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**AN APPLICATION OF THE FINITE DIFFERENCE METHOD TO ESTIMATE  
THE SHELF LIFE OF A PACKAGED MOISTURE SENSITIVE  
PHARMACEUTICAL TABLET**

**By**

**Jai Neung Kim**

**A THESIS**

**Submitted to  
Michigan State University  
in partial fulfillment of the requirements  
for the degree of**

**MASTER OF SCIENCE**

**School of Packaging**

**1992**

**ABSTRACT**

**AN APPLICATION OF THE FINITE DIFFERENCE METHOD TO ESTIMATE  
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PHARMACEUTICAL TABLET**

By

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A mathematical model for predicting the shelf life of packaged moisture sensitive pharmaceutical tablet was developed based on the unsteady steady state mass transfer of water through the package and the tablet. A computer program was developed to solve the mathematical model, using the finite difference method. The computer program was run for a variety of numerical values including the main variables such as the diffusion coefficient and solubility of water in the packaging material and the diffusion coefficient of water in the tablet.

A distinctive characteristic of this shelf life computer model is that it fully takes into account the unsteady state nature of the shelf life of a packaged moisture sensitive product.

There was not experimental validation of the shelf life values calculated with this computer program at this time. However for limiting cases that calculated values agreed very well with the analytical solutions.

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**Dedicated to My Parent, Mr. and Mrs. Kim,  
and My Wife, Mrs. Kid**

## **ACKNOWLEDGEMENT**

The author wishes to express his thanks to his advisor, Dr. Ruben Hernandez for his valuable advise, sincere assistance and providing good research topic and also the author gives thanks to the CFPPR at School of Packaging for providing the financial assistance for this project.

The author is deeply indebted to Dr. Gary Burgess, for his sincere guidance, assistance and encouragement in the course of his graduate study.

Genuine appreciation is extended to the members of the research guidance committee, Drs. Bruce Harte and Eric Grulke for reviewing this manuscript. Special thanks go to Dr. Lapael for his sincere help to check computer program.

Last but not least, the author wishes to express deepest appreciation to his parents, Mr. D. K. Kim and Mrs. O. S. Kim, his wife, Mrs. H. J. Kim, and his son, J. W. Kim for their love and support.



## TABLE OF CONTENTS

	Page
<b>LIST OF TABLES .....</b>	<b>viii</b>
<b>LIST OF FIGURES .....</b>	<b>ix</b>
<b>LIST OF APPENDIXES .....</b>	<b>x</b>
<b>LIST OF SYMBOLS .....</b>	<b>xi</b>
<b>I. INTRODUCTION .....</b>	<b>1</b>
<b>II. LITERATURE REVIEW .....</b>	<b>3</b>
2.1. Water in the food and pharmaceutical product .....	3
2.2. Water vapor transmission mechanism .....	6
2.3. Shelf life simulation models .....	24
2.4. Finite difference method .....	38
<b>III. DEVELOPMENT OF THE MATHEMATICAL MODEL .....</b>	<b>40</b>
3.1. Assumptions .....	40
3.2. Presentation of the solution .....	41
<b>Calculation water vapor concentrations</b>	
3.3. Calculation of water vapor concentration in the outside of the package ( $C_E$ ) .....	42
3.4. Calculation of water vapor concentration of the packaging material in equilibrium with concentration of outside package $C_E$ , ( $C_{LE}$ ). .....	43
3.5. Calculation of the initial concentration of water vapor inside the surface of the packaging material, in headspace and in the product .....	44
3.6. Calculation of water vapor concentrations of water vapor in packaging material ( $C_{LN,i}$ ) at time $t$ .....	46
3.7. Calculation of water vapor concentrations in the inside surface of the packaging mater- ial ( $C_{LH}$ ), the headspace ( $C_H$ ), and inside sur- face of spherical shape product ( $C_{RH}$ ) at time $t$ .....	49
3.8. Calculation of water vapor concentrations inside the product ( $C_{RU,i}$ ) at time $t$ .....	52
3.9. Calculation of the total water gain for the product .....	57

<b>IV. THE COMPARISON BETWEEN FINITE DIFFERENCE SOLUTION AND ANALYTICAL SOLUTION .....</b>	<b>59</b>
4.1 The solution for water diffusion equation in the packaging material .....	59
4.2 The solution for water diffusion equation in the product .....	60
<b>V. DATA ANALYSIS OF THE COMPUTER PROGRAM .....</b>	<b>63</b>
5.1. Input data .....	63
5.2. The effect of numbers of shells on in which the product is divided for calculation purpose .....	69
5.3. The effect of diffusion coefficient of water in the packaging material and in the tablet on the shelf life .....	73
5.4. The effect of solubility of water in the packaging material and diffusion coefficient of water in the tablet on the shelf life ....	79
<b>VI. CONCLUSION .....</b>	<b>83</b>
<b>APPENDIXES .....</b>	<b>86</b>
<b>REFERENCES .....</b>	<b>128</b>

## LIST OF TABLES

Table	page
1. Published diffusion coefficient and solubility of water .....	16
2. Published diffusion coefficient of foods .....	23
3. Concentrations profile of the analytical solution and finite difference solution .....	61
4. Comparison of moisture gain between the analytical solution and the finite difference solution	62
5. Sorption isotherm data of multivitamin tablet	67
6. Experimental G.A.B. constants of multivitamin tablet .....	67
7. Data used in simulation .....	68
8.A. Effect of the number of shells of the spherical shape on the shelf life (hours).....	70
8.B. Effect of the number of shells of the circular plate shape product on the shelf life (hours) .....	70
9.A. Effect of diffusion coefficient of water in the packaging material and the spherical shape of tablet on the shelf life (hours) ..	74
9.B. Effect of diffusion coefficient of water in the packaging material and the circular plate shape tablet on the shelf life (hours) .....	74
10. Sorption isotherm data in concentration (g/cm <sup>3</sup> )	77
11. The analytical solution in limiting case .....	78
12.A. Effect of the solubility of packaging material and the diffusion coefficient of water in the spherical shape tablet on shelf life (hours) .....	80
12.B. The effect of solubility of packaging material and diffusion coefficient of water in the circular plate shape tablet on shelf life (hours) .....	80

## LIST OF FIGURES

Figure	page
1. Diagram showing package and product system and the corresponding values of water concentrations .....	xi
2. Water activity and food stability diagram .....	5
3. Typical sorption isotherm curve of food .....	18
4. Finite different method .....	39
5. Package and product diagram .....	40
6. The concentration matrix .....	42
7. Subdivision of packaging material into N thin layers	46
8. Headspace and interface concentrations .....	49
9. Subdivision of spherical product into U shells. The thickness $\Delta R$ of each shell is $\Delta R=R/U$ .....	52
10. Concentrations within shells .....	57
11. Multivitamin tablet blister package .....	64
12. Effect of number of shells of the spherical shape product on the shelf life (hours) .....	71
13. Effect of number of shells of the circular plate shape product on the shelf life (hours) .....	72
14. Effect of diffusion coefficient of water in the packaging material and in the spherical shape tablet on the shelf life (hours) .....	75
15. Effect of diffusion coefficient of water in the packaging material and in the circular plate shape on the shelf life (hours) .....	76
16. Effect of solubility of water in the packaging material and diffusion coefficient of water in the spherical shape tablet on shelf life (hours) .....	81
17. Effect of solubility of water in the packaging material and diffusion coefficient of water in the circular plate shape tablet on the shelf life(hours)	82
18. Package and product .....	104

## **LIST OF APPENDIXES**

<b>Appendix</b>	<b>page</b>
1. Procedure to calculate Henry's law constant ...	86
2. The stability of dimensionless constant .....	88
3. Finite difference calculation scheme and water gain formula for products like plates .....	90
4. Calculation of the analytical solution.....	94
5. Computer program .....	108

## LIST OF SYMBOLS

### 1. General symbols

A	Surface area
A <sub>w</sub>	Water activity
B	Constant
b	Constant for particular food
b <sup>*</sup>	Hole affinity constant
C	Concentration, g/cm <sup>3</sup>
C <sub>i</sub>	The penetrant concentration
C <sub>s</sub>	The sorbed concentration
C <sub>H</sub> <sup>*</sup>	Hole saturation constant
C <sub>T</sub>	Total solute concentration
C <sub>B</sub>	Solute concentration due to absorption
C <sub>D</sub>	Solute concentration due to adsorption
C <sub>i</sub>	Penetrant concentration at upstream penetration membrane surface
C <sub>g</sub>	Guggenheim constant
D	Diffusion coefficient of solute
D <sub>i</sub>	Initial mass diffusion
D <sub>eff</sub>	Effective diffusion coefficient
D'	Effective vapor pressure diffusion coefficient
f	Conversion factor
H	Henry's law constant
H <sub>q</sub>	Total heat of sorption of the multilayers
H <sub>m</sub>	Total heats of sorption of first layers n the primary sites
ΔH <sub>s</sub>	Molar Heat of sorption
K	Constant
k	Factor
k'	Thermal conductivity
L	Thickness of polymer film
M	Moisture content in dry basis
M <sub>i</sub>	Initial moisture content
M <sub>c</sub>	critical moisture content
m	Mass of water
M <sub>B</sub>	Moisture content of environment
M <sub>w</sub>	Molecular weight of water
M <sub>m</sub>	Water content corresponding to saturation
M <sub>s</sub>	Experimental water content
M <sub>i</sub>	Calculated water content
P	Permeability
p	Pressure
p <sub>sat</sub>	Saturation vapor pressure
p <sub>w</sub>	Partial pressure of water
p <sub>T</sub>	Total pressure
τ	Time lag

RH	Relative Humidity
R	Gas constant (1.98 cal/gmole °K)
R <sub>g</sub>	Gas constant (82.1 atm. cm <sup>3</sup> /gmole °K)
S	Solubility
T	Temperature
t	Time
t <sub>1/2</sub>	Half time
t <sub>p</sub>	Time lag of the closed volume experiment
V <sub>1</sub>	Solute volume fraction
V <sub>1</sub> <sup>L</sup>	Langmuir volume fraction contribution to solute volume fraction
V <sub>1</sub> <sup>FH</sup>	Flory-Huggins contribution to the solute volume fraction
W <sub>i</sub>	Dry weight of product

## 2. The symbols used in mathematical model

### 2.1 The name of variables and unit

T	Temperature of outside package (°C)
RH <sub>B</sub>	Relative humidity of outside package (%)
AH	Absolute humidity at given temperature (g H <sub>2</sub> O/g air)
D <sub>L</sub>	Water diffusion coefficient of polymer packaging material (cm <sup>2</sup> /sec)
H <sub>L</sub>	Henry's law constant of polymer packaging material (g H <sub>2</sub> O/cm <sup>3</sup> PKG)/(g H <sub>2</sub> O/cm <sup>3</sup> air)
L	Thickness of polymer packaging material (cm)
A <sub>L</sub>	Surface area of polymer packaging material (cm <sup>2</sup> )
V <sub>L</sub>	Inner volume of package (cm <sup>3</sup> )
N	Number of divided layers of polymer packaging material thickness
D <sub>R</sub>	Water diffusion coefficient of vitamin tablet (cm <sup>2</sup> /sec)
M <sub>i</sub>	Initial moisture content of vitamin tablet (g H <sub>2</sub> O/ 100g dry Product)
M <sub>C</sub>	Critical moisture content of vitamin tablet (g H <sub>2</sub> O/ 100g dry Product)
W <sub>i</sub>	Dry weight of vitamin tablet (g)
R <sub>i</sub>	Radius of spherical shape vitamin tablet (cm)
R <sub>p</sub>	Radius of circular plate shape vitamin tablet (cm)
T <sub>p</sub>	Thickness of circular plate shape vitamin tablet (cm)
a, b, c	G.A.B sorption isotherm constant of vitamin tablet
U	Number of divided shells of vitamin tablet
t	Time

## 2.2 Subscript

E External environment  
 L Packaging Material  
 R Product inside package  
 i Initial time  
 c Critical, center  
 sat Saturation in the air

## 2.3 Symbols used for concentrations of water

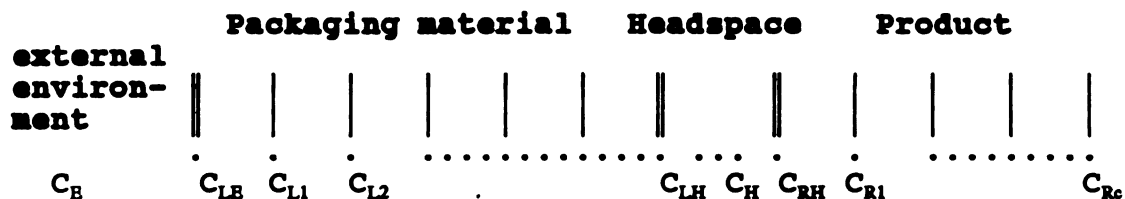


Figure 1. Diagram showing the partitions of package and product system and the corresponding values of water concentrations

$C_E$  The concentration of water vapor outside the package (constant).

$C_{LE}$  The concentration of absorbed water vapor on the outside surface of the package (constant).

$C_{L,N}$  The concentration of water vapor inside of the packaging material (variable).

$C_{LH}$  The concentration of diffused water vapor on the inside surface of the package (variable).

$C_H$  The uniform concentration of water vapor in the headspace (variable).

$C_{RH}$  The concentration of absorbed water vapor on the surface of the product from headspace (variable).

$C_{R,U}$  The concentration of water vapor inside of the product (variable).

$C_{Rc}$  The concentration of diffused water vapor at the center of the product (variable).



## **I. INTRODUCTION**

Estimation of transfer of the moisture through packaging material and product is essential to the shelf-life of moisture sensitive pharmaceutical and food products packaged in polymeric packaging material.

Experimental determination of the shelf life of moisture sensitive food and pharmaceutical products, requires a considerable amount of time and money. There is need, then to develop computer programs to estimate the shelf life of packaged product. The availability of many computer models is important not only in the reducing cost and time in the estimation of shelf life but also provides a tool to optimize packaging design.

Several predictive models have been prepared in the past. In most cases, the model is based on moisture transport through the packaging material at steady state conditions and/or equilibrium moisture content of the products. However there is a need for taking in consideration the unsteady state transport of moisture, especially with the availability of high barrier polymeric structures.

In this study, the shelf life of moisture sensitive

water in the packaging material and diffusion coefficient of water in the product and geometry of product on shelf life of moisture sensitive product were examined.

**The specific objectives of this research were:**

1. To develop a mathematical model for predicting the shelf life of moisture sensitive products based on the unsteady state mass transfer of water through the package and the packaged product.
2. To develop a computer program based on the finite difference to calculate the shelf life of moisture sensitive product during storage.
3. To examine the effect of the main variables such as diffusion coefficient and solubility of water in the packaging material, and diffusion coefficient of water in the product on the shelf life of moisture sensitive product.

## **II. LITERATURE REVIEW**

### **2.1. Water in the food and pharmaceutical product**

Interaction between water and components of food and pharmaceutical product plays an essential role in the physical, chemical modifications that may occur during the preservation of packaged or non-packaged food and pharmaceutical product. These molecular interactions affect the water structure, conformation and reactivity of the macromolecule and the water retention, especially by ions and small molecules.

Solute -water interactions in aqueous biological media are important in the reaction mechanisms related to hydration. This is of particular interest for stored foods where a slow hydration may occur and affect enzymic activity, browning reactions and microbial growth, and hence the quality of the preserved foodstuff.

In the intermediate range of water activities the non-enzymic browning reaction or Maillard reaction shows a maximum of reaction rate. (Heiss,1968),(Heiss et al,1971), (Labuza, 1970). Non-enzymic browning is caused by reactions between reducing sugars and the amino groups of amino acids and protein, leading to losses of nutritive value, brown

discoloration and off-flavors. Primary condensation products between reducing sugars and amino acids (Amadori compounds) can be isolated and analyzed in different ways, and these serve as indicator compounds for early detection of the Maillard reaction during heat processing (e.g. drying) and storage; in the lower moisture range, browning- being a consecutive reaction is suppressed, whereas Amadori compounds may still be formed (Eichner et al, 1981,1983).

The maximum in reaction rate is due to the fact, at lower moisture contents, diffusion of the reactants is very slow, whereas at higher moisture contents a dilution due to water produced by the reaction causes an inhibitory effect and, according to mass action law, a slowing down of the reaction rate.

Storage conditions for foods to undergo the Maillard reaction should be chosen such that the water activity remains below or above the maximum. In the latter case additional measures like application of heat or addition of preservatives must be taken. Moreover, care should be taken that formation of browning intermediates during the drying process is minimized in order to reduce the shelf-life by cutting down part of the induction period before the onset of undesirable sensory changes (Eichner et al, 1981,1983).

On the other hand, at very low water activities fat autooxidation, which is a radical chain reaction between unsaturated fatty acids and oxygen, is promoted (Maloney, 1966). If water activity is increased, the reaction rate is slowed down at first. This is due to stabilization of fatty acid hydroperoxidees, which are reactive intermediates, by hydrogen bonding with water. At higher water contents fat oxidation may be promoted again, which can partly be explained by an increase in the mobility of heavy metal ions catalyzing fat oxidation (Labuza, 1972a).

Interval of water activities or moisture contents critical respectively for different types of deteriorative changes during storage are shown in Figure 2.

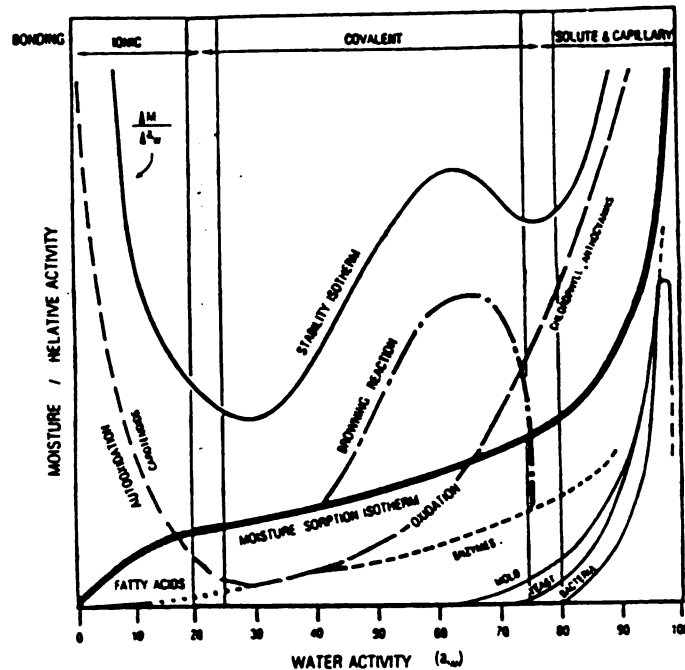


Figure 2. Water activity and food stability diagram

## **2.2. Water Vapor Transmission Mechanism**

### **2.2.1. Water Vapor Transmission Through Packaging Material**

Prolonging the consumer-acceptable shelf life of food product is the major benefit bestowed by the use of packaging. The first step in defining packaging requirements is quantifying the transport properties and the critical factors of quality loss as well as the variables that influence them. The importance of transport behavior of gases and vapors in polymeric films has become apparent with the accelerating development of highly impermeable or selectively permeable packaging film for diverse applications in the food and pharmaceutical industries.

#### **2.2.1.1 Sorption Mechanisms of Polymeric Films**

A sorption isotherm is an equation that describes the relationship between the equilibrium concentration of the penetrant in the polymer and the concentration of water surrounding the solid at a constant temperature. Classically, there are four basic types of isotherm observed in polymer systems. These isotherms depend on the degree of penetrant-polymer interaction. Type I follows Henry's law where the concentration is linearly dependent upon pressure. Type II is characteristic in systems where only a unimolecular layer of sorbed substance forms of a concave curve towards the pressure

axis. Type III sorption is characteristic of multilayer adsorption where the attractive forces between penetrant and solid are greater than those between the molecules of the penetrant themselves, giving a sigmoid shaped curve. When the forces between the penetrant and the substrate are relatively small, the sorption process occurs essentially randomly as the results of absorption or adsorption due to van der Waals type forces. Another interpretation of type III isotherm considers that it is the result of two simultaneous sorption process. One process, dominant at low penetrant concentrations, corresponds to a type II isotherm due to preferential sorption of penetrant onto a limited number of acting sites in the solid.

The other concurrent process is a type IV sorption, so the superposition of the two curves gives the observed type III isotherm.

Langmuir (1918) equation for sorption is limited to monolayer formation leads to a type II isotherm. The Langmuir equation can be expressed as follows,

$$S = \frac{C^*}{P} = \frac{C_H^* P}{1 + b^* P} \quad (1)$$

where  $b^*$  is the hole affinity constant,  $C_H^*$  is the hole saturation constant,  $C^*$  is the sorbed concentration, and  $p$  is

the corresponding pressure. Langmuir's equation works best when the energies of adsorption are high, as in chemisorption, or when the absorbed molecules are quite large. In both cases, the penetrant molecules are rendered relatively immobile by the adsorption process. However, at high concentration or low temperatures, discrepancies often appear in the direction of more sorption than predicted by the Langmuir equation. This is especially apparent when the energies of adsorption are in the range characteristic of physical adsorption. These discrepancies may be due to the formation of multilayer rather than monolayer.

The magnitude of the solubility for a penetrant in a polymer increase with :

- a. the chemical similarity of the penetrant-polymer
- b. the larger the molar volume of the condensed penetrant
- c. the lower the percent cross linking and the crystallinity of polymer.

The sorption of a penetrant by the polymer may have a important effect on the polymer properties. In addition to the plasticizing action of the sorbed penetrant there may be swelling and dimensional distortion of the polymer. (Rogers, 1964)

Michaels et al. (1963) also reported that the sorption of



helium, nitrogen, oxygen, argon and methane in glassy, amorphous and glassy crystalline polyethylene terephthalate for pressure up to 10 atmosphere obey Henry's law, but carbon dioxide at 25°C and 40°C and ethane at 25°C in the same pressure range derived from Henry's law. The carbon dioxide isotherms lead Michaels et al. (1963) to propose a dual-mode sorption model of ordinary dissolution and adsorption in microvoids (holes) for gas sorption in glassy amorphous polymers. It was assumed that the total amount of solute sorbed in the polymer,  $C_T$ , consisted of two thermodynamically distinct molecular population :

$$C_T = C_B + C_D \quad (2)$$

where  $C_B$  and  $C_D$  are the concentrations due to absorption and adsorption. Concentration  $C_B$  was represented by Henry's law,

$$C_D = H p \quad (3)$$

where  $H$  is the Henry's law constant.

The concentration,  $C_B$ , was represented by a Langmuir isotherm:

$$C_T = C_B + C_D = H p + \frac{C_H^* p}{1 + b^* p} \quad (4)$$

Hernandez et al. (1991) have proposed to modify equation

(4) by using the Flory-Huggins equation to describe non-specific solution rather than Henry's law. The modified dual-mode sorption model represents the sorption of water vapor by an amorphous polyamide at 23°C . This modification allowed the model to fit over the activity range,  $0 < A_w < 1.0$  . For convenience, the modified dual mode sorption model was expressed in terms of volume fraction and solute activity :

$$V_1 = V_1^{FH} + V_1^L \quad (5)$$

Where  $V_1^{FH}$  refers to the Flory-Huggins contribution to the solute volume fraction and  $V_1^L$  is Langmuir volume fraction contribution.  $V_1^{FH}$  can be determined by numerical methods, such as Newton-Raphson technique and equation (5) become :

$$V_1 = FH(A_w, \chi) + \frac{KA_w}{1 + BA_w} \quad (6)$$

where  $K = C_H' f d p_{\text{sat}}$ ,  $B = b' p_{\text{sat}}$ ,  $p_{\text{sat}}$  is saturation vapor pressure, and  $f$  is a conversion factor.

#### 2.2.1.2 Mass Transfer Mechanism Through The Polymeric Film

Two usual types of mechanisms of mass transfer through materials are the capillary flow transport and the activated diffusion. Capillary flow involves molecules traveling

through pinholes and/or high porous media such as paper, glassine, cellulosic membranes, etc. Activated diffusion consists of solubilization of the penetrants into an effectively non-porous film at the inflow (upstream) surface, diffusion through the film under a concentration gradient and release from the outflow (downstream) surface at the lower concentration (Stannett, 1988). The mass transport of a penetrant basically includes three steps: adsorption, diffusion, desorption. Adsorption and desorption depend upon the solubility of the penetrant in the film, i.e. the thermodynamic compatibility between the polymer and the penetrant. Diffusion is the process by which mass is transported from one part of system to another as a result of random molecular motion. Within the water matrix, the process is viewed as a series of activated jumps from one vaguely defined "cavity" to another. Qualitatively, The diffusion rate increases with the increase of the number of size of cavities caused by the presence of substances such as plasticizer. On the other hand, the structural entities such as crosslinks or degree of crystallinity decrease the size or number of cavities and thereby decrease the diffusion rate (Roger, 1985).

When a penetrant diffuses through a polymeric film in which it is soluble, there is a transient state before the steady state is established. Two approach are used to

quantify the unsteady state process.

#### 2.2.1.3 The Method to Calculate Diffusion Coefficient

There are two usual methods to calculate diffusion coefficient of polymer film. One is integral permeation method. In this technique, the penetrant pressure  $p_1$  at the upstream face of the polymer is generally held constant. Meanwhile the downstream pressure,  $p_2$ , while measurable, is negligible relative to the upstream pressure. The relationship between thickness of polymer film and diffusion coefficient is as follows,

$$\tau = L^2 / 6D \quad (7)$$

where  $L$  is thickness of polymer film,  $D$  is diffusion coefficient and  $\tau$  is known as the "time lag" (Daynes, 1920).

By use of eqn.(7), diffusion coefficient can be calculated. Permeability constants can be determined from the steady state portion of the curve the time-lag method. Solubility constant can be calculated by following equation (Barrer, 1939).

$$S = P / D \quad (8)$$

Solubility constant determined by the time-lag method, however, are less precise for more soluble gases. Precise

solubility can be determined by the equilibrium-sorption method.

For a penetrant-independent diffusivity, the steady-state flow through a plane sheet is approximately reached after a period amounting to  $2.7 \tau$  (Crank, 1975).

If the diffusivity,  $D$ , is not constant, but depends upon  $C$ , then a mean value of the diffusivity,  $D$ , may be defined as

$$D = \left( \frac{1}{C_1} \right) \int_0^{C_1} D(C) dC \quad (9)$$

where  $C_1$  is the penetrant concentration at up stream penetrant membrane surface.

The other method is the differential permeation methods which has been used by Ziegel et al. (1969) and Felder (1978) to improve the previously mentioned method. In this technique, the membrane serves as a barrier between two flowing gas streams, penetrant and carrier, each at atmospheric pressure. The permeation rate is obtained by analyzing the downstream effluent gas to determine the penetrant concentration, and multiplying the concentration by the gas flow rate. The permeation rate,  $\phi$ , is measured as a function of time, until the steady state permeation rate,  $\phi_{\infty}$ ,

is obtained. For a flat membrane,  $\phi_{\infty}$  given as

$$\phi_{\infty} = (P A/L) (p_1 - p_2) \quad (10)$$

Four techniques have been used for estimating the diffusivity from a curve of the differential permeation methods.

The first estimation technique, the so-called half-time method, is to designate the time  $t_{1/2}$  at which  $\phi$  is equal to 0.5  $\phi_{\infty}$ . For a flat membrane this becomes (Pollack, 1959)

$$D = \frac{L^2}{7.199 t_{1/2}} \quad (11)$$

The second estimation technique is similar to a treatment given by Jost (1952) for diffusion into or out of a thin slab

$$\ln\left(1 - \frac{\phi}{\phi_{\infty}}\right) = \ln 2 + \ln \sum_{n=1}^{\infty} -(-1)^n \exp\left(\frac{-n^2 \pi^2 D t}{L^2}\right) \quad (12)$$

As time becomes sufficiently large, all terms other than  $n=1$  in the series vanish; hence, the linear portion of a plot of  $\ln(1-\phi/\phi_{\infty})$  versus  $t$  has an intercept of  $\ln 2$  at  $t=0$  and a slope related to the diffusivity by

$$D = -L^2 (\text{slope}) / \pi^2 \quad (13)$$

Third estimation method used by Roger et al. (1960), is based on the Holstein relation (Crank, 1975) for small time as shown below

$$\ln(\phi_{t_{\frac{1}{2}}}) = \ln[2C(\frac{D}{\pi})^{\frac{1}{2}}] - \frac{L^2}{4Dt} \quad (14)$$

The slope of a plot of  $\ln(\phi_{u/2})$  versus  $1/t$  yields  $(-L^2/4D)$  from which  $D$  can be calculated. The advantage of this method is that it does not require knowledge of the value of  $\phi_{\infty}$ .

The fourth estimation method is a moment technique used by Felder et al. (1978, 1975, 1976) who defined a quantity,  $t_p$ , equivalent to the time lag of the closed volume experiment.

$$t_p = \int_0^{\infty} [1 - \frac{\phi(t)}{\phi_{\infty}}] dt \quad (15)$$

Once  $t_p$  is determined, the diffusivity for a flat membrane may be estimated as

$$D = L^2 / 6 t_p \quad (16)$$

It is not easy to cite the reported diffusion coefficient and solubility of packaging material for water.

Here is several reported values of diffusion coefficient and solubility of packaging material for water.

Table 1. Published Diffusion Coefficient and Solubility data (Brandrup, 1989)

Packaging material	Temp. (°C)	Diffusion coefficient (cm <sup>2</sup> /sec)	Solubility (cm <sup>3</sup> STP /cm <sup>3</sup> Pa)
Rigid PVC	25 - 80	$2.4 \times 10^{-8}$	$206 \times 10^{-13}$
P.S	25	$1.4 \times 10^{-7}$	
PEM	25 - 60	$1.02 \times 10^{-7}$	$2333 \times 10^{-13}$

#### 2.2.2. Water Vapor Transmission Into The Product

##### 2.2.2.1 Sorption Mechanism For Product

The water contained in a hygroscopic food is bound within the food in some chemical or physical manner or in a combination of these. It is an intimate part of the food but does not materially change the physical or chemical properties. Experimental evidences indicate that the predominant mechanism is adsorption. The molecules of the material attract and physically hold the water molecules. Thus binding is assumed to be a surface phenomenon, although moisture of solution, hydration, and chemical combination may also be present in limited amounts.

In general, the sorption of water in foodstuffs and



pharmaceutical product is expressed in sorption isotherm curve. The water in a food and pharmaceutical product with a certain moisture content produces a water vapor pressure,  $p$ , which is less than the saturated water vapor pressure of pure water,  $p_m$ , at the same temperature as the food. The ratio of these pressure,  $p/p_m$ , is the equilibrium relative humidity for that particular moisture content and temperature of the food.

The equilibrium moisture curve is a graphic expression of the relationship between the moisture content of food and its equilibrium relative humidity.

Sorption can be divided into several regions depending on the state of the water present. It should be noted from Figure 3. that region A corresponds to the adsorption of a monomolecular film of water; region B, to adsorption of additional layers over this monolayer; and region C to condensation of water in the pores of the food followed by dissolution of the soluble material present.

Several mathematical equations have been reported in the literature for describing water sorption isotherms of food material. Recently, G.A.B sorption isotherm was reported. It is a three-parameter equation with physically meaningful coefficients which fits data very well up to 0.9  $A_w$  in many cases. Mathematically speaking, several three-

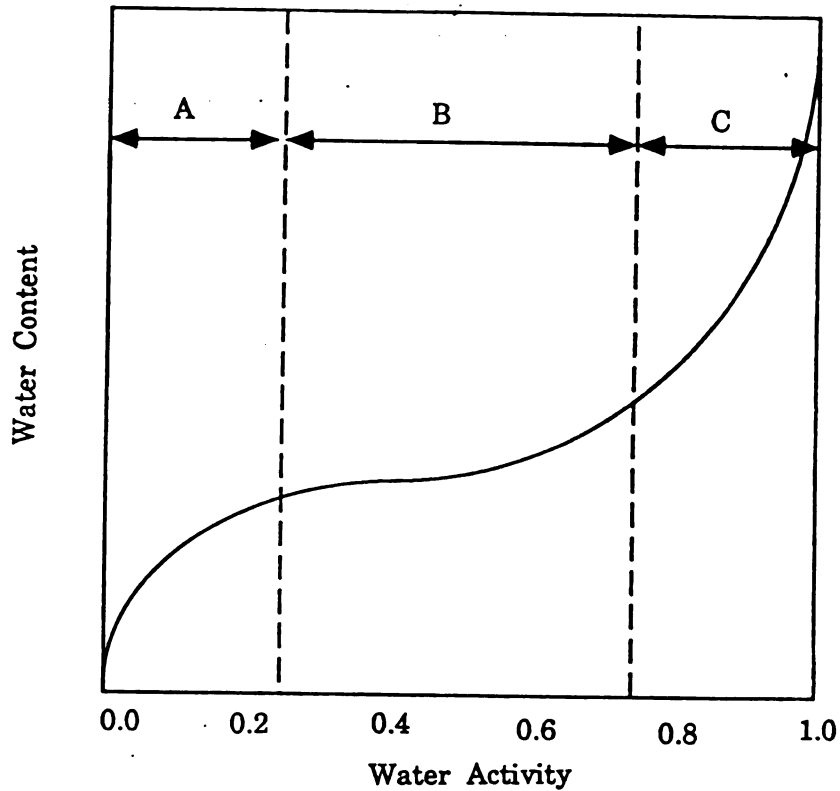


Figure 3. Typical Sorption Isotherm Curve of Food and Pharmaceutical products

parameter equation can be transformed into formulae similar to the Guggenheim-Anderson-De Boer (G.A.B.) model; the relation is (Van Den Berg, 1978);

$$\frac{M}{M_m} = \frac{C_g kAw}{(1-kAw)(1-kAw+C_g kAw)} \quad (17)$$

where  $A_w$  is water activity,  $M$  is water content on dry basis,  $M_m$  is water content corresponding to saturation of all primary adsorption sites by one water molecule (formally called the monolayer in B.E.T. theory),  $C_g$  is the Guggenheim constant=

$C' \exp(H_1 - H_m)/RT$ ,  $H_q$  is total heat of sorption of the multilayers (which differs from the heat of condensation of pure water),  $H_m$  is total heat of sorption of first layer on primary sites,  $k$  is a factor correcting properties of the multilayer molecules with respect to the bulk liquid [ $k = k' \exp(H_1 - H_q)/RT$ ], and  $H_1$  is heat of condensation of pure water vapor.

This model can be considered as an extension of the B.E.T. multimolecular localized homogeneous adsorption model taking into account the modified properties of the sorbate in the multilayer region.

A quadratic regression is easily conducted on experimental values for computer-fitting procedure. The original parameters were deduced after solving the previous equation system (Van den Berg, 1981). From eqn. (17)

$$\frac{A_v}{M} = aA_v^2 + bA_v + c \quad (18)$$

$$a = \frac{k}{M_m} \left[ \frac{1}{C_g} - 1 \right]$$

$$b = \frac{1}{M_m} \left[ 1 - \frac{2}{C_g} \right]$$

$$c = \frac{1}{M_m C_g k}$$

The quality of the fit was judged from the value of the relative percent root mean square (%RMS)

$$\%RMS = 100 \sqrt{\frac{\sum_{i=1}^N \frac{[M_x - M_x^*]^2}{M_x}}{N}} \quad (19)$$

where N is number of experimental points,  $M_x$  is experimental water content, and  $M_x^*$  is calculated water content. With above equation, they reported several G.A.B constant of starch.

#### 2.2.2.2 Mass Transfer Into Product

In order to calculate the change in the moisture content of a product, sorption isotherm and eventually mass transfer coefficient of water with respect to the product are necessary to know the diffusion coefficient of water. In most of the sorption modeling studies, it is assumed that the surface of food product reaches equilibrium instantaneously. This is necessary because of it make easier the calculation.

Thus, the diffusion coefficients calculated based on this assumption may be viewed as effective diffusion coefficient which account for both integral and external resistance to moisture transfer.

### 2.2.2.3 Method to calculate the diffusion coefficient in the product.

Various methods have been developed to estimate diffusion coefficients. One method of the calculation is determine the  $D_{eff}$  as a function of the material properties of the food and its surrounding atmosphere (King, 1968; Bluestein, 1971; Roman et al., 1982).

$$D_{eff} = \frac{M_w D' p_w^0}{\rho_s R_v T} \frac{p}{p - p_w} \left( \frac{\partial RH}{\partial M} \right)_T \left( \frac{\alpha}{1 + \alpha} \right) \quad (20)$$

Where

$$\alpha = \frac{k' R R_v T^3}{(\Delta H_s)^2 D' R H p_w^2}$$

$D'$  is effective vapor space diffusion coefficient,  $\text{cm}^2/\text{sec}$   
 $\Delta H_s$  is molar heat of sorption,  $\text{cal./gmole}$ ,  $k'$  is thermal conductivity of solid and sorbed moisture,  $\text{cal/sec.cm.}^\circ\text{K}$ ,  $M_w$  is molecular weight of water,  $18\text{g/gmole}$ ,  $p_w$  is partial pressure of water,  $\text{atm}$ ,  $p$  is total pressure,  $\text{atm}$ ,  $p_w^0$  is vapor pressure of water,  $\text{atm}$ ,  $RH$  is relative humidity,  $p_w/p_w^0$ ,  $R$  is gas constant,  $1.98 \text{ cal/gmole }^\circ\text{K}$ ,  $R_v$  is  $82.1 \text{ atm.cm}_3/\text{gmole.}^\circ\text{K}$ ,  $M$  is moisture content (dry basis),  $T$  is absolute temperature,  $^\circ\text{K}$ , and  $\rho_s$  is density of the solid with no moisture,  $\text{g/cm}^3$ .

Second methods include solving numerically the Fick's

second law of diffusion and then finding the value of  $D_{eff}$  which minimizes the error in sum of squares between the actual and predicted values of the moisture content (Zhang et al., 1984; Baskshi and Singh, 1980; Misra and Young, 1980; Steffe and Singh, 1980; Whitaker and Young, 1972).

$$D = D_i \left( \frac{\rho_i}{\rho} \right)^{n_j} \exp[-n^2(C - C_i)] \quad (21)$$

where  $D$  is mass diffusivity,  $D_i$  is initial mass diffusivity at a given dry bulb temperature,  $m_2/hr$ ,  $\rho$  is dry mass density,  $kg/m^3$ ,  $\rho_i$  is initial dry mass density,  $kg/m^3$ ,  $C$  is concentration at any time,  $kg/m^3$ , and  $C_i$  is concentration at initial time,  $kg/m^3$ .

A third method is to use an analytical solution to Fick's first law such as the one given below for a moisture transfer in one dimension in a semi-infinite slab:

$$\Gamma_{1s} = \frac{M - M_E}{M_i - M_E} = \frac{8}{(\Pi)^2} \sum_{n=0}^{\infty} (2n+1)^2 \exp\left(\frac{-D_{eff}(2n+1)^2(\Pi)^2 t}{4L^2}\right) \quad (22)$$

where  $M_E$  is equilibrium moisture content,  $M_i$  is initial moisture content,  $M$  is moisture content at time  $t$ ,  $L$  is thickness of slab. Eqn.(22) assumes a uniform initial moisture content, constant surface moisture content and a constant density.

Hanson et al. (1971) and Roman et al. (1982) have used the following in determining effective or apparent diffusion coefficient:

$$D_{eff} = -\left(\frac{4L^2}{\pi^2}\right) * slope \quad (23)$$

where the slope is obtained from a plot of the  $\ln R$  versus time. This method is especially useful when a break in the  $R$  vs time plot is observed. A  $D_{eff}$  can be obtained for each portion of the curve. Lomauro et al. (1985) reported diffusion coefficient of several food by use of eqn (23).

Table 2. Published diffusion coefficients of foods

Product	Aw	Thickness (mm)	Initial Weight(g)	Diffusion Coef. $m^2/hr \times 10^7$
Flour	0.11	3.6	4.0	0.139 (0.006)
Flour	0.75	8.3	28.3	1.52 (0.826)
Nonfat	0.75	3.1	2.0	0.767 (-)
Dry milk				
Freeze-dried	0.75	2.7	0.9	0.146 (0.015)
apple				
Freeze-dried	0.75	2.5	0.5	0.274 (0.009)
turnip				
Freeze-dried	0.75	10.9	6.2	1.105 (0.212)
raw ground				
beef				
Oatmeal cookie	0.75	10.1	12.8	0.143 (0.015)
Shredded wheat	0.75	2.9	2.0	0.199 (0.026)

### 2.3. Shelf Life Simulation Models

Since the early 1940's, numerous studies on the simulation model of shelf life of foods have been published.

Heiss (1958) developed shelf life predictive model by using concepts of mass transfer. He discussed the relationship between the moisture sorption properties of foods, the packaging permeability with respect to water vapor, and the shelf life of the product and developed a mathematical model describing the moisture change of a packaged moisture sensitive product for constant temperature and humidity.

$$t = \frac{W_s}{A} \left( \frac{\Delta P}{P} \right) \int_{M_i}^{M_e} \frac{dM}{M_s - F(M)} \quad (24)$$

where P is permeability value, A is the surface area of package, W<sub>s</sub> is the dry weight of the contents, Δp is water amount difference, f(M) is sorption isotherm, p<sub>De</sub> is external water amount, and M is amount of water.

M. Karel (1967) reported the shelf life simulation model based on Heiss' model. Following is a summary of Karel's model.

(a). Moisture sorption isotherm are assumed to be linear



according to eqn.(25).

$$M = b (p/p_{\text{sat}}) \quad (25)$$

Where  $M$  is moisture content (g of  $H_2O$ )/g of solid),  $p$  is partial pressure of water in the food,  $p_{\text{sat}}$  is saturated vapor pressure of water, and  $b$  is constant for the particular food.

(b). There is linear relationship between water vapor pressure difference and the transmission rate.

$$dm / dt = P A ( \Delta p / L ) \quad (26)$$

Where  $dM/dt$  is water vapor transmission rate,  $\Delta p$  is water vapor pressure difference,  $L$  is thickness of the packaging material,  $A$  is area of the package, and  $P$  is permeability.

(c). The critical moisture content,  $M_c$ , for the particular food is assume or determined, assuming the linearity of the isotherm.

$$dM / dt = P A ( \Delta p / W_s L ) \quad (27)$$

Where  $W_s$  is the weight of solids in the package.

(d). The relative humidity at which the package will be stored is known.

$$\frac{dM}{dt} = PA \frac{P_E - P_i}{P_{sat} W_s L} = PA \frac{M_E - M_i}{b W_s L} \quad (28)$$

Finally, by integration, following equation was obtained,

$$t = - \left( \frac{b W_s L}{PA} \right) \ln \frac{M_E - M_C}{M_E - M_i} \quad (29)$$

Where  $t$  is time of storage,  $M_E$  is equilibrium moisture content of external environment,  $M_i$  is initial moisture content,  $M_C$  is critical moisture content, and  $b$  is sorption isotherm constant.

Limits of accuracy of Karel's model are :

- a. The assumed linearity of the moisture absorption
- b. The assumed proportionality between the pressure Difference and rate of water vapor transfer. This linearity does hold for hydrophobic materials, but not for hydrophilic materials.
- c. Rapid equilibrium of moisture content within the product is also often only partially true. It holds best for condition in which moisture transfer is slow.
- d. The assumed homogeneity of water vapor transfer through the package is also often incorrect. Seal areas, and crease areas are known to transmit water more rapidly than the flat portions of the package.

Labuza et al. (1972b) modified the Karel's model by lifting the assumption of the linear sorption isotherm. Labuza et al. combined non-linear sorption isotherm, such as Oswin isotherm, Kuhn isotherm, and Mizarahi isotherm and also calculated shelf life when chemical reactions with water occur. Their model is described as follows;

The rate of transport of water vapor is

$$\frac{dm}{dt} = \frac{P}{L} A [p_e - p_i] \quad (30)$$

where  $m$  is mass of water transported across film, g,  $t$  is time in day,  $P$  is permeability of film in water, mil/mm Hg.day,  $L$  is film thickness in mil,  $A$  is area of film, m<sup>2</sup>,  $p_e$  is vapor pressure of water outside of film, mmHg, and  $p_i$  is vapor pressure of water inside of film, mmHg.

Initial vapor pressure in the product then is solely determined by the water sorption isotherm of the food, which is a property of the food as given by equation (31)

$$M = f(A_w)_T = F[p_i - p_e]_T \quad (31)$$

where  $M$  is moisture content in g H<sub>2</sub>O per g solids,  $A_w$  is equilibrium water vapor activity,  $T$  is constant temperature. In the case of linear sorption isotherm,

$$M = b Aw + c$$

Where  $M$  is moisture content,  $b$  is slope, and  $c$  is constant.

$$\frac{dM}{dt} = \frac{dm}{dtW_s} = \left[ \frac{P}{L} \right] \frac{P_{sat}A}{b} [M_s - M] \quad (32)$$

$$t = \frac{W_s L}{P_{sat} A} \frac{b}{P} \ln \frac{M_s - M_i}{M_s - M_c} \quad (33)$$

where  $p_{sat}$  is saturated water vapor pressure at given constant temperature,  $W_s$  is dry weight of food,  $M_s$  is moisture content of food as predicted by the isotherm equation if exposed to the external package relative humidity,  $M_i$  is initial moisture content, and  $M_c$  is critical moisture content.

Clifford et al. (1977) reported a shelf life prediction model considering the moisture content in package head space under following assumptions :

- a. The shelf life of a product depends solely on moisture content.
- b. The moisture content of the packaged product is in equilibrium with the humidity inside the package.
- c. The relative humidity inside the package ( if the outside relative humidity and temperature are constant) is determined by the permeability of the package.

- d. The relationship between the moisture content of the product and the relative humidity can be represented by equilibrium moisture sorption isotherm curve.

Based on the above assumptions,

$$m_t = m_1 + m_2 \quad (34)$$

where  $m_t$  is total weight of water in package and food system,  $m_1$  is the weight of the water in product,  $m_2$  is the weight of the water in head space of package.

$$m_1 = M ( W_p / 100g ) \quad (35)$$

Where  $M$  is moisture content (g moisture /100 g dry product) and  $W_p$  is weight of the dry product.

The moisture content dependent on the internal humidity at constant temperature.

$$M = f ( RH_i ), \text{ therefore, } m_1 = W_p f ( RH_i ) \quad (36)$$

Using ideal gas law (water vapor is not an ideal gas, but the introduced error in this can be negligible).

$$m_2 = 18 ( V / R T ) P_{sat} ( RH_i / 100 ) \quad (37)$$

Where  $V$  is the volume of head space of the package,  $T$  is temperature in  $^{\circ}\text{K}$ ,  $R$  is gas constant,  $p_{\text{sat}}$  is saturated water vapor pressure at  $T$  temperature, and  $RH_i$  is the relative humidity inside package.

$$M = \frac{W_s}{100} f(RH_i) + 18 \frac{V}{RT} P_{\text{sat}} \frac{RH_i}{100} \quad (38)$$

Rate of penetration :

$$\frac{dm}{dt} = P \frac{A}{L} \frac{P_{\text{sat}}}{100} (RH_E - RH_i) \quad (39)$$

where  $P$  is permeability constant of the packaging material,  $A$  is surface area of the package,  $L$  is wall thickness, and  $RH_E$  is external relative humidity.

$$\frac{dm}{dt} = P \frac{A}{L} \frac{P_{\text{sat}}}{100} (RH_E - RH_i) = \frac{d}{dt} \left[ \frac{W_s}{100} f(RH_i) + 18 \frac{V}{RT} P_{\text{sat}} \frac{RH_i}{100} \right] \quad (40)$$

In the case of that sorption isotherm has linear relationship:

$$(m_i = a + b RH_i)$$

$$P \frac{A}{L} \frac{P_{\text{sat}}}{100} (RH_E - RH_i) = \frac{d}{dt} \left[ \frac{W_s}{100} (a + b RH_i) + 18 \frac{V}{RT} P_{\text{sat}} \frac{RH_i}{100} \right] \quad (41)$$

By integration, shelf life can be calculate by eqn. (43).

$$\frac{dH_i}{dt} = \frac{P \frac{A}{L} \frac{P_s}{100}}{18 \frac{P_s}{100} \frac{V}{RT} + \frac{bW_s}{100}} (H_o - H_i) \quad (42)$$

$$t = \frac{P \frac{A}{L} \frac{P_{sat}}{100}}{18 \frac{P_{sat}}{100} \frac{V}{RT} + \frac{bW_s}{100}} \ln \left[ \frac{(RH_g - RH_i)}{(RH_g - RH_t)} \right] \quad (43)$$

Peppas et al (1980) developed a model to account for the sensitivity of both packaged dehydrated food and hydrophobic packaging materials to vapor sorption. The author started with the general Nernst-Plank's diffusion equation applicable to the transport of n penetrants through polymeric films.

$$N_i = -CD_{im}d_i + X_i \sum_{j=1}^n \left( \frac{N_j}{D_{ij}} \right) / \sum_{j=1}^n \left( \frac{X_j}{D_{ij}} \right) \quad (44)$$

where  $N_i$  is the total mole flux of species i,  $X_i$  is the mole fraction of species i, C is the total concentration,  $D_{ij}$  is multicomponent diffusivity for the diffusion of i in a mixture, and  $d_i$  is the driving force for transport of the ith component through the system.

The following assumption were used:

- a . Homogeneous polymeric film.
- b . Only water vapor diffusing through film.
- c . Henry's law dissolution constant application to link the in-film water concentration with the external

water vapor pressure.

d . Small solubility of the water vapor in the film.

e . Sealed package without external/internal pressure difference.

Based on the above assumptions, Nernst-plank's equation is modified into a simplified equation for water vapor transport.

$$\frac{dM}{dt} = \frac{PA}{W_s} (Aw_s - Aw_i) \quad (45)$$

Where M is mass of water absorbed per mass of dry food product, W<sub>s</sub> is mass of packaged food product, P is water vapor permeability, A is surface area, and Aw<sub>s</sub>, Aw<sub>i</sub> are external and internal water activities.

They conjugated above the equation with several non-linear sorption isotherm which can be applied to food in various range water activities, such as Langmuir, Halsey, B.E.T, Oswin and Freundlich isotherm by using numerical method.

In the case of B.E.T sorption isotherm application :  
B.E.T sorption isotherm :

$$\frac{Aw}{m(1-Aw)} = \frac{1}{m_s C} + \frac{C-1}{m_s C} Aw \quad (46)$$



combining eqn.(45) and (46)

$$\int_{Aw_1}^{Aw_2} \frac{1 + (C-1)Aw^2}{(Aw_2 - Aw)(1 - Aw)^2 [1 + (C-1)Aw]^2} = \beta t \quad (47)$$

where,

$$\beta = \frac{PA}{W_s} \frac{1}{Cm_s}$$

With this equation, they predicted the water vapor activity in packages.

Also they applied diffusion theory to solute-polymer systems exhibiting thermodynamic compatibility, namely, the solubility of the solute in the film is not negligible. In this case, the molar fraction of water in the film  $X_w$  must be included in the equation.

Wang (1985) had described a model for predicting the shelf life of moisture sensitive product stored at constant temperature and relative humidity condition. The basic equation used was

$$t = \frac{W_s}{PP_{sat_{M_1}}} \int_{M_1}^{M_2} \frac{dM}{[Aw_E - f(M)]} \quad (48)$$

where  $t$  is time,  $W$ , is dry weight of product,  $P$  is permeability of the package,  $p_{\infty}$  is saturated vapor pressure of water,  $dM$  is moisture content difference,  $M_i$  is initial moisture content,  $M_t$  is moisture content at time  $t$ ,  $Aw_g$  is water activity external to the package, and  $f(M)$  is intermolecular water activity as function of moisture content.

Lee (1987) upgraded Wang's model by introducing the temperature of the package/environment system as a variable. Another modification included the use of the modified B.E.T sorption isotherm equation to fit the experimental sorption data of the product.

The effect of temperature on the permeability constant is expressed in following equations;

$$P = D_o S_o \exp\left(-\frac{E_d + E_s}{RT}\right) \quad (49)$$

$$P = P_o \exp\left(-\frac{E_a}{RT}\right) \quad (50)$$

The modified B.E.T. equation :

$$Q_o = \frac{BCJ}{(C_{sat} - C) \left[1 + (B-1) \left(\frac{C}{C_{sat}}\right)\right]} \quad (51)$$

where  $C_{\infty}$  is the saturation concentration of the solute,  $C$  is

the measured concentration of the solute, remaining in solution at equilibrium which is equivalent to relative humidity (RH),  $J$  is number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface,  $q_c$  is the number of moles of solute adsorbed per unit weight at concentration  $C$ , and  $B$  is constant.

Above equation describing the moisture content as a function of temperature and relative humidity can then be expressed as :

$$M = \frac{B(RH)J}{(C_{sat} - RH) [1 + (B-1) (\frac{RH}{C_{sat}})]} \quad (52)$$

Where  $M$  is moisture content (g water/ 100g solids).

By combining the permeability of the package, He developed moisture change model, as follows :

$$\frac{dm}{dt} = \frac{PAp_{sat}}{L} (Aw_E - Aw_I) \quad (53)$$

Since  $dM = dm / W_s$  (54)

Therefore,

$$\int_0^t dt = \frac{W_s L}{PA} p_{sat} \int_{M_I}^{M_E} \frac{dM}{(Aw_E - Aw_I)} \quad (55)$$

Water activity can be described as the function of

moisture content.

$$Aw_i = f(M) \quad (56)$$

The basic mathematical model for shelf life prediction :

$$t = \frac{W_s L}{P P_{sat}} \int_{M_i}^{M_t} \frac{dM}{[Aw_s - F(M)]} \quad (57)$$

To take into account the temperature variation of the equilibrium sorption isotherm, the B.E.T. equations were applied to obtain the equilibrium moisture content and the associated relative humidity values of the product at the desired temperature. The resultant isotherm data was then fitted by the described polynomial equation and substituted into eqn.(57) for shelf life estimation.

However, the basic mathematical model (eqn(57)) which Lee used is almost the same as Labuza's model which was developed 20 years ago and it has also the limits of Labuza's model.

Kirloskar (1991) combined the Lee' model with more two sorption isotherms such as Chen's and Henderson's isotherm by using Newton-Raphson method for solving equation. However, the basic mathematical model which she used also is the same as the model which Lee used. The basic mathematical model for shelf life prediction is the same as Wang's model, eqn.(48).

But Kirloskar used two different non linear sorption isotherms, Chen's and Henderson equation.

Chen equation :

$$M = \frac{k - \ln(-\ln A_w)}{a} \quad (58)$$

Henderson equation :

$$M = \exp\left(\frac{1}{n} [\ln(-\ln(1 - A_w)) - \ln K]\right) \quad (59)$$

Effect on temperature on sorption isotherm :

$$M(T) = F [ A_w \quad b(T), c(T), d(T) ] \quad (60)$$

$$A(M, T) = f [ M, B(T), C(T), D(T) ] \quad (61)$$

By using the Newton-Raphson method, she solved the equation which contained the effect of temperature on the permeability and sorption isotherm equation.

#### 2.4. FINITE DIFFERENCE METHOD

Exact solutions to differential equations governing moisture movement can be obtained for simple geometries; sphere, slab or a cylinder (Crank, 1975). The solutions are obtained for only each fixed geometry, but when the total package, product and headspace of package are considered at the same time, the solution become more complicated and often does not exist. Numerical techniques can be utilized for the more complex but closer to real life situations. Among numerical methods available to solve the governing differential equations for moisture transfer are the Finite difference and finite element analysis. Even though the finite difference method often results in long computation times, it is easier to use and the results are very correct for simple geometry such as sphere and plate type than finite element analysis. The finite difference method of analysis is based on the approximation by difference derivative at a point.

From Figure 4, the first order differential equation and the second order differential equation can be expressed in finite difference scheme.

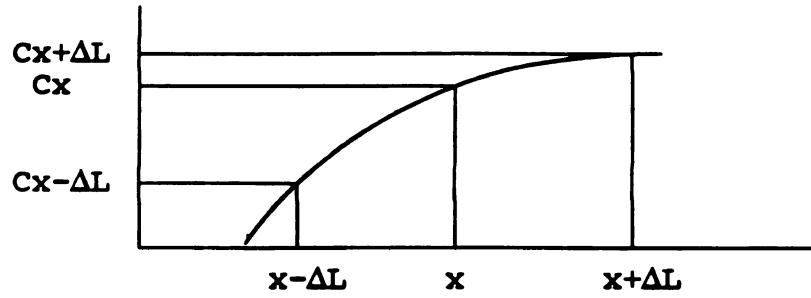


Figure 4. Finite different method

The first order differential equation is

$$\frac{\partial C}{\partial X} = \frac{\Delta C}{\Delta X} = \frac{C_{x+\Delta L} - C_x}{x+\Delta L - x} = \frac{C_{x+\Delta L} - C_x}{\Delta L} \quad (62)$$

The second order differential equation can be obtained from eqn. (62) .

$$\frac{\partial^2 C}{\partial X^2} = \frac{\frac{C_{x+\Delta L} - C_x}{\Delta L} - \frac{C_x - C_{x-\Delta L}}{\Delta L}}{\Delta L} = \frac{C_{x+\Delta L} - 2C_x + C_{x-\Delta L}}{\Delta L^2} \quad (63)$$

### III. DEVELOPMENT OF THE MATHEMATICAL MODEL

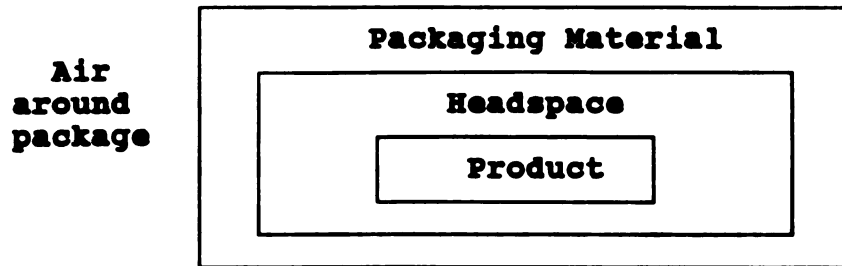


Figure 5. Package and Product Diagram

#### 3.1. ASSUMPTIONS

The mathematical model was developed based on the following assumptions:

- 1) Water is transferred through the polymer packaging material and product by molecular diffusion.
- 2) Sorption isotherms of packaging material and product are known.
- 3) The shelf life of the product depends on physical and/or chemical qualities which are solely related to the moisture content of the product.
- 4) The temperature and the relative humidity outside the package are constant.
- 5) Sorption/desorption hysteresis in the product is negligible.



- 6) The water vapor concentration in the headspace surrounding the product is always homogeneous.
- 7) Initial concentrations of water in the product, headspace, and packaging material are all in thermodynamical equilibrium.
- 8) The diffusion coefficients of the polymer and product depend only on temperature.
- 9) Product has simple geometry such as a sphere or circular plate. In the latter case, transfer of water occurs only through both circular faces and not through the edge.

### 3.2. PRESENTATION OF THE SOLUTION

The solution is presented in matrix form as shown in Figure 6. An entry in the matrix gives the concentration of water at a particular location (column) and time (row). The water concentration in the external environment is considered as a constant ( $C_E$ ) during the run, the initial water concentration of packaging material, headspace, and product are denoted by  $C_{LN,0}$ ,  $C_{H,0}$ , and  $C_{RU,0}$ , respectively.

Fick's Law, Henry's Law, and the ideal Gas Law allow us to calculate the concentration of water within the three regions (packaging ( $C_{LN,i}$ ), headspace ( $C_{H,i}$ ), product ( $C_{RU,i}$ ) through a mass balance. The finite difference

(F.D.) method was applied to solve the set of differential equation generated. Computer schemes will be developed which will allow for the remainder of the table to be filled in. This will be done row by row from left and right.

Time	A i r  $C_E$	Layers			Head space  $C_H$	Shells		
		0	.....	N		0	....	U
		$C_{LE}$	.....	$C_{LH}$		$C_{RH}$	....	$C_{RC}$
$t=0$	$C_E$	$C_{LE}$	$C_{LN,0}$	$C_{LH,0}$	$C_{H,0}$	$C_{RH,0}$	$C_{RU,0}$	$C_{RC,0}$
$t=1\Delta t$	$C_E$	$C_{LE}$	$C_{LN,t}$	$C_{LH,t}$	$C_{H,t}$	$C_{RH,t}$	$C_{RU,t}$	$C_{RC,t}$
$t=2\Delta t$	$C_E$	$C_{LE}$	$C_{LN,t}$	$C_{LH,t}$	$C_{H,t}$	$C_{RH,t}$	$C_{RU,t}$	$C_{RC,t}$
$t=3\Delta t$	$C_E$	$C_{LE}$	$C_{LN,t}$	$C_{LH,t}$	$C_{H,t}$	$C_{RH,t}$	$C_{RU,t}$	$C_{RC,t}$

.	.	.	.	.	..	.	.	....	.
Air around package		packaging material			Head space	product			

Figure 6. The concentration matrix

### CALCULATION OF THE WATER VAPOR CONCENTRATIONS

#### 3.3. CALCULATION OF THE WATER VAPOR CONCENTRATION IN THE OUTSIDE PACKAGE ( $C_E$ )

With given temperature and relative humidity values for the storage conditions,  $C_E$  can be calculated based on psychrometric data. The absolute humidity, AH, obtained from a psychrometric chart at saturation temperature is given in

1 gram of moisture per a gram of air. Since 1 gm of air occupies a volume of

$$V = \frac{nRT}{P} = \frac{\left(\frac{1g}{28.8g/mole}\right) \left(45.59 \frac{ml \cdot atm}{mole \cdot ^\circ R}\right) T}{1atm}$$

$$V = 1.5829 T \quad (64)$$

where V is in ml and T is in  $^\circ R$ . If room temperature is  $23^\circ C$ , it is  $532^\circ R$ . The concentration of water in air at saturation (gram/ml) is

$$C_{sat} = \frac{AH}{1.5829 T} \quad (65)$$

$$C_R = (RH/100) C_{sat}$$

The concentration at any other relative humidity then is

$$C_R = (RH/100) (AH/1.5829 T) \quad (66)$$

#### 3.4. CALCULATION OF THE WATER VAPOR CONCENTRATION OF THE PACKAGING MATERIAL IN EQUILIBRIUM WITH $C_E$ , $C_{LE}$

To get  $C_{LE}$ , Henry's Law can be applied. Accordingly the concentration at the outside interface of the polymer packaging material is related to the concentration in the

surrounding air and the solubility of water in the material,

$$C_{LE} = H_L C_E \quad (67)$$

where  $H_L$  is the Henry's Constant in  $(g \text{ H}_2\text{O}/\text{cm}^3 \text{ polymer})/(g \text{ H}_2\text{O}/\text{cm}^3 \text{ air})$  and depends only on the packaging material and temperature. The procedure to calculate  $H_L$  in  $(g \text{ H}_2\text{O}/\text{cm}^3 \text{ polymer})/(g \text{ H}_2\text{O}/\text{cm}^3 \text{ air})$  from solubility in  $\text{cm}^3 \text{ H}_2\text{O}/(\text{cm}^3 \text{ polymer} \times \text{Pa})$  or  $g \text{ H}_2\text{O}/g \text{ polymer}$  is given in Appendix 1.  $C_{LE}$  is constant for an entire set of calculations at given temperature and relative humidity.

**3.5. CALCULATION OF THE INITIAL WATER VAPOR CONCENTRATIONS INSIDE THE SURFACE OF THE PACKAGING MATERIAL ( $C_{LE}|_{t=0}$ ), IN HEADSPACE ( $C_H|_{t=0}$ ), AND IN THE PRODUCT ( $C_{RH}$  TO  $C_{RE}|_{t=0}$ ).**

Product has initial moisture content ( $M_i$ ). We assume that the initial concentrations of water vapor in headspace ( $C_H|_{t=0}$ ), in the product ( $C_{RH}|_{t=0}$ ) and on internal surface of packaging material are all in equilibrium. Therefore, we can calculate the initial concentration of water vapor in product with  $M_i$ .

$$C_{RH}|_{t=0} = M_i W_s / (100 V_R) \quad (68)$$

where  $C_{RH}|_{t=0}$  is in g/ml of product,  $M_i$  is in g  $H_2O$ /100 g dry product,  $W_i$  is dry weight of product in grams, and  $V_R$  is volume of product in ml. Accordingly, the concentration of water vapor within product is  $C_{RH}|_{t=0}$ .

To get  $C_H|_{t=0}$  with  $C_{RH}|_{t=0}$ , we can use either Henry's Law or any other sorption isotherm. The sorption isotherm of many food as well as a pharmaceutical tablet can be very well represented by the three parameter G.A.B equation. The G.A.B sorption isotherm is given in eqn.(18).

The initial moisture content ( $M_i$ ) of product can be used in eqn.(18) to get  $A_w|_{t=0}$  in headspace. By using of eqn.(65), the initial homogenous water vapor concentration in the headspace,  $C_H|_{t=0}$ , can be calculated at a given temperature, once  $A_w|_{t=0}$  is obtained from eqn.(18).

$$C_H|_{t=0} = A_w|_{t=0} \times C_{sat}$$

where  $C_{sat}$  is given in eqn.(65).

Therefore,

$$C_H|_{t=0} = A_w|_{t=0} \frac{AH}{1.5829T} \quad (69)$$

The initial water concentration at package internal **interface**,  $C_{LH}|_{t=0}$ , is considered to be in equilibrium with the

initial headspace concentration. The concentration on the surface of the packaging material can be obtained directly from the headspace concentration using Henry's Law for water/package material.

$$C_{LH}|_{t=0} = H_L C_H|_{t=0} \quad (70)$$

According to assumption number 7 on page 41, initially, concentration of water vapor inside packaging material are is homogenous and equal to  $C_{LH}|_{t=0}$ .

### 3.6. CALCULATION OF WATER VAPOR CONCENTRATIONS IN THE PACKAGING MATERIAL ( $C_{LN,t}$ ) AT TIME $t$ .

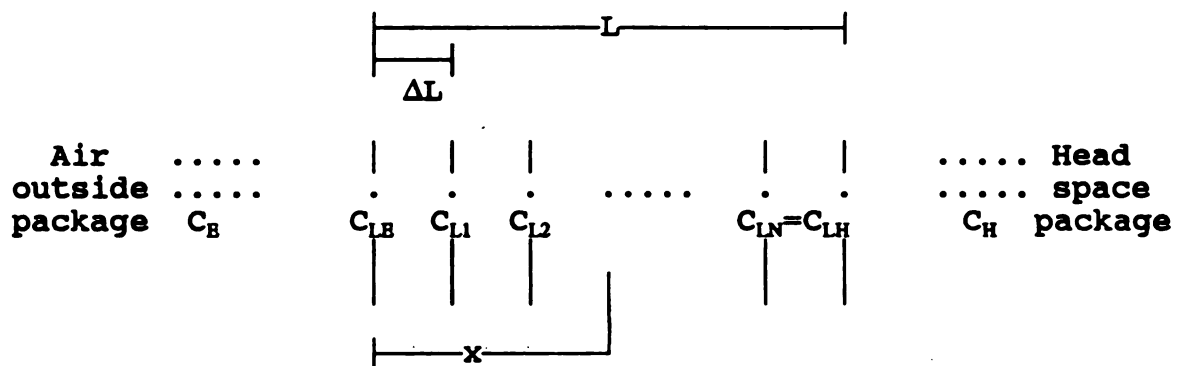


Figure 7. Subdivision of the packaging material into  $N$  thin layers,  $\Delta L$  thick.  $\Delta L = L/N$ .

A mass balance on a "layer" of thickness  $dx$  of packaging material located a distance  $x$  into the material (measured from the left side) as indicated in Fig.6 will be

given by

$$\begin{array}{ccccc} \text{(Flow into)} & - & \text{(Flow out of)} & = & \text{(rate of increase)} \\ \text{left face} & & \text{right face} & & \text{inside layer} \end{array}$$

or

$$-D_L \frac{\partial C}{\partial X} \Big|_x A_L - (-D_L \frac{\partial C}{\partial X} \Big|_{x+\Delta L} A_L) = A_L dX \frac{\partial C}{\partial t}$$

simplifying will obtain

$$\frac{\partial^2 C}{\partial X^2} = \frac{1}{D_L} \frac{\partial C}{\partial t} \quad (71)$$

where  $C$  is the concentration of water (grams/ ml of packaging material),  $D_L$  is the diffusion coefficient for water in the packaging material, and  $A$  is the surface area of the package. Equation (71) is subject to the following

initial Condition : at  $t = 0$ ,  $0 \leq x < L$ ,  $C_L = C_{LH}$

$$x = L, \quad C_L = C_R \Big|_{t=0}$$

and boundary Condition : for  $t > 0$ ,  $x = 0$ ,  $C_L = C_{LH}$

Applying the Finite difference general expressions indicated by eqn.(62) and (63) to eqn.(71) gives the following

$$\frac{\partial C}{\partial X} = \frac{C_{x+\Delta L} - C_x}{\Delta L} \Big|_t \quad (72)$$

$$\frac{\partial^2 C}{\partial X^2} = \frac{C_{x+\Delta L} - 2C_x + C_{x-\Delta L}}{\Delta L^2} \Big|_t \quad (73)$$

$$\frac{\partial C}{\partial t} = \frac{C_{t+\Delta t} - C_t}{\Delta t} \Big|_x \quad (74)$$

where  $\Delta L$  is the thickness of a layer as indicated in Fig.7 and  $\Delta t$  is the time step. Substituting eqn.(72), (73), and (74) into the eqn.(71) and rearranging,

$$C_{X,t+\Delta t} = QC_{X-\Delta L,t} + (1-2Q)C_{X,t} + QC_{X+\Delta L,t} \quad (75)$$

where  $Q = D_L \Delta t / (\Delta L)^2$ .  $Q$  depends on the geometry of product. Whenever we change the geometry of product, we have to check stability of this  $Q$  value. For the numerical stability of the computer, normally, it must be less than 0.3. A detailed explanation is given in Appendix 2.

This equation relates the concentration at time  $\Delta t$  later (next row in Fig.6) to the concentrations in the previous row.

In terms of the boxes in the matrix in Fig.6, this scheme can be presented as :

$$Q = D_L \Delta t / (\Delta L)^2$$

Q	1-2Q	Q
	$C_{LN,t}$	

which indicate that the unknown concentration in the box marked  $C_{LN,t}$  in Fig. 6 can be determined as the weighed sums of



the concentrations in the previous row. The scheme may be used only up to the (N-1)st layer ( the last column marked  $C_{LH,t}$ ) since the diffusion eqn.(71) applies to points inside the material only.

**3.7. CALCULATION OF WATER VAPOR CONCENTRATIONS IN THE INSIDE SURFACE OF THE PACKAGING MATERIAL ( $C_{LH}$ ), THE HEADSPACE ( $C_H$ ), AND THE INSIDE SURFACE OF SPHERICAL SHAPE PRODUCT ( $C_{RH}$ ) AT TIME  $t$**

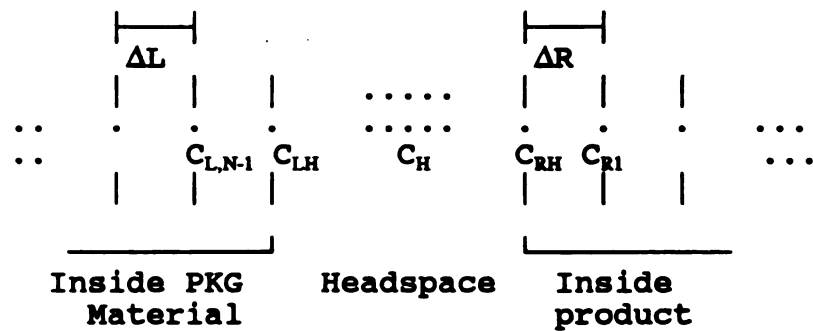


Figure 8. Headspace and interface concentrations

A mass balance on water around the headspace will relate the concentrations of diffusing water vapor at the inside surface of the package  $C_{LH}$ , the headspace  $C_H$ , and at the surface of the product  $C_{RH}$  at any time  $t > 0$ .

The headspace mass balance is as follows:

$$\begin{array}{rcl}
 \text{(Flow out of)} & - & \text{(Flow into )} = \text{(rate of increase)} \\
 \text{the inside} & & \text{the inside} & & \text{in headspace} \\
 \text{surface of} & & \text{surface of} & & \\
 \text{package} & & \text{Product} & & 
 \end{array}$$

or

$$(-DA \frac{\partial C}{\partial X})_{PKG} - (-DA \frac{\partial C}{\partial R})_{product} = V_H \frac{\partial C_H}{\partial t} \quad (76)$$

where  $V_H$  is the volume of air in the headspace.

Equation (76) is subject to the following

Initial Condition : at  $t = 0$ ,  $C_H = C_H|_{t=0}$

Eqn.(76) can be casted into F.D. form, and the following expression is obtained.

$$-(DA)_L \frac{C_{LH} - C_{L,N-1}}{\Delta L} |_t - (DA)_R \frac{C_{RS} - C_{R1}}{\Delta R} |_t = V_H \frac{C_H|_{t+\Delta t} - C_H|_t}{\Delta t}$$

And rearranging,

$$C_H|_{t+\Delta t} = C_H|_t + a1(C_{L,N-1} - C_{LS})_{PKG} + b1(C_{R1} - C_{RS})_{Product} \quad (77)$$

where

$$a1 = \frac{\Delta t}{V_H} \left( \frac{DA}{\Delta L} \right)_L$$

$$b1 = \frac{\Delta t}{V_H} \left( \frac{DA}{\Delta R} \right)_R$$

For numerical stability,  $a1$  and  $b1$  have following relationship,

$$\frac{b1 * C_{RH}|_{t=0}}{a1 * C_{LH}|_{t=0}} < 1000$$

a detailed explanation is given in Appendix 2.

In terms of the matrix locations in Figure 6, this F.D. scheme can be written as,

$C_{L,N-1}$	$C_{LH}$	$C_H$	$C_{RH}$	$C_{R1}$
a1	-a1	1	-b1	b1
		$C_{H,t}$		

The concentration on the internal surface of the packaging material (marked  $C_{H,t}$  in Fig.6) is obtained directly from the headspace concentration using Henry's Law.

$$C_{LH} = H_L C_H \quad (78)$$

The product surface concentration,  $C_{RH}$ , is obtained by using the G.A.B sorption isotherm given by eqn.(18).

$$A_w = C_H / C_{\infty} \quad (79)$$

Initially the headspace concentration,  $C_H$ , is calculated using eqn.(77), and  $C_{\infty}$  is calculated by eqn.(65). After time  $>0$ ,  $A_w$  in eqn.(18) is calculated by eqn.(79). Then  $A_w|_{t+\Delta t}$  can be calculated by G.A.B sorption isotherm in eqn.(18) to calculate moisture content at surface of product, M.

$$M = \frac{A_N|_{t+\Delta t}}{a(A_N|_{t+\Delta t})^2 + b(A_N|_{t+\Delta t}) + c} \quad (80)$$

where  $M$  is in gm  $H_2O/100$  gm dry product.

Therefore,  $C_{RH} = M W_p / (100 V_R)$  (81)

where  $W_p$  is dry weight of product,  $V_R$  is volume of product.

### 3.8. CALCULATION OF WATER VAPOR CONCENTRATIONS INSIDE THE PRODUCT ( $C_{RU,t}$ ) AT TIME $T$ .

Two simple geometries for the product were studied, spherical and circular plate.

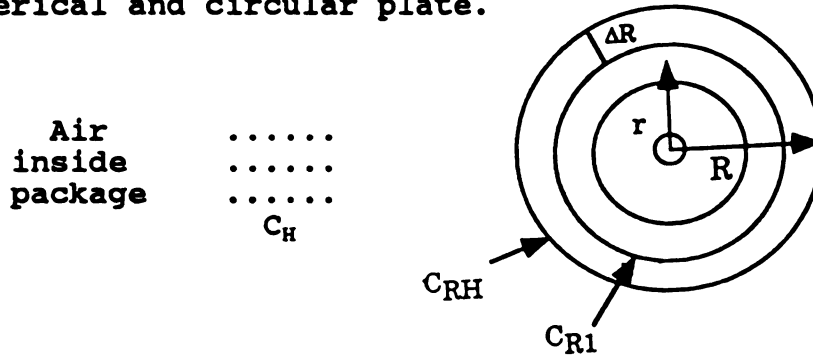


Figure 9. Subdivision of a spherical product into  $U$  shells. The thickness  $\Delta R$  of each shell is  $\Delta R = R/U$

In order to find the concentration of the diffused water vapor within the product, a mass balance is done on water in the one shell in Fig.9,

$$\begin{array}{ccccc}
 \text{( Amount )} & - & \text{( Amount )} & = & \text{(rate of )} \\
 \text{leaving} & & \text{entering} & & \text{increase} \\
 \text{outer} & & \text{inner} & & \text{inside} \\
 \text{surface} & & \text{surface} & & \text{shell}
 \end{array}$$

tahr can be rewritten as

$$-D_R \frac{\partial C}{\partial r} \Big|_r (4\pi r^2) - [-D_R \frac{\partial C}{\partial r} \Big|_{r+dr} (4\pi (r+dr)^2)] = (4\pi r^2 dr) \frac{\partial C}{\partial t}$$

$$D_R \left[ \frac{\frac{\partial C}{\partial r} \Big|_{r+dr} (r+dr)^2 - \frac{\partial C}{\partial r} \Big|_r r^2}{dr} \right] = r^2 \frac{\partial C}{\partial t}$$

Writing the left hand side as  $D_R \partial/\partial r (r^2 \partial C/\partial r)$  and rearranging gives

$$\frac{2}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} = \frac{1}{D_R} \left( \frac{\partial C}{\partial t} \right) \quad (82)$$

Initial Condition : at  $t = 0$ ,  $0 \leq r \leq R$ ,  $C_R = C_{RH} \Big|_{t=0}$

The Finite Difference expressions which come from eqn.(62) and (63) for the derivatives in the above equation (82) are

$$\frac{\partial C}{\partial r} = \frac{C_{r+\Delta R} - C_r}{\Delta R} \Big|_t \quad (83)$$

$$\frac{\partial^2 C}{\partial r^2} = \frac{C_{r+\Delta R} - 2C_r + C_{r-\Delta R}}{\Delta R^2} \Big|_t \quad (84)$$

$$\frac{\partial C}{\partial t} = \frac{C_{t+\Delta t} - C_t}{\Delta t} \Big|_r \quad (85)$$

Substituting eqn.(83), (84), and (85) into eqn.(82) and rearranging gives,

$$C_{r,t+\Delta t} = GC_{r-\Delta R,t} + [1 - 2G(\frac{\Delta R}{r} + 1)] C_{r,t} + G(1 + 2\frac{\Delta R}{r}) C_{r+\Delta R,t} \quad (86)$$

Where  $G = D_r(\Delta t) / (\Delta R)^2$ . For numerical stability,  $G$  must be less than 0.3. A detailed explanation is given in Appendix 2.

The equation relates the concentration at time  $\Delta t$  later (next row in Fig.6) to the concentration in the previous row. In terms of the boxes in the matrix in Fig.6, this scheme can be presented as :

G	$1 - 2(\Delta R/r + 1)G$	$G(1 + 2\Delta R/r)$
	$C_{RU,i}$	

which says that the unknown concentration in the box marked  $C_{RU,i}$  in Fig. 6 can be determined as the weighted sums of the concentrations in the previous row. The weights are shown in

the boxes.

There is only one position in the matrix where this scheme will not work, and this is the center of product, because  $\partial C/\partial r=0$  there. Therefore, a different scheme is needed to calculate the concentration at the center. Applying Fick's Law to the center shell (sphere),

$$D_R \frac{C_{R,U-1} - C_{RC}}{\Delta R} \Big|_t 4\pi (\Delta R)^2 = \frac{4}{3} \pi (\Delta R)^3 \left[ \frac{C_{t+\Delta t} - C_t}{\Delta t} \Big|_{\text{center}} \right]$$

or

$$C_C \Big|_{t+\Delta t} = C_C \Big|_t + 3G(C_{U-1} - C_C) \Big|_t \quad (87)$$

3G	1-3G
	$C_{RC,t}$

At this point, we are able to calculate the concentrations in all of the columns in the solutions matrix in Fig.6 up to and including the one labelled headspace.

To calculate  $C_E$  in the first column, we use eqn.(66) with T and RH for the storage conditions. To get  $C_{LE}$  in the second column, we use eqn.(67).

Using initial moisture content ( $M_i$ ), we can calculate the

remainder of the initial concentrations in the same rows by assumptions with in eqn.(68), (69), and (70).

To get  $C_B$  and  $C_{LB}$  in row 2 in Fig.6, we can follow the same procedure as for initial step. This applies to the remaining rows also.

To get the concentrations inside the packaging material (marked  $C_{LN,i}$  in Fig.6), we use the F.D. scheme in eqn.(75) proceeding left to right.

We then use the F.D. scheme in eqn.(77) to get  $C_H$  (marked  $C_{H,i}$  in Fig.6) and then go back and get  $C_{LH}$  (marked  $C_{LH,i}$  in Fig.6) using eqn.(78). We now use eqn.(81) to get  $C_{RH}$  (marked  $C_{RH,i}$  in Fig.6) and the F.D. scheme in eqn.(86) and (87) to get the remaining concentrations (marked  $C_{RU,i}$  and  $C_{RC,i}$  in Fig.6).

This completes the F.D. scheme for the model. Every column in a given row may now be determined using the same equations and the values for the concentration in the previous row. The entire matrix in Fig. 6 can therefore be generated. If the product is not spherical, then the procedure is the same but the F.D. schemes in eqn.(86) and eqn.(87) are different. The appropriate schemes for the plate shaped products is shown in Appendix 3.



### 8. CALCULATION OF THE TOTAL WATER GAIN FOR THE PRODUCT

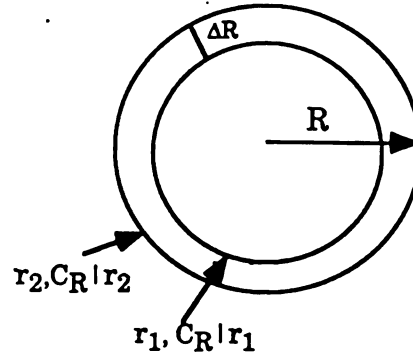


Figure 10. Concentrations within shells

The amount of water contained in the product (M) in g H<sub>2</sub>O at any instant is the concentration integrated over the volume,

$$M = \int_0^R C(4\pi r^2 dr) \quad (88)$$

It is assumed that water concentrations within each shell varies linearly. Therefore, the concentration of water at distant  $r$  in between  $r_1$  and  $r_2$  ( $\Delta R$ ) in Fig.10 is given by

$$C_R|_r = C_R|_{r_1} + \frac{C_R|_{r_2} - C_R|_{r_1}}{r_2 - r_1} (r - r_1) \quad (89)$$

Substituting eqn.(89) into eqn.(88)

$$M_{r_1} = \int_{r_1}^{r_2} \left[ C_R|_{r_1} + \frac{C_R|_{r_2} - C_R|_{r_1}}{\Delta R} (r - r_1) \right] 4\pi r^2 dr \quad (90)$$

and rearranging

$$\begin{aligned} M_{r_1} &= 4\pi (C_R|_{r_1} - (C_R|_{r_2} - C_R|_{r_1}) \frac{r_1}{\Delta R}) \int_{r_1}^{r_2} r^2 dr + (4\pi \frac{C_R|_{r_2} - C_R|_{r_1}}{\Delta R}) \int_{r_1}^{r_2} r^3 dr \\ &= \frac{4\pi}{3} (r_2^3 - r_1^3) \left[ C_R|_{r_1} \left(1 + \frac{r_1}{\Delta R}\right) - C_R|_{r_2} \frac{r_1}{\Delta R} \right] + \pi (r_2^4 - r_1^4) \left( \frac{C_R|_{r_2} - C_R|_{r_1}}{\Delta R} \right) \end{aligned}$$

Finally, the total moisture content of product after time  $t$  ( $M_t$ ) in g  $H_2O$  /100 g dry product is given by

$$M_t = (100/W_s) \sum_{i=1}^U M_{r_i} \quad (91)$$

#### **IV. THE COMPARISON BETWEEN FINITE DIFFERENCE SOLUTION AND ANALYTICAL SOLUTION**

In order to check the finite difference solutions, they were compared to the analytical solutions in some limiting cases. For the analytical solutions of the diffusion equations in the packaging material was developed by Crank (1975) when the penetrant concentrations of both side of packaging material are constant. For the analytical solutions of diffusion equations of two different shaped products were solved in Appendix 4 for limiting case, when there is no package, the product is exposed in environment.

##### **4.1. THE SOLUTION FOR WATER DIFFUSION EQUATION IN THE PACKAGING MATERIAL**

Crank (1975) solved the analytical solution for diffusion equation in a plane sheet under the unsteady state, when surface concentrations of both side are constant. Initial and boundary conditions are as follows,

Initial condition :  $t = 0, 0 < x < L, C = f(x)$

Boundary condition :  $t > 0, x = 0, C_L = C_{LE}$

$x = L, C_L = C_{LH}$

where  $C_{LE}$  is the water concentration of outside surface of plane sheet (at  $x = 0$ ),  $C_{LH}$  is the water concentration of inside surface of plane sheet ( at  $x = L$  )

The solution in the form of a trigonometrical series is

$$C = C_s + (C_{LH} - C_s) \frac{x}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_{LH} \cos(n\pi) - C_s}{n} \sin\left(\frac{n\pi x}{L}\right) \exp(-D_L n^2 t \pi^2 / L^2) \quad (100)$$

where  $D_L$  is the diffusion coefficient of packaging material,  $L$  is thickness of packaging material.

The analytical solution (eqn. (100)) and the finite difference solution (eqn.(75)) were compared and the results are shown in Table 3. Two different solutions generated the exactly equal output.

#### 4.2. THE SOLUTION FOR WATER DIFFUSION EQUATION IN THE PRODUCT

The moisture gain of the analytical solution which is solved in Appendix 4 and finite difference solution were compared for both spherical shaped product and circular plate shape product were compared in Table 4.

Equation (121) is used as the analytical solution , equation (86-1) and (91-1) as the finite difference solution for circular plate shape product. Equation (137) is used as the analytical solution , equation (86), (87) and (91) as the finite difference solution for spherical shaped product.

From Table 4, the finite difference solution of circular plate shaped product is fitted well to the analytical solution, but the finite difference solution of spherical shaped product is higher percent error than that of circular plate shaped product.

Table 3. Concentrations profile of the analytical solution and finite difference solution (g/cm<sup>3</sup>)

time (sec)	shape	Position in packaging material (cm)					
		x=0	x=2	x=4	x=6	x=8	x=10
25	F	80	42.3	16.69	4.81	0.99	0
	A	80	42.17	16.47	4.62	0.90	0
50	F	80	52.42	29.74	14.33	5.37	0
	A	80	52.37	29.66	14.24	5.31	0
100	F	80	57.14	36.97	21.06	9.28	0
	A	80	57.12	36.94	21.02	9.25	0
150	F	80	59.84	41.26	25.29	11.86	0
	A	80	59.83	41.27	25.28	11.85	0
200	F	80	61.46	43.89	27.89	13.46	0
	A	80	61.46	43.89	27.89	13.46	0
250	F	80	62.45	45.49	29.49	14.45	0
	A	80	62.45	45.49	29.49	14.45	0
300	F	80	63.14	46.61	30.61	15.14	0
	A	80	63.14	46.61	30.61	15.14	0

F is the solution of finite difference

A is the analytical solution

Data used in comparison :  $C_{1\infty} = 80 \text{ g/cm}^3$ ,  $C_{1x} = 0 \text{ g/cm}^3$ ,

$D_1 = 0.1 \text{ cm}^2/\text{sec}$ ,  $L = 10 \text{ cm}$

**Table 4. Comparison of moisture gain between the analytical solution and the finite difference solution (g/100 g dry product)**

Time (hrs)	Plate shape			Time (hrs)	Spherical shape		
	A	F	% error		A	F	% error
0.08	3.23	3.1	4.38	0.06	3.5	3.24	7.2
0.57	3.29	3.3	1.71	1.92	3.55	3.38	4.8
1.06	3.35	3.32	0.83	3.18	3.61	3.47	4.0
1.46	3.4	3.38	0.47	3.82	3.64	3.5	3.8
1.83	3.44	3.43	0.26	4.45	3.66	3.53	3.8
2.28	3.48	3.48	0	5.09	3.68	3.55	3.7
2.69	3.52	3.52	0	5.72	3.71	3.57	3.7
3.18	3.56	3.56	0	6.35	3.73	3.6	3.8

A is the analytical solution

F is the finite difference solution

Data used in comparison :

Diffusion coefficient of the product is  $1 \times 10^{-4}$  cm<sup>2</sup>/sec

Radius of spherical shaped product is 0.697 cm

Initial moisture content is 3 gH<sub>2</sub>O/100g dry product

critical moisture content is 4 gH<sub>2</sub>O/100g dry product

Thickness of circular plate shaped product is 0.5 cm

Concentration on the outside surface of product is 0.05 g/cm<sup>3</sup>

## **V. DATA ANALYSIS OF THE COMPUTER PROGRAM**

As an application of the computer program, the shelf-life of a multivitamin tablet with known sorption equilibrium isotherm is calculated. The tablet was packed in a blister package as indicated in Figure 11. The computer program analysis includes the study of the following variables on the shelf life of moisture sensitive product, diffusion coefficient and solubility constant of the water in packaging material, and diffusion coefficient of water in the product.

### **5.1. INPUT DATA**

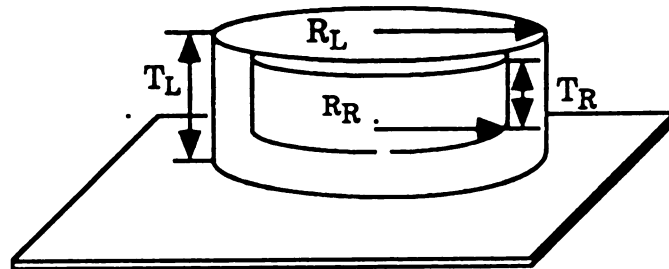
#### **5.1.1. External environmental conditions surrounding the package**

Since the sorption isotherm of the tablet was previously determined at 28°C (Kirloskar, 1990), the following conditions we selected:

- a. Temperature (T) = 28 °C.
- b. External environment relative humidity of outside  
(RHE) = 70 %
- c. Equivalent to an absolute humidity of outside (AH) =  
0.0243 gH<sub>2</sub>O/g air.

### 5.1.2. Geometry and dimensions of packaging and product

Geometry and dimension of package and product used for this simulation is shown in Figure 13. Accordingly, the surface area of packaging material related to diffusion of water, the inner volume of packaging material, the total area, and volume of the product are as follows, thickness of packaging material is taken in 0.005 cm.



$$\begin{aligned}
 R_L &= 1 \quad \text{cm} & T_L &= 0.7 \quad \text{cm} \\
 R_R &= 0.95 \quad \text{cm} & T_R &= 0.5 \quad \text{cm}
 \end{aligned}$$

Figure 11. Multivitamin tablet blister package



Surface area of blister package,  $A_L$ , and the inner volume,  $V_L$ , of the package can be calculated by the following equations.

$$A_L = \pi R_L^2 + 2\pi R_L T_L = \pi (1)^2 + 2(\pi)(1)(0.7) = 7.54 \text{ cm}^2$$

$$V_L = \pi R_L^2 T_L = \pi (1^2)(0.7) = 2.2 \text{ cm}^3$$

The area of the blister package exposed to the diffusion of water through the blister package does not consider the back of the blister generally made of aluminum foil. With respect to the tablet, it was assumed that the diffusion phenomena takes place only through the two circular face but not through the side area. Therefore, the surface area ( $A_R$ ) and volume ( $V_R$ ) of the circular plate shaped product can be calculated as follows;

$$A_R = 2 * \pi R_R^2 = 2\pi (0.95^2) = 5.67 \text{ cm}^2$$

$$V_R = (\pi R_R^2) T_R = \pi (0.95^2)(0.5) = 1.42 \text{ cm}^3$$

In order to compare the values of the shelf life, the volume and weight was kept constant. This gives a spherical radius of 0.697 cm. The surface area ( $A_R$ ) is calculated by

$$A_R = 4\pi R_R^2 = 4\pi (0.697^2) = 6.1 \text{ cm}^2$$

### 5.1.3. Diffusion coefficient ( $D_L$ ) and Henry's constant ( $H_L$ ) of packaging material

In order to minimize computing time, rigid polyvinylchloride (PVC) was selected as a packaging material to run the program. The diffusion coefficient and solubility of water in rigid PVC was obtained from Polymer Handbook (Brandrup, 1989).

$$D_L = 0.024 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$S_L = 870 \times 10^{-13} \text{ cm}^3 \text{ (STP) H}_2\text{O} / \text{cm}^3 \text{ PKG}$$

$S_L$  should be converted to Henry's law constant in  $(\text{gH}_2\text{O}/\text{cm}^3 \text{ polymer}) / (\text{gH}_2\text{O}/\text{cm}^3 \text{ Air})$  as indicated by eqn (92) in Appendix 1. Henry's constant ( $H_L$ ), of rigid PVC is 93.28  $(\text{gH}_2\text{O}/\text{cm}^3 \text{ PKG}) / (\text{gH}_2\text{O}/\text{cm}^3 \text{ Air})$ .

### 5.1.4. G.A.B constant

Table 5 presents experimental moisture sorption equilibrium data of multivitamin tablet (M) as a function of relative humidity (RH) at 21°C, 28°C, and 33°C, obtained by Kirloskar (1991)

With the above sorption isotherm data, G.A.B constants  $a, b$ , and  $c$  in eqn.(18) were calculated according to eqns.

(18) and (19) and given in Table 6.

Table 5. Sorption isotherm data of multivitamin tablet

21 °C		28 °C		33 °C	
RH	M	RH	M	RH	M
21.6	3.44	21.4	3.27	21.4	3.62
32	3.98	31.2	3.73	29.6	4.20
45	4.56	43.5	4.32	42	4.73
55.1	4.83	53.5	4.62	52	5.13
62.5	5.42	62	5.25	62	5.81
78.5	7.13	77.5	6.95	77	7.56
88.5	8.33	88	8.15	88	8.59

RH is Relative Humidity in %

Mo is Equilibrium Moisture content in gH<sub>2</sub>O/100g dry Wt.

Table 6. Exprimental G.A.B constants of the multivitamin tablet

Temp.	a	b	c
21 °C	-0.2425096	0.3329983	0.006503889
28 °C	-2.511928	0.3379882	0.003707545
33 °C	-2.340032	0.3200488	0.008387779

#### 5.1.5. Initial and critical moisture content

The initial moisture content was taken as 3 gH<sub>2</sub>O/100g dry product, the critical moisture content was considered 4 gH<sub>2</sub>O/100g dry product, and dry mass of product was taken as 1.7 g. These numbers were selected to keep the computer time within a reasonable range.

## 5.1.6. Data used in simulation

All data used in simulation are summarized Table 7.

Table 7. Data used in simulation

Components	Symbol	Values	Units
External environment	T	28	°C
	RH <sub>R</sub>	70	%
	AH	0.0243	g H <sub>2</sub> O/g Air
Package (Rigid PVC)	D <sub>L</sub>	0.24	$\times 10^{-7}$ cm <sup>2</sup> /sec
	H <sub>L</sub>	93.28	$\frac{\text{g H}_2\text{O}}{\text{cm}^3 \text{ PKG}}$
			$\frac{\text{g H}_2\text{O}}{\text{cm}^3 \text{ Air}}$
	L	0.005	cm
	A <sub>L</sub>	7.54	cm <sup>2</sup>
	V <sub>L</sub>	2.2	cm <sup>3</sup>
Product Pharmaceutical tablet	N	5	
	D <sub>R</sub>	1	$\times 10^{-5}$ cm <sup>2</sup> /sec
	M <sub>I</sub>	3	$\frac{\text{g H}_2\text{O}}{100\text{g dry weight of product}}$
	M <sub>C</sub>	4	"
	W	1.7	g
	R(S)	0.697	cm (Spherical shape)
	R(P)	0.95	cm (Circular plate shape)
	T <sub>R</sub> (P)	0.5	cm (Circular plate shape)
	a	-0.2511928	-
	b	0.3379882	-
	c	0.003707545	-
	U	5	

## **5.2. THE EFFECT OF NUMBERS OF SHELLS IN WHICH THE PRODUCT IS DIVIDED FOR CALCULATION PURPOSE**

The number of shells of in which the product is divided (U) was expected to effect the accuracy of the shelf life calculations and computing time. According to the finite difference method, as U increases, the computing results are more accurate, but computing time is longer. Therefore, it is necessary to find out the minimum U value to obtain an acceptable accuracy of the shelf-life of and running time. Table 8.A and 8.B and Figure 12 and 13 show the results when value ranged from 10 to 80 shells.

From the Table 8.A and 8.B and Figure 12 and 13, it is apparent that a U equal to 80 for spherical shaped product and 60 for circular plate shaped product will yield an error less than 0.2%.

**Table 8.A Effect of number of shells of the spherical shape product on the shelf life (hours)**

Shelf life	Number of shells							
	10	20	30	40	50	60	70	80
(hrs)	462.5	496.8	504.8	509.0	511.8	513.2	514.6	515.3

Diffusion coef. of polymer PKG material =  $2.4 \times 10^{-8}$  cm<sup>2</sup>/sec  
 Henry's law constant = 93.28 (gH<sub>2</sub>O/cm<sup>3</sup> PKG)/(gH<sub>2</sub>O/cm<sup>3</sup> air)  
 Diffusion coefficient of Product =  $1 \times 10^{-8}$  cm<sup>2</sup>/sec  
 Other data are the same as data in Table 7

**Table 8.B Effect of number of shells of the circular plate shape product on the shelf life (hours)**

Shelf life	Number of shells							
	10	20	30	40	50	60	70	80
(hrs)	281.0	313.2	322.2	326.4	329.2	330.6	332.0	332.6

Diffusion coef. of polymer PKG material =  $2.4 \times 10^{-8}$  cm<sup>2</sup>/sec  
 Henry's law constant = 93.28 (gH<sub>2</sub>O/cm<sup>3</sup> PKG)/(gH<sub>2</sub>O/cm<sup>3</sup> air)  
 Diffusion coefficient of Product =  $1 \times 10^{-8}$  cm<sup>2</sup>/sec  
 Other data are the same as data in Table 7

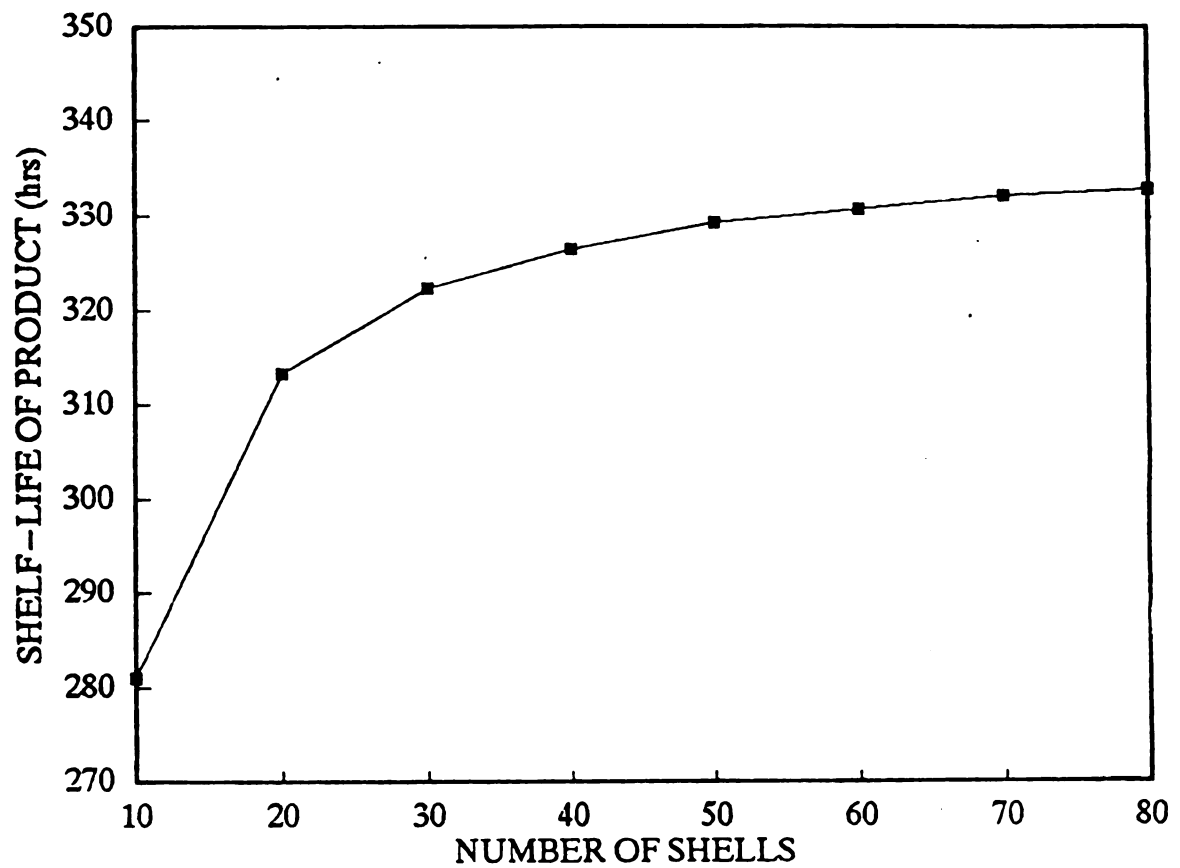


Figure 12. Effect of number of shells of the spherical shape product on the shelf life (hours)

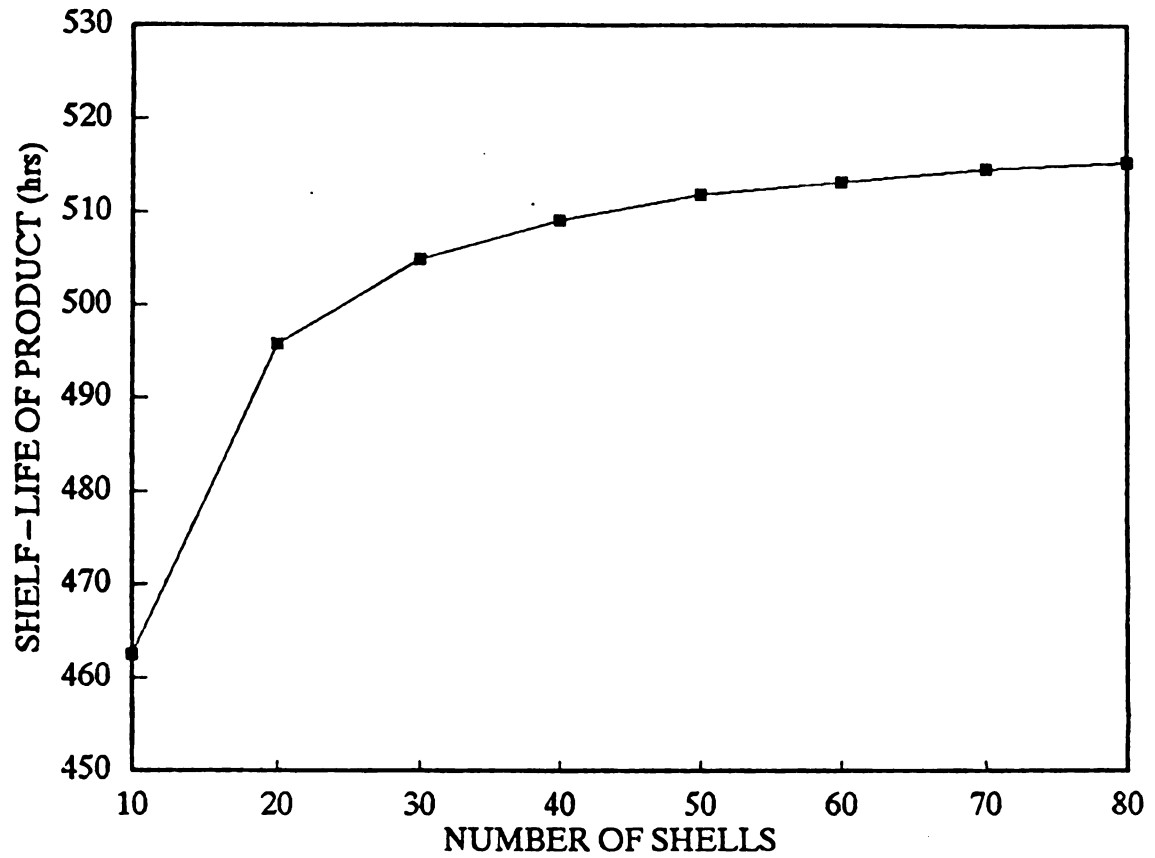


Figure 13. Effect of number of shells of the circular plate shape product on the shelf life (hours)



### 5.3. THE EFFECT OF DIFFUSION COEFFICIENT OF PACKAGING MATERIAL AND TABLET ON SHELF-LIFE

The effect of the diffusion coefficient of the tablet and the diffusion coefficient of the packaging material, on the product shelf life is presented in Table 9.A and 9.B and Figure 14 and 15.

From the Table 9.A and 9.B and Figure 14 and 15. It can be observed that as the diffusion coefficient of packaging material and tablet increase, the shelf life tends to decrease and reaches plateau. Amount of water absorbed in product is limited by the water vapor transmission rate of packaging material, in that range, diffusion coefficient of packaging material is dominating factor in water vapor transport. When diffusion coefficient of product is similar to the that of packaging material each other, the diffusion coefficient of the product has great effect on the shelf life.

It can be seen that after the diffusion coefficient of the product reaches a value of  $1 \times 10^{-7} \text{ cm}^2/\text{sec}$ , the self life value does not change significantly. In this case, the analytical solution was obtained in Appendix 4.

**Table 9.A. Effect of the diffusion coefficient of packaging material and the spherical shape tablet on the shelf life (hours)**

Diff. Coef of PKG (cm <sup>2</sup> /sec)	Diffusion coef. of the tablet (cm <sup>2</sup> /sec)					
	1E-9	5E-9	1E-8	5E-8	1E-7	5E-7
2.4*10 <sup>-9</sup>	5149	3516	3564	3594	3515	3706
2.4*10 <sup>-8</sup>	2420	735	515	352	356	357
2.4*10 <sup>-7</sup>	2113	450	242	73.8	51.5	35.2

Number of shells of tablet = 80

Henry's law constant = 93.28 (gH<sub>2</sub>O/cm<sup>3</sup> PKG)/(gH<sub>2</sub>O/cm<sup>3</sup> air)

Other data are the same as data in Table 5, except for diffusion coefficient of packaging material and tablet

**Table 9.A. Effect of the diffusion coefficient of packaging material and the circular plate shapetablet on the shelf life (hours)**

Diff. Coef of PKG (cm <sup>2</sup> /sec)	Diffusion coef. of the tablet (cm <sup>2</sup> /sec)					
	1E-9	5E-9	1E-8	5E-8	1E-7	5E-7
2.4*10 <sup>-9</sup>	3343	1728	1461	1214	1180	1180
2.4*10 <sup>-8</sup>	1764	506	335	173	146	121
2.4*10 <sup>-7</sup>	1563	331	176	50.5	33.4	17.3

Number of shells of tablet = 60

Henry's law constant = 93.28 (gH<sub>2</sub>O/cm<sup>3</sup> PKG)/(gH<sub>2</sub>O/cm<sup>3</sup> air)

Other data are the same as data in Table 5, except for diffusion coefficient of packaging material and tablet

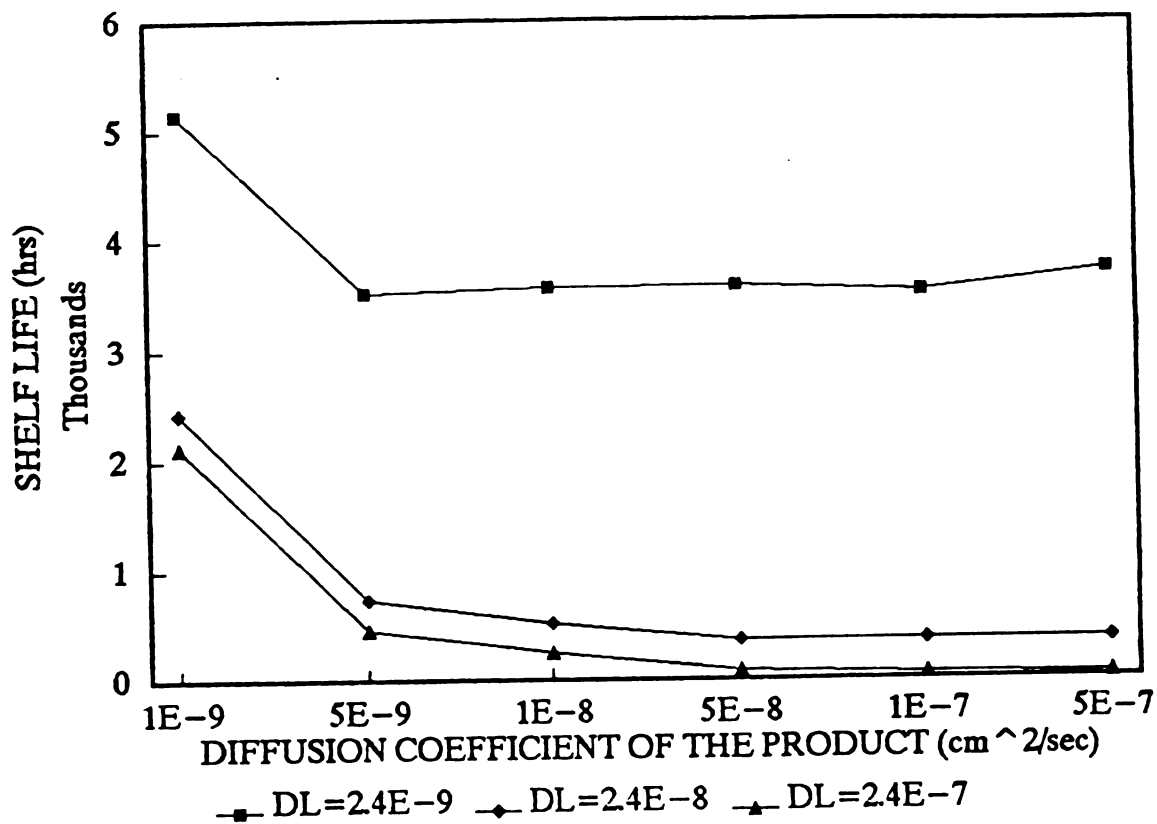


Figure 14. Effect of diffusion coefficient of packaging material and the spherical shape tablet on the shelf life (hours), where DL is diffusion coefficient of polymer packaging material ( $\text{cm}^2/\text{sec}$ )

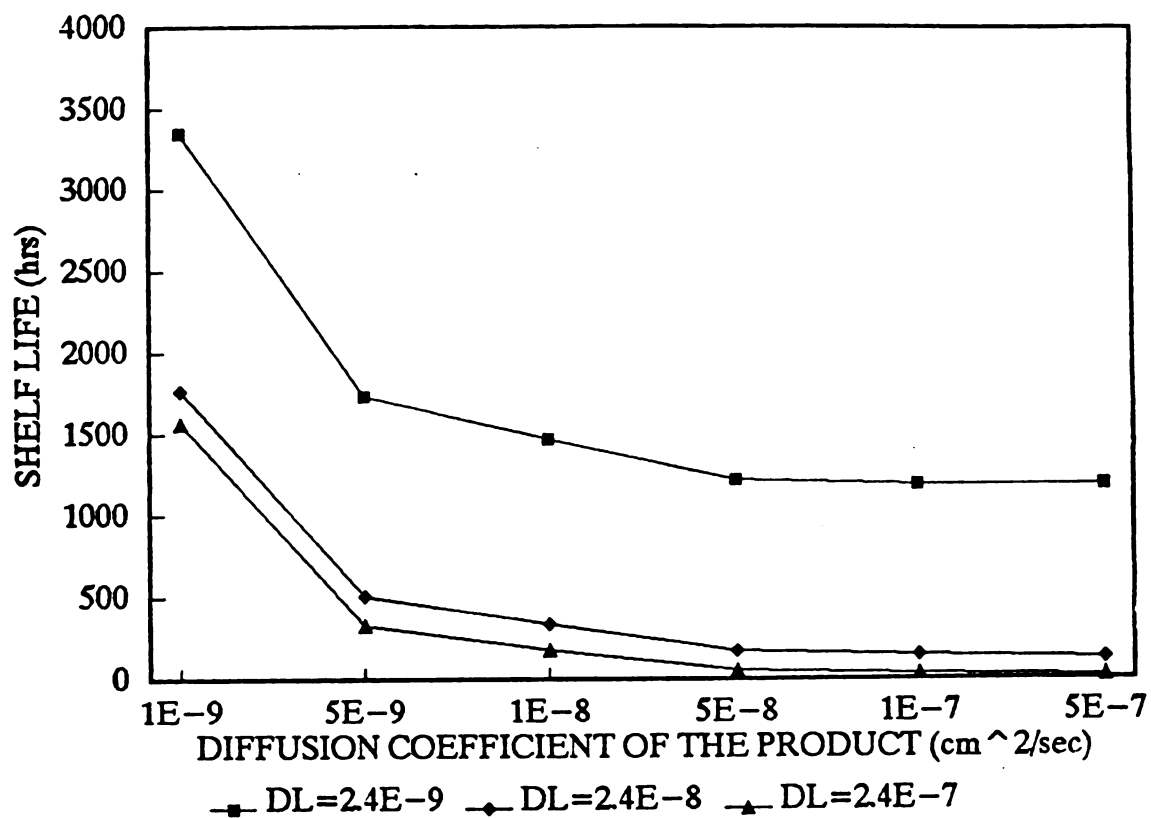


Figure 15. Effect of diffusion coefficient of packaging material and the circular plate shape tablet on the shelf life (hours), where DL is diffusion coefficient of polymer packaging material ( $\text{cm}^2/\text{sec}$ )

### 5.3.1 THE ANALYTICAL SOLUTION IN LIMITING CASE WHEN DIFFUSION COEFFICIENT OF THE PRODUCT IS VERY LARGE

By eqn.(142) in Appendix 4, with the same data used in the above case, the results of analytical solutions are  
From eqn.(142), shelf-life is

$$t = \frac{(V_R + ZV_R)L}{H_L D_L A_L Z} \ln \frac{C_{HI} - C_E}{C_{HC} - C_E}$$

From eqn.(142), the unknown data is  $Z$ ,  $C_{HI}$ ,  $C_{HC}$  and  $C_E$

$C_H$  and  $C_R$  can be calculated by following two equations

$$C_H = C_{sat} \times RH / 100$$

$$C_R = M \times W_s / (100 V_p)$$

The calculation results are shown in Table 10.

Table 10. Sorption isotherm data in concentration (g/cm<sup>3</sup>)

RH	M	$C_H$	$C_R$
21.4	3.27	0.0061	0.039
31.2	3.73	0.0088	0.044
43.5	4.32	0.0123	0.051

It was assumed that there is linearity in G.A.B sorption isotherm from 3 (gH<sub>2</sub>O/100g dry product) to 4 (gH<sub>2</sub>O/100g dry product).

The linearity is

$$C_H = Z C_R + F$$

From Table 10,  $Z = 0.497$  and  $F$  is  $-1.34$

$$C_{RI} = 3 \text{ (gH}_2\text{O/ 100g dry prod.)} \times Ws$$

$$C_{RC} = 4 \text{ (gH}_2\text{O/ 100g dry prod.)} \times Ws$$

Therefore,  $C_{HI} = Z C_{RI} + F$

$$C_{HC} = Z C_{RC} + F$$

All other data are the same as in the Table 7.

The shelf life which are calculated from analytical solution is shown in Table 11.

Table 11. The analytical solution in limiting case

Diffussion coefficient of packaging material (cm <sup>2</sup> /sec)	Shelf life (hrs)
2.4 x 10 <sup>-9</sup>	1151.4
2.4 x 10 <sup>-8</sup>	115.4
2.4 x 10 <sup>-7</sup>	15.7

These results are fitted very well with the results of circular plate shaped product in Table 9. Therefore, in this limiting cases, the finite difference solution is very accurate.

#### 5.4. THE EFFECT OF SOLUBILITY OF PACKAGING MATERIAL AND DIFFUSION COEFFICIENT OF PRODUCT ON SHELF-LIFE

The effect of solubility coefficient of water in packaging material at 63.28, 93.28, 120.28 (gH<sub>2</sub>O/cm<sup>3</sup> PKG)/(gH<sub>2</sub>O/cm<sup>3</sup> air) was evaluated . Table 12.A and 12.B and Figure 16 and 17 show the results as a function of diffusion coefficient of the product.

From the Table 12.A and 12.B and Figure 18 and 19, solubility of packaging material appears to have a relatively larger significance at values of higher diffusion. Indeed, the shelf life almost duplicates when going from one solubility of 120 to 63 units at a  $D_L = 10^{-6}$ , however at  $D_L = 5 \times 10^{-9}$  the effect is not significant in its percent change.

**Table 12.A. Effect of solubility of packaging material and diffusion coefficient of the spherical shape product on the shelf life (hours)**

Solubility of packaging material	Diffusion coefficient of product(cm <sup>2</sup> /sec)					
	5E-9	1E-8	5E-8	1E-7	5E-7	1E-6
63.28	423	236	81.5	60.6	47.3	50.6
93.28	408	219	67.5	48.0	32.3	33.6
120.28	399.3	211	60.3	40.0	27.1	24.3

solubility of packaging material is in (gH<sub>2</sub>O/cm<sup>3</sup> polymer PKG)/(gH<sub>2</sub>O/cm<sup>3</sup> air)

Number of shells of tablet = 80

Diffusion coef. of polymer PKG material =  $2.4 \times 10^{-7}$  cm<sup>2</sup>/sec

Critical moisture content = 3.960

Other data are the same as data in Table 5, except for diffusion coefficient of tablet

**Table 12.B. Effect of solubility of packaging material and diffusion coefficient of the circular plate shape product on the shelf life (hours)**

Solubility of packaging material	Diffusion coefficient of product(cm <sup>2</sup> /sec)					
	5E-9	1E-8	5E-8	1E-7	5E-7	1E-6
63.28	341	186	58.5	40.5	23.0	20.1
93.28	331	176	50.5	33.4	17.3	14.4
120.28	325	171	46.2	29.6	14.3	11.8

solubility of packaging material is in (gH<sub>2</sub>O/cm<sup>3</sup> polymer PKG)/(gH<sub>2</sub>O/cm<sup>3</sup> air)

Number of shells of tablet = 60

Diffusion coef. of polymer PKG material =  $2.4 \times 10^{-7}$  cm<sup>2</sup>/sec

Other data are the same as data in Table 5, except for diffusion coefficient of tablet



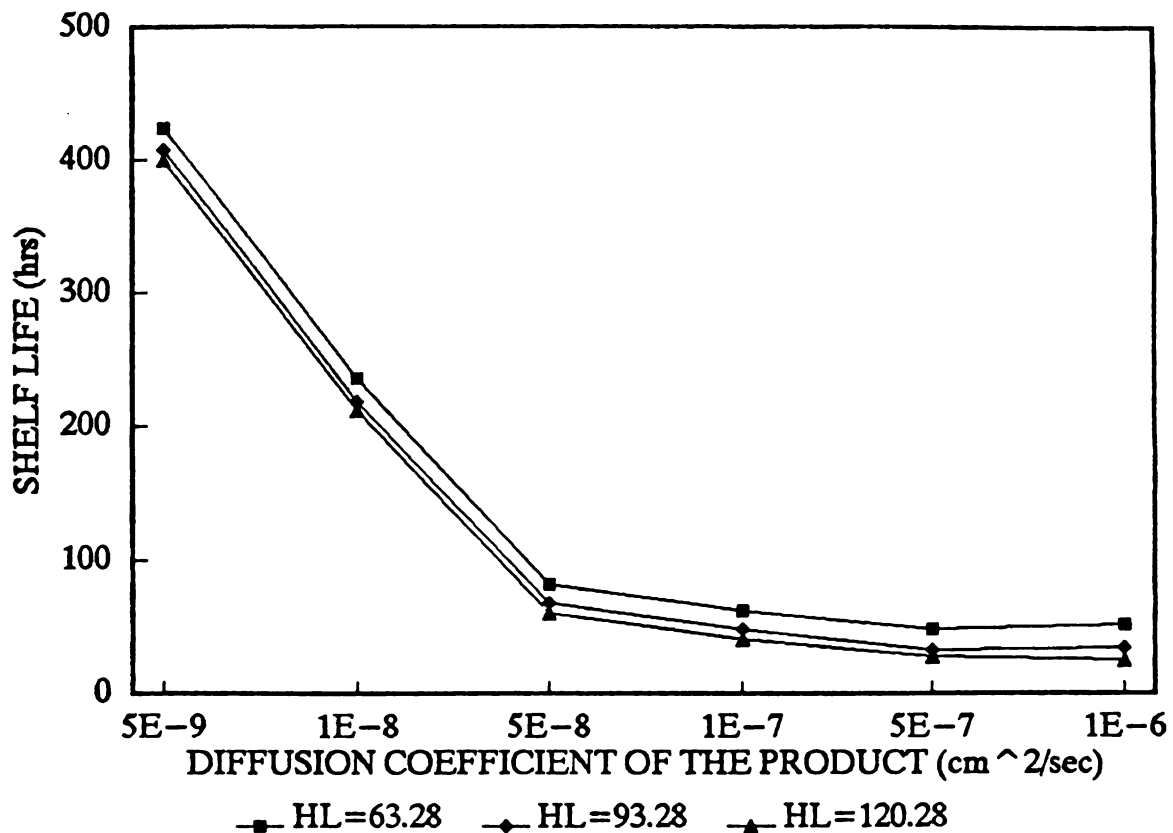


Figure 16. Effect of solubility of packaging material and diffusion coefficient of the spherical shape product on the shelf life (hours), where HL is solubility of polymer packaging material ( $\text{gH}_2\text{O}/\text{cm}^3$  polymer)/( $\text{gH}_2\text{O}/\text{cm}^3$  air)

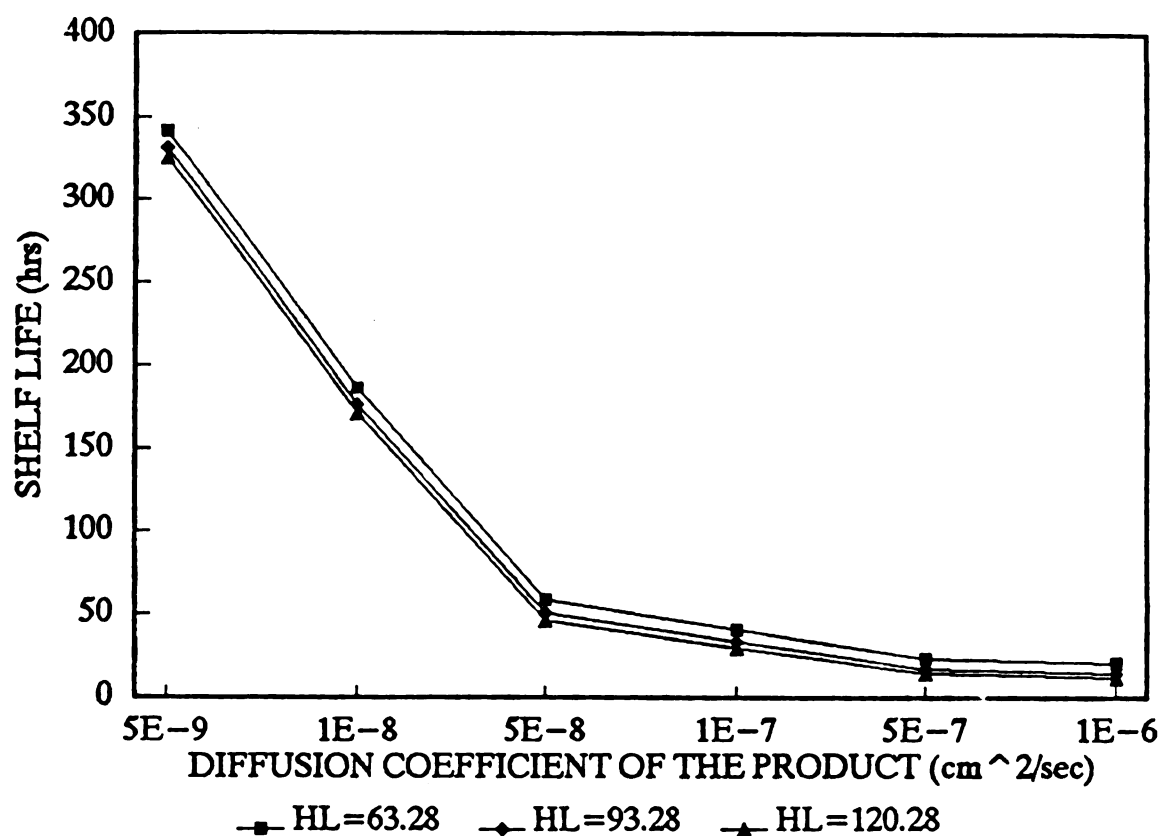


Figure 17. Effect of solubility of packaging material and diffusion coefficient of the circular plate shape product on the shelf life (hours), where HL is solubility of polymer packaging material ( $\text{gH}_2\text{O}/\text{cm}^3$  polymer) / ( $\text{gH}_2\text{O}/\text{cm}^3$  air)

## VI. CONCLUSIONS

1. The finite difference method applied to the calculation of the shelf life is a promising tool for the packaging design in the case of moisture sensitive product.
2. In limiting cases, the calculated shelf life values agreed well with the shelf life calculated based on the analytical solutions. The percent error in the case of spherical shaped tablet is 3.8% and for the circular plate shaped tablet is 0.1%.
3. As the diffusion coefficient of packaging material and tablet increase, the shelf life tends to decrease and reach plateau. When the diffusion coefficient of water in the product and that of packaging material is similar each other, the diffusion coefficient of water in the product has the great effect on the shelf. But when diffusion coefficient of water in the packaging material is much lower than that of the product, the amount of water taken by product is limited by the water vapor transmission rate of packaging material, in that range, diffusion coefficient of packaging material is dominating factor in water vapor transport.

4. Solubility of packaging material has the same effect of diffusion coefficient of water in the packaging material and the product. It appears to have a relatively larger significance at values of higher diffusion. Indeed, the shelf life almost duplicates when going from one solubility of 120 to 63 units at a  $D_L = 10^{-6}$ , however at  $D_L = 5 \times 10^{-9}$  the effect is not significant in its percent change.
5. When the diffusion coefficient of water in the product ( about  $1 \times 10^{-7}$  cm<sup>2</sup>/sec) is much higher than diffusion coefficient of the packaging material ( $2.4 \times 10^{-9}$ ,  $2.4 \times 10^{-8}$ ,  $2.4 \times 10^{-7}$  cm<sup>2</sup>/sec), the estimated shelf life of the circular plate shape product agreed well with those of the analytical solution.
6. When the critical moisture content of the product is taken as equilibrium moisture content value at the surface of the product, the shelf life is much shorter than when the critical moisture content is defined as the average through the product.
7. The finite difference method used in the computer program had some limits in terms of the computer running time. When the diffusion coefficient of packaging material is  $2.4 \times 10^{-9}$  cm<sub>2</sub>/sec, in order to get shelf life to reach from

3% moisture content to 4%, with IBM main frame, it took about 10 hours.

## **APPENDIX**

## **APPENDIX 1**

### **PROCEDURE TO CALCULATE HENRY'S LAW CONSTANT**

# PROCEDURE TO CALCULATE HENRY'S LAW CONSTANT

Normally, solubility of polymer is given in  $\text{cm}^3$  (STP)  $\text{H}_2\text{O}/(\text{cm}^3 \text{PKG Pa})$  or  $\text{g H}_2\text{O}/(\text{g PKG Pa})$ . But we need Henry's law constant in  $(\text{g H}_2\text{O}/\text{cm}^3 \text{PKG})/(\text{g H}_2\text{O}/\text{cm}^3 \text{Air})$  in our mathematical model. Therefore, we need to convert the unit of solubility [ $\text{cm}^3$  (STP)  $\text{H}_2\text{O}/(\text{cm}^3 \text{PKG Pa})$  or  $\text{g H}_2\text{O}/(\text{g PKG Pa})$ ] to the unit of Henry's law constant [ $(\text{g H}_2\text{O}/\text{cm}^3 \text{PKG})/(\text{g H}_2\text{O}/\text{cm}^3 \text{Air})$ ].

1. Procedure to convert solubility unit in  $\text{cm}^3$  (STP)  $\text{H}_2\text{O}/(\text{cm}^3 \text{PKG Pa})$  to Henry's law constant unit in  $(\text{g H}_2\text{O}/\text{cm}^3 \text{PKG})/(\text{g H}_2\text{O}/\text{cm}^3 \text{Air})$

- 1). Partial pressure at given condition (p) :

$$p = \left( \frac{P_{\text{sat}}}{760 \text{ mmHg}} \right) (1.013 \times 10^5) \frac{RH_{\%}}{100}$$

where p is in Pa,  $p_{\text{sat}}$  is saturated vapor pressure at given temperature in mmHg, RHE is relative humidity of environment surrounding package in %.

- 2). Mass of water vapor occupied in  $1 \text{ cm}^3$  ( $m_{\text{H}_2\text{O}}$ )

Applying gas law,

$$m_{\text{H}_2\text{O}} = \frac{MPV}{RT}$$

where M is 18, p is 1 atm, R is 82.06 (atm.cc/gmole. $^{\circ}$ K), T is



273.15 °K, and V is in cc.

$$m_{H_2O} = 8.03448 \times 10^{-4} V$$

Therefore, Solubility in  $g_{H_2O}/cm^3$  PKG is

$$S = 8.03448 \times 10^{-4} V p$$

where V is solubility in  $cm^3$  (STP)  $H_2O/$  ( $cm^3$  PKG Pa), p is partial pressure of water vapor in Pa.

### 3). Concentration in environment surrounding package

This is given in eqn.(3).

$$C_E = \left( \frac{RH}{100} \right) \left( \frac{AH}{1.5829T} \right) \quad (92)$$

where T is in °R.

### 4). Henry's law constant

$$H_L = S/C_E \quad (g \ H_2O / cm^3 \ PKG) / (g \ H_2O / cm^3 \ Air)$$

### 2. Procedure to calculate $H_L$ from unit in $g \ H_2O / (g \ PKG)$ to unit in $(g \ H_2O / cm^3 \ PKG) / (g \ H_2O / cm^3 \ Air)$

$$S = W \times d$$

where S is solubility in  $g \ H_2O / cm^3$  PKG, W is solubility in  $g \ H_2O / g \ PKG$ , and d is density of PKG.

$$\text{Therefore,} \quad H_L = S / C_E \quad (93)$$

### THE STABILITY OF DIMENSIONLESS CONSTANT

This computer program has 4 dimensionless constants, Q, G, A1, B1. Each constant has certain range of values needed to maintain stability of the calculations. This is because the finite difference method is based on numerically very small  $\Delta t$ ,  $\Delta L$ , and  $\Delta R$ . Each dimensionless constant is as follows:

$$Q = (D_L * \Delta t) / \Delta L^2 \quad (94)$$

$$G = (D_R * \Delta t) / \Delta R^2 \quad (95)$$

$$a1 = \Delta t * D_L * A_L / (V_H * \Delta L) \quad (96)$$

$$b1 = \Delta t * D_R * A_R / (V_H * \Delta R) \quad (97)$$

Dimensionless constant Q is used to solve the diffusion equation on packaging material. In equation (75). Each concentration has to have positive influence,  $(1-2Q)$  must be greater than zero, therefore, Q value must be Less than 0.5.

Once Q value is fixed, G value can be determined by following equation,

$$\Delta t = Q * \Delta L^2 / D_L \quad (98)$$

Accordingly, G can be determined by substituting eqn.(98) into eqn.(95).

But in eqn.(94),  $\Delta L$  is  $L/N$ , where  $N$  is number of the divided layers of packaging material and it is determined as small as possible to reduce computing time as long as it has no error, also  $D_L$  is predetermined. Therefore, only by controlling  $\Delta t$ ,  $Q$  value can be fixed, as above mentioned, finite difference method based on that the  $\Delta t$  is very small. Accordingly,  $Q$  value varies from 0.3 to 0.0001 for simulation of this.

Dimensionless constant  $a_1$  and  $b_1$  are used to calculate the headspace and interface concentration. In equation (77), each concentration has following relationship;

$$C_H|_{t+\Delta t} - C_H|_t > 0$$

at  $t=0$ ,

$$a_1 * C_{LH}|_{t=0} > k * b_1 * C_{RH}|_{t=0}$$

where  $k$  is numerical ratio of two initial concentration of internal surface of packainge ( $C_{LH}|_{t=0}$ ) and product ( $C_{RH}|_{t=0}$ ). For example, when  $C_{LH}|_{t=0}$  is  $1 \cdot 10^{-7}$  g/cm<sup>3</sup> of packaging and  $C_{RH}|_{t=0}$  is  $1 \cdot 10^{-4}$  g/cm<sup>3</sup> of product,  $k$  value, numerical ratio of two concentration is  $10^3$ .

## **APPENDIX 2**

### **THE STABILITY OF DIMENSIONLESS CONSTANT**

### **APPENDIX 3**

#### **FINITE DIFFERENCE CALCULATION SCHEME AND WATER GAIN FORMULA FOR PRODUCTS SHAPED LIKE PLATES**

# **FINITE DIFFERENCE CALCULATION SCHEME AND WATER GAIN FORMULA FOR PRODUCTS SHAPED LIKE PLATES**

When the shape of product is not spherical, then the procedure is the same but F.D. scheme in eqn.(86), (87) and total moisture content of product in eqn.(91) are different for plate type. Eqn.(86-1), (87-1), and (91-1) for plate type can be drawn as follows.

## **1. CALCULATION OF WATER VAPOR CONCENTRATIONS INSIDE THE PRODUCT**

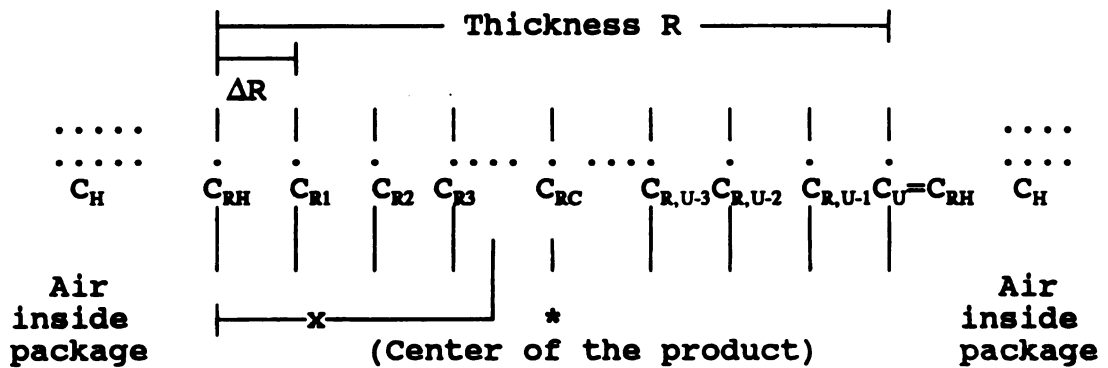


Figure 21. Subdivision of the plate type product into  $U$  layers. Here, the product is taken to be a plate and the thickness  $\Delta R$  of each layer is  $\Delta R = R/U$ .

In order to find the concentration of diffused water vapor in the product, we apply a mass balance to one of the shells in Fig.21 and use Fick's Law for the rates into and out of the layer,

$$\begin{array}{ccccc}
 \text{( Amount )} & - & \text{( Amount )} & = & \text{(rate of )} \\
 \text{entering} & & \text{leaving} & & \text{increase} \\
 \text{inner} & & \text{outer} & & \text{inside} \\
 \text{surface} & & \text{surface} & & \text{Shell}
 \end{array}$$

$$-D_R \frac{\partial C}{\partial r} \Big|_r A_R - (-D_R \frac{\partial C}{\partial r} \Big|_{r+\Delta R}) = A_R dr \frac{\partial C}{\partial t}$$

$$\frac{\partial^2 C}{\partial r^2} = \frac{1}{D_R} \left( \frac{\partial C}{\partial t} \right) \quad (99)$$

C is the concentration,  $D_R$  is the diffusion coefficient for water in the product, and  $A_R$  is the surface area of the product.

Initial Condition : at  $t = 0$ ,  $0 \leq r \leq R$ ,  $C = C_{RH} \Big|_{t=0}$

Boundary Condition : at  $t > 0$ ,  $r = 0$ ,  $C = C_{RH}$

The Finite Difference expressions for the derivatives in the above equation are,

$$\frac{\partial C}{\partial r} = \frac{C_{r+\Delta R} - C_r}{\Delta R} \Big|_t$$

$$\frac{\partial^2 C}{\partial r^2} = \frac{C_{r+\Delta R} - 2C_r + C_{r-\Delta R}}{\Delta R^2} \Big|_t$$

$$\frac{\partial C}{\partial t} = \frac{C_{t+\Delta t} - C_t}{\Delta t} \Big|_r$$

where  $\Delta R$  is the thickness of a layer in Fig.6 and  $\Delta t$  is the time step. Substituting this into the diffusion equation and

rearranging,

$$C_{r,t+\Delta t} = GC_{r-\Delta R,t} + (1-2G)C_{r,t} + GC_{r+\Delta R,t} \quad (86-1)$$

where  $G = D_R \Delta t / (\Delta R)^2$ . For stability,  $G$  must be less than 0.3. Detail explanation is given in Appendix 2.

This equation relates the concentration at time  $\Delta t$  later (next row in Fig.6) to the concentrations in the previous row. In terms of the boxes in the matrix in Fig.6, this scheme can be presented as :

Q	1-2Q	Q
	$C_{RU,t}$	

which says that the unknown concentration in the box marked  $C_{RU,t}$  can be determined as the weighted sums of the concentrations in the previous row. The weights are shown in the boxes.

For plate shape product, concentration of water vapor at center of product is the concentration of water vapor at  $(U/2)$ th layer, therefore above scheme can be used until  $U/2$  layer. The concentration at center of the product is obtained from new boundary condition that the flow rate through the left layer is zero because  $D_R \partial C / \partial r = 0$ .



Therefore,  $C_{U/2-1} = C_{U/2} (= C_{R_0}) = C_{U/2+1} \quad (87-1)$

and  $C_{RH} = C_{R,U}, \quad C_{R1} = C_{R,U-1}, \quad C_{R2} = C_{R,U-2} \dots$

## 2. CALCULATION OF THE TOTAL WATER GAIN FOR THE PRODUCT

Net gain at any time is the sum of average concentrations of each layer times volumes.

$$M_t = (100/W) \left[ \frac{C_{R0} + C_{R1}}{2} A_R \Delta R + \frac{C_{R1} + C_{R2}}{2} A_R \Delta R + \dots + \frac{C_{R,U-1} + C_{R,U}}{2} A_R \Delta R \right]$$

$$= (100/W) (A_R \Delta R) [C_{R0} + C_{R1} + C_{R2} + \dots + C_{R,U-1} + C_{R,U}] \quad (91-1)$$

## **APPENDIX 4**

### **CALCULATION OF THE ANALYTICAL SOLUTION**

## CALCULATION OF THE ANALYTICAL SOLUTION

### 1. ANALYTICAL SOLUTION OF DIFFUSION EQUATION TO CALCULATE THE TOTAL GAIN IN THE CIRCULAR PLATE SHAPED PRODUCT.

Diffusion equation of water in the circular plate shaped product was given in eqn.(99).

$$\frac{\partial^2 C(x, t)}{\partial x^2} = \frac{1}{D_R} \left( \frac{\partial C(x, t)}{\partial t} \right)$$

Equation (99) is subject to the following

initial condition : at  $t = 0$ ,  $C(x, t) = C_{RI}$

boundary condition : at  $x = 0$ ,  $C(x, t) = C_{RH}$  for all time

at  $x = L$ ,  $C(x, t) = C_{RH}$

#### 1.1 The separation variable technique

General solution can be obtained by using separation variable technique,

putting  $C(x, t) = X(x)T(t)$  (100)

applying eqn.(100) to eqn.(99) and rearranging,

$$D_R X''(x) T(t) = X(x) T'(t)$$

dividing  $X(x)T(t)$ , and letting it be equal to  $-\lambda^2$

$$X(x)''/X(x) = (1/D_R) T(t)'/T(t) = -\lambda^2$$

then,

$$X(x)''/X(x) = -\lambda^2 \quad (101)$$

$$(1/D_R) T(t)'/T(t) = -\lambda^2 \quad (102)$$

so eqn.(100) becomes,

$$X(x)'' + \lambda^2 X(x) = 0 \quad (103)$$

the general solution of eqn.(103) is

$$X(x) = C_1 \sin \lambda x + C_2 \cos \lambda x \quad (104)$$

eqn.(101) becomes,

$$T'(t) + \lambda^2 D_R T(t) = 0 \quad (105)$$

the general solution of eqn.(105) is

$$T(t) = C_3 \exp (-\lambda^2 D_R t) \quad (106)$$

applying eqn.(104) and (106) to eqn.(100), and rearranging,  $C(x,t)$  becomes

$$C(x,t) = (C_4 \sin \lambda x + C_5 \cos \lambda x) \exp (-\lambda^2 D_R t) \quad (107)$$

## 1.2. Calculation of constants in the general solution

### 1.2.1 When $\lambda = 0$ ,

from eqn.(103) and (105)

$$X(x) = C_6 + C_7 x, \quad T(t) = C_8$$

therefore, the general solution of eqn.(107) is

$$C(x,t) = C_9 + C_{10} x \quad (108)$$

boundary condition; at  $x = L$ ,  $C(x,t) = C_{RH}$ ,

$$C_9 = C_{RH}, \quad C_{10} = 0$$

therefore,

$$C(x,t) = C_{RH}$$

### 1.2.2 When $\lambda \neq 0$

$$C(x, t) = \sum_{\lambda=1}^{\infty} (C_{11} \sin \lambda x + C_{12} \cos \lambda x) \exp(-\lambda^2 D_R t)$$

therefore,  $C(x, t)$  becomes

$$C(x, t) = C_{RH} + \sum_{\lambda=1}^{\infty} (C_{11} \sin \lambda x + C_{12} \cos \lambda x) \exp(-\lambda^2 D_R t) \quad (109)$$

boundary condition again, at  $x = 0$ ,  $C(x, t) = C_{RH}$ ,

$$C_{RE} = C_{RE} + \sum_{\lambda=1}^{\infty} C_{12} \exp(-\lambda^2 D_R t) \quad (110)$$

therefore,  $C_{12}$  must be zero.

boundary condition : at  $x = L$ ,  $C(x, t) = C_{RH}$

$$C_{RE} = C_{RE} + \sum_{\lambda=1}^{\infty} C_{11} \sin(\lambda L) \exp(-\lambda^2 D_R t) \quad (111)$$

In order to satisfy above equation,  $\sin \lambda L$  should be zero.

therefore,  $\lambda L = n \pi$  ( $n = 1, 2, 3, 4 \dots$ )

$C(x, t)$  is

$$C(x, t) = C_{RH} + \sum_{n=1}^{\infty} (C_n \sin \frac{n\pi x}{L}) \exp(-\frac{n^2 \pi^2 D_R t}{L^2}) \quad (112)$$

**Initial condition : at  $t = 0$ ,  $C(x, t) = C_{RI}$**

**applying eqn.(112) to initial condition,**

$$C_{RI} = C_{RH} + \sum_{n=1}^{\infty} (C_n \sin \frac{n\pi x}{L}) \quad (113)$$

**In order to find  $C_n$  in eqn.(113), multiply  $\sin(k\pi x/L)$  and integrating from 0 to L.**

$$\sum_{n=1}^{\infty} \int_0^L (C_n \sin \frac{n\pi x}{L}) (\sin \frac{k\pi x}{L}) dx = \int_0^L (C_{RI} - C_{RH}) \sin(\frac{k\pi x}{L}) dx \quad (114)$$

**when  $k \neq n$ , integration of right term in eqn.(114) is 0**

**when  $k = n$ , integration of left term in eqn.(114) is**

$$\int_0^L C_n (\sin^2 \frac{n\pi x}{L}) = \int_0^L [\frac{1 - \cos(2 \frac{n\pi x}{L})}{2}] = C_n \frac{L}{2} \quad (115)$$

**Rearranging eqn.(115),**

$$C_n (\frac{L}{2}) = \int_0^L [(C_{RI} - C_{RH}) \sin \frac{k\pi x}{L}] = (C_{RI} - C_{RH}) \frac{L}{k\pi} (1 - \cos k\pi)$$

**Therefore,**

$$C_n = \frac{2(C_{RI} - C_{RH})}{k\pi} (1 - \cos k\pi) \quad (116)$$

applying eqn.(116) to eqn.(112)

rearranging, and finally the analytical solution to calculate water vapor concentration in the product is obtained.

$$C(x, t) = C_{RH} + \frac{2(C_{RI} - C_{RH})}{\pi} \sum_{n=1}^{\infty} \left( \frac{1 - \cos n\pi}{n} \right) \sin\left(\frac{n\pi x}{L}\right) \exp\left(-\frac{n^2 \pi^2 D_R t}{L^2}\right) \quad (117)$$

if n is even,  $1 - \cos(n\pi) = 0$ , if n is odd,  $1 - \cos(n\pi) = 2$ .

Therefore,

$$C(x, t) = C_{RH} + \frac{4(C_{RI} - C_{RH})}{\pi} \sum_{n=1,3,5..}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi x}{L}\right) \exp\left(-\frac{n^2 \pi^2 D_R t}{L^2}\right) \quad (118)$$

### 1.3. Analytical solution for total gain

Mass at any time,  $M(t)$ , is

$$M(t) = \int_0^L C(x, t) A_R dx \quad (119)$$

applying  $C(x, t)$  in eqn.(118) to eqn.(119)

$$M(t) = A_R \int_0^L \left[ C_{RH} + \frac{4(C_{RI} - C_{RH})}{\pi} \sum_{n=1,3,5..} \frac{1}{n} \sin\left(\frac{n\pi x}{L}\right) \exp\left(-\frac{n^2 \pi^2 D_R t}{L^2}\right) \right] dx$$

$$M(t) = A_R \left[ C_{RH} x + \frac{4(C_{RI} - C_{RH})}{\pi} \sum_{n=1,3,5..} \frac{1}{n} \exp\left(-\frac{n^2 \pi^2 D_R t}{L^2}\right) \int_0^L \left(\sin \frac{n\pi x}{L}\right) dx \right]$$

where (120)

$$\int_0^L \left(\sin \frac{n\pi x}{L}\right) dx = \left[ \frac{L}{n\pi} \cos \frac{n\pi x}{L} \right]_0^L = 2 \frac{L}{n\pi}$$

therefore,

$$M(t) = A_R L \left[ C_{RH} + \frac{8(C_{RI} - C_{RH})}{\pi} \sum_{n=1,3,5..} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_R t}{L^2}\right) \right]$$

rearranging,

$$\frac{M(t)}{M_\infty} = \left[ 1 - \frac{8\left(1 - \frac{C_{RI}}{C_{RH}}\right)}{\pi^2} \sum_{n=1,3,5..} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_R t}{L^2}\right) \right] \quad (121)$$



## 2. ANALYTICAL SOLUTION OF DIFFUSION EQUATION TO CALCULATE THE TOTAL GAIN IN THE SPHERICAL SHAPE PRODUCT.

Diffusion equation of water in the spherical product was given in eqn.(82).

$$\frac{\partial C}{\partial t} = \frac{2}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} D_R$$

if let  $U = rC$ , equation (82) becomes

$$\frac{\partial^2 U(r, t)}{\partial r^2} = \frac{1}{D_R} \left( \frac{\partial U(r, t)}{\partial t} \right) \quad (122)$$

Equation (82) is subject to the following

initial condition : at  $t = 0$ ,  $U(r, t) = rC_{RI}$

boundary condition : at  $r = 0$ ,  $U(r, t) = 0$

at  $r = R$ ,  $U(r, t) = RC_{RH}$

### 2.1 The separation variable technique

Using the same procedure from eqn.(100) to eqn.(106), general solution of eqn.(122) can be obtained

$$U(r, t) = (A_4 \sin \lambda r + A_5 \cos \lambda r) \exp (-\lambda^2 D_R t) \quad (123)$$

### 2.2. The calculation of constant in the general solution

Using the same procedure from eqn.(107) and (108),

$U(r, t)$  becomes

$$U(r, t) = A_2 r + A_3 + \sum_{\lambda=1}^{\infty} (A_9 \sin \lambda r + A_{10} \cos \lambda r) \exp(-\lambda^2 D_R t) \quad (124)$$

applying boundary condition again,

boundary condition : at  $r = 0$ ,  $U(r, t) = 0$

$$0 = A_3 + \sum_{\lambda=1}^{\infty} A_{10} \exp(-\lambda^2 D_R t)$$

therefore,  $A_3$  and  $A_{10}$  must be zero.

$$U(r, t) = A_2 r + \sum_{\lambda=1}^{\infty} A_9 \sin(\lambda r) \exp(-\lambda^2 D_R t) \quad (125)$$

applying eqn.(125) to boundary condition,

boundary condition : at  $r = R$ ,  $U(r, t) = r C_{RH}$

$$R C_{RH} = A_2 R + \sum_{\lambda=1}^{\infty} A_9 \sin(\lambda R) \exp(-\lambda^2 D_R t) \quad (126)$$

In order to satisfy the equation,  $A_2$  must be  $C_{RH}$  and  $\sin \lambda R$  should be zero.

$$\lambda R = n \cdot \pi \quad (n = 1, 2, 3, 4 \dots)$$

Therefore,  $U(r, t)$  is

$$U(r, t) = rC_{RH} + \sum_{n=1}^{\infty} (A_n \sin \frac{n\pi r}{R}) \exp(-\frac{n^2 \pi^2 D_R t}{R^2}) \quad (127)$$

Initial condition : at  $t = 0$ ,  $U(x, t) = rC_{RI}$

applying eqn.(127) to initial condition,

$$rC_{RI} = rC_{RH} + \sum_{n=1}^{\infty} (A_n \sin \frac{n\pi x}{R}) \quad (128)$$

In order to find  $A_n$  in eqn.(128), multiply  $\sin(k\pi x/L)$  and integrating from 0 to L

$$\sum_{n=1}^{\infty} \int_0^R (A_n \sin \frac{n\pi r}{R}) (\sin \frac{k\pi r}{R}) dr = \int_0^R (C_{RI} - C_{RH}) \sin(\frac{k\pi r}{R}) dr \quad (129)$$

when  $k \neq n$ , integration of light term in eqn.(129) is 0

when  $k = n$ , integration of left term in eqn.(129) is

$$\int_0^R A_n (\sin^2 \frac{n\pi r}{R}) = \int_0^R [\frac{1 - \cos(2 \frac{n\pi r}{R})}{2}] = A_n \frac{R}{2}$$

therefore,  $A_n$  is

$$A_n = 2 \frac{R}{k\pi} [(C_{RH} - C_{RI}) \cos k\pi] \quad (130)$$

Finally, the general solution becomes

$$rC(r, t) = rC_{LH} + 2R \frac{(C_{RH} - C_{RI})}{\pi} + \sum_{n=1}^{\infty} \frac{\cos k\pi}{n} \sin \frac{n\pi r}{R} \exp\left(-\frac{n^2\pi^2 D_R t}{R^2}\right) L$$

rearranging, and finally the analytical solution to calculate water vapor concentration in the product is obtained. therefore,  $C(r, t)$  is

$$C(r, t) = C_{RH} + \frac{2R(C_{RH} - C_{RI})}{\pi} \sum_{n=1}^{\infty} \left( \frac{\cos n\pi}{n} \right) \frac{1}{r} \sin\left(\frac{n\pi r}{R}\right) \exp\left(-\frac{n^2\pi^2 D_R t}{R^2}\right) \quad (132)$$

### 2.3. Analytical solution for total gain

Mass at any time,  $M(t)$ , is

$$M(t) = \int_0^L C(r, t) 4\pi r^2 dr \quad (133)$$

applying  $C(r, t)$  in eon.(132) to eon.(133)

$$M(t) = 4\pi \left[ C_{RH} \int_0^R r^2 dr + \frac{2R(C_{RH} - C_{RI})}{\pi} \sum_{n=1}^{\infty} \frac{\cos n\pi}{n} e^{\left(-\frac{n^2\pi^2 D_R t}{R^2}\right)} \int_0^R r \sin \frac{n\pi r}{R} dr \right]$$

where (134)

$$\int_0^R r \sin \frac{n\pi r}{R} dr = -\frac{R^2}{n\pi} \cos n\pi$$

therefore

$$M(t) = 4\pi \left[ C_{RH} \frac{R^3}{3} + \frac{2R^3 (C_{RI} - C_{RH})}{\pi} \sum_{n=1}^{\infty} \frac{\cos^2 n\pi}{(n^2)} \exp \left( -\frac{n^2 \pi^2 D_R t}{R^2} \right) \right]$$

rearranging

(135)

$$M(t) = 4\pi R^3 C_{RH} \left[ 1 - \frac{6}{\pi^2} \left( 1 - \frac{C_{RI}}{C_{RH}} \right) \sum_{n=1}^{\infty} \frac{1}{(n^2)} \exp \left( -\frac{n^2 \pi^2 D_R t}{R^2} \right) \right] \quad (136)$$

$$\frac{M(t)}{M_{\infty}} = 1 - \frac{6}{\pi^2} \left( 1 - \frac{C_{RI}}{C_{RH}} \right) \sum_{n=1}^{\infty} \frac{1}{(n^2)} \exp \left( -\frac{n^2 \pi^2 D_R t}{R^2} \right) \quad (137)$$

### 3. ANALYTICAL SOLUTION FOR LIMITING CASE WHEN DIFFUSION COEFFICIENT OF PRODUCT IS VERY LARGE

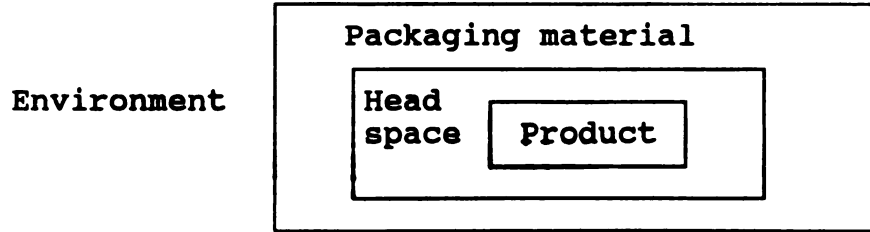


Figure 18. Package and product

Mass balance of package and product system will be given by

$$\begin{array}{ccccc} \text{( Mass tranfer )} & - & \text{( Mass transfer )} & = & \text{( rate of )} \\ \text{rate into} & & \text{rate into} & & \text{accumuation in} \\ \text{package} & & \text{product} & & \text{head space} \end{array}$$

It is assumed that the concentration profile inside the package reaches steady state quickly so that it is linear. By applying Fick's law and Henry's law,

### 3.1. Mass transfer rate into package :

$$D_{LA_L} \frac{\partial C}{\partial X} = D_{LA_L} \left( \frac{C_{LH} - C_{LB}}{L} \right) = D_{LA_L} H_L \frac{C_E - C_H}{L}$$

$$C_{LB} = H_L C_E$$

$$C_{LH} = H_L C_H$$

It is assumed also that G.A.B has lineality from 3% moisture content to 4%.

$$C_H = Z C_R + F$$

Therefore, mass transfer rate into package is

$$H_L D_{LA_L} \left( \frac{C_E - C_H}{L} \right) = \frac{D_{LA_L} H_L}{L} \left( C_E - F - Z \frac{m}{V_P} \right)$$

### 3.2. Mass transfer rate into product : $dm/dt$

### 3.3 Mass rate of accumulation in headspace :

$$\frac{d}{dt} (V_{HS} C_H) = V_{HS} \frac{d}{dt} (Z C_R + F) = Z \frac{V_{HS}}{V_P} \frac{dm}{dt}$$

## 3.4 Mass balance

$$\frac{H_L D_L A_L}{L} (C_E - F - Z \frac{m}{V_P}) - \frac{dm}{dt} = Z \frac{V_{HS}}{V_P} \frac{dm}{dt} \quad (138)$$

rearranging

$$\frac{dm}{dt} + \left( \frac{H_L D_L A_L Z}{(V_P + Z V_{HS}) L} \right) m = \frac{V_P H_L D_L A_L}{(V_P + Z V_{HS}) L} (C_E - F)$$

its general solution is

$$m(t) = K e^{(-at)} + \frac{b}{a} \quad (139)$$

where

$$a = \frac{H_L D_L A_L Z}{(V_P + Z V_{HS}) L}$$

$$b = \frac{V_P H_L D_L A_L}{(V_P + Z V_{HS}) L} (C_E - F)$$

$$b/a = V_P (C_E - F) / Z$$

initial condition :  $t=0$ ,  $m=m_1$ ,  $m_1 = k + b/a$ ,  $k = m_1 - b/a$

$$m_1 = C_{RI} \times V_P,$$

therefore,

$$m(t) = \left[ C_{RI} V_P - \frac{(C_E - F) V_P}{Z} \right] \exp(-at) \quad (140)$$

$$C_R(t) = \frac{m(t)}{V_P} = \left[ C_{RI} - \frac{(C_E - F)}{Z} \right] \exp(-at) \quad (141)$$

rearranging

$$e^{-at} = \frac{ZC_{RC} + F - C_E}{ZC_{RI} + F - C_E} = \frac{C_{HC} - C_E}{C_{HI} - C_E}$$

therefore,

$$t = \frac{(V_P + ZV_{HS})L}{H_L A_L D_L Z} \ln \frac{C_{HI} - C_E}{C_{HC} - C_E} \quad (142)$$

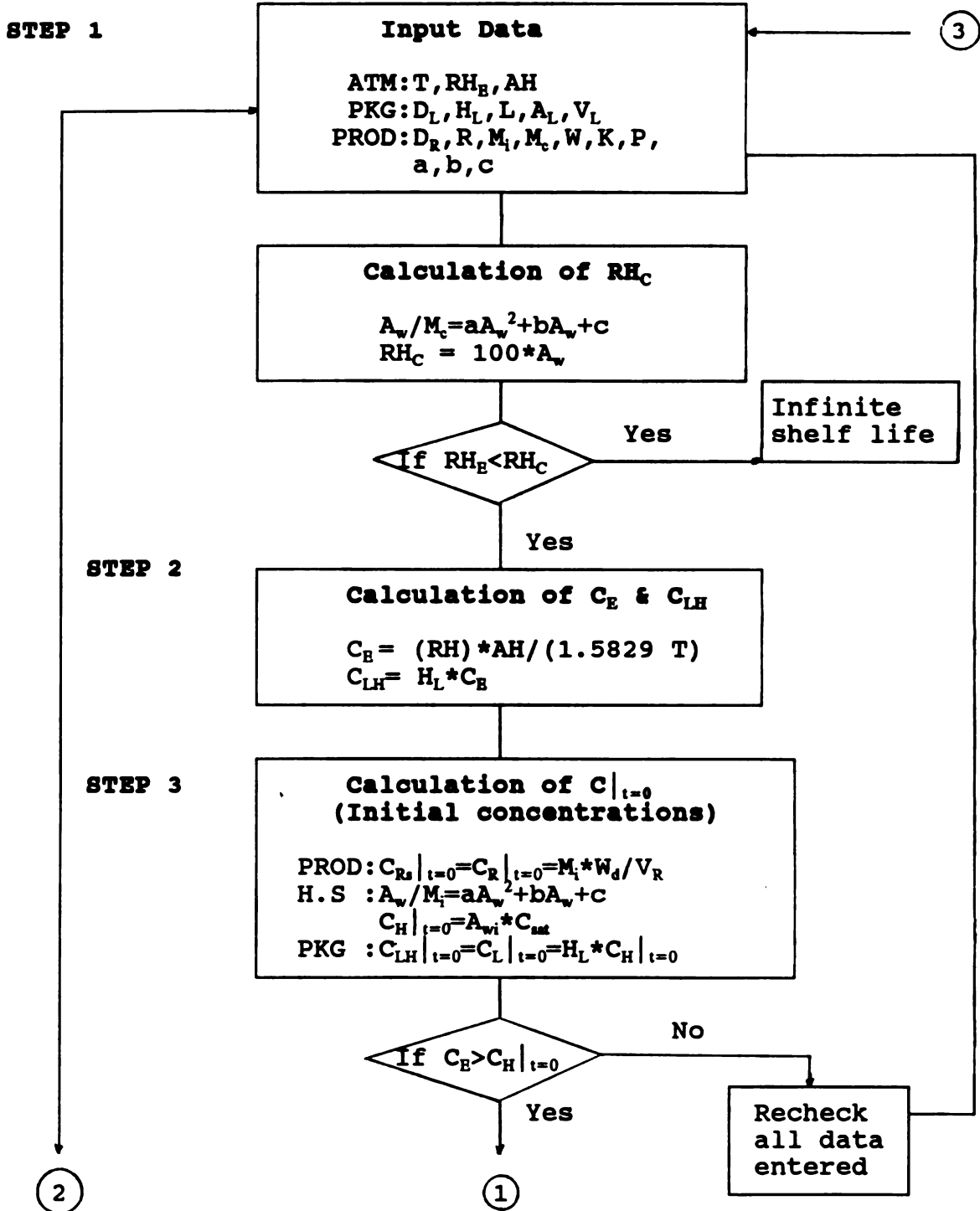


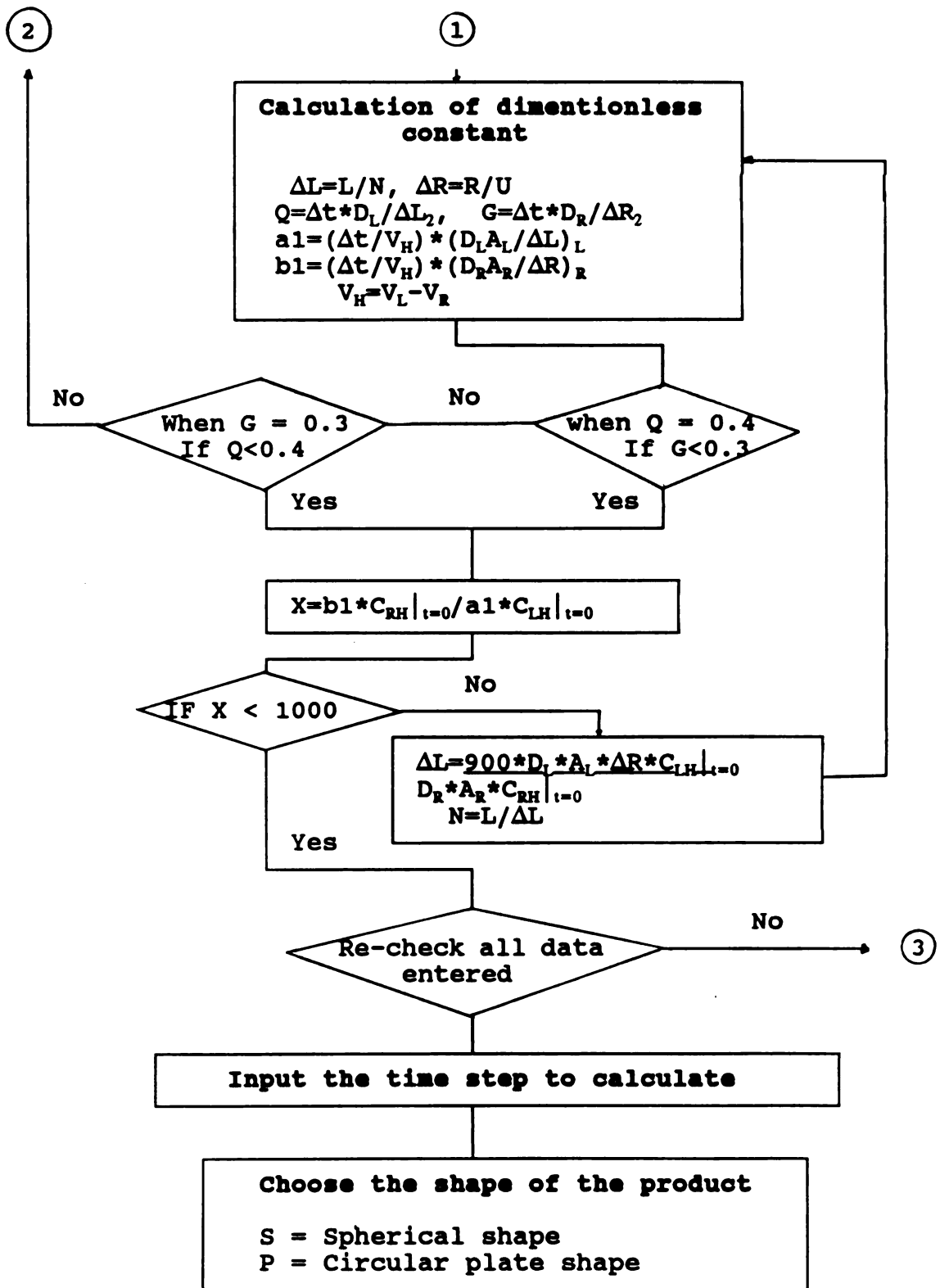
## **APPENDIX 5**

### **COMPUTER PROGRAM**

# COMPUTER PROGRAM

## 1. Flow Chart of Program

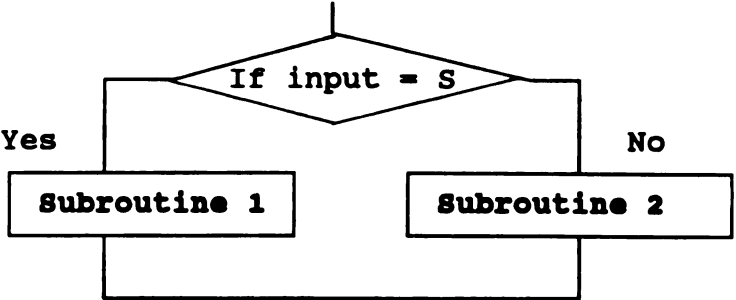




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④

**STEP 6**



**STEP 8**



## SUBROUTINE 1 : SPHERICAL SHAPE PRODUCT

STEP 4

Calculation of  $C_{LN,i}$  after time step  $\Delta t$   
( In Packaging Material)

$$\frac{\partial^2 C}{\partial x^2} = \frac{1}{D_L} \frac{\partial C}{\partial t}$$

$$C_{x,i+\Delta t} = Q * C_{x-\Delta L,i} + (1-2Q) * C_{x,i} + Q * C_{x+\Delta L,i}$$

⑦

STEP 5

Calculation of  $C_H, C_{RH}, C_{LH}$  after time step  $\Delta t$

$$C_H|_{t+\Delta t} = a1 * C_{L9}|_t - a1 * C_{LH}|_t + C_H|_t - b1 * C_{RH}|_t + b1 * C_{R1}|_t$$

$$C_{LH}|_{t+\Delta t} = H_L * C_H|_{t+\Delta t}$$

$$A_w|_{t+\Delta t} = C_H|_{t+\Delta t} / C_{ms}$$

$$M|_{t+\Delta t} = A_w|_{t+\Delta t} / [a * (A_w|_{t+\Delta t})^2 + b * (A_w|_{t+\Delta t}) + c]$$

$$C_{RH}|_{t+\Delta t} = M|_{t+\Delta t} * W / V_R$$

STEP 6

Calculation of  $C_{RU,i}$  after time step  $\Delta t$   
( In Product )

$$\frac{2}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} = \frac{1}{D_R} \left[ \frac{\partial C}{\partial t} \right]$$

$$C_{R1} \text{ to } C_{R9} : C_{r,i+\Delta t} = G * C_{r-\Delta R,i} + [1 - 2G(\Delta R/r + 1)] * C_{r,i} -$$

$$+ G * (1 + 2\Delta/r) * C_{r+\Delta R,i}$$

$$C_{Rc} : C_{Rc}|_{t+\Delta t} = 3G * C_{R9}|_t + (1 - 3G) * C_{Rc}|_t - k\Delta t (C_{Rc}|_t)^p$$

STEP 7

Calculation of Total Gain

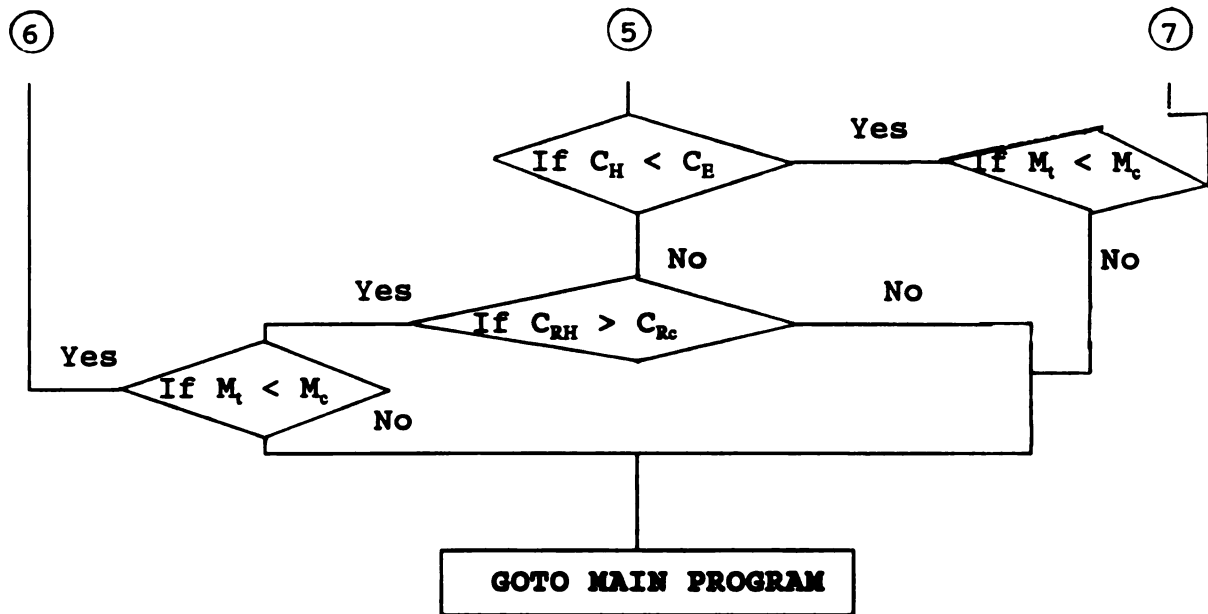
$$M_i = \frac{4\pi}{3} (r_i^3 - r_{i+1}^3) [C_R|_{r(i+1)} (1 + r_i/\Delta R) - C_R|_{r(i+1)} r_i/\Delta R]$$

$$\pi (r_{i+1}^4 - r_i^4) [(C_R|_{r(i+1)} - C_R|_n) / \Delta R]$$

$$M_t = (100/W) (M_1 + M_2 + \dots + M_U)$$

⑥

⑤



## SUBROUTINE 2 : CIRCULAR PLATE SHAPE PRODUCT

STEP 4

Calculation of  $C_{LN,t}$  after time step  $\Delta t$   
( In Packaging Material)

⑦

$$\frac{\partial^2 C}{\partial x^2} = \frac{1}{D_L} \frac{\partial C}{\partial t}$$

$$C_{x,t+\Delta t} = Q * C_{x-\Delta L,t} + (1-2Q) * C_{x,t} + Q * C_{x+\Delta L,t}$$

STEP 5

Calculation of  $C_H, C_{RH}, C_{LH}$  after time step  $\Delta t$

$$C_H|_{t+\Delta t} = a1 * C_{L9}|_t - a1 * C_{LH}|_t + C_H|_t - b1 * C_{RH}|_t + b1 * C_{R1}|_t$$

$$C_{LH}|_{t+\Delta t} = H_L * C_H|_{t+\Delta t}$$

$$A_w|_{t+\Delta t} = C_H|_{t+\Delta t} / C_{as}$$

$$M|_{t+\Delta t} = A_w|_{t+\Delta t} / [a * (A_w|_{t+\Delta t})^2 + b * (A_w|_{t+\Delta t}) + c]$$

$$C_{RH}|_{t+\Delta t} = M|_{t+\Delta t} * W / V_R$$

STEP 6

Calculation of  $C_{RU,t}$  after time step  $\Delta t$   
( In Product )

$$\frac{\partial^2 C}{\partial x^2} = \frac{1}{D_L} \left( \frac{\partial C}{\partial t} \right)$$

$$C_{R1} \text{ to } C_{Rc} : C_{r,t+\Delta t} = G * C_{r-\Delta R,t} + [1-2G] * C_{r,t} - G * C_{r+\Delta R,t}$$

$$C_{RH} = C_{R,U}, \quad C_{R1} = C_{R,U-1}, \quad C_{R2} = C_{R,U-2}, \dots$$

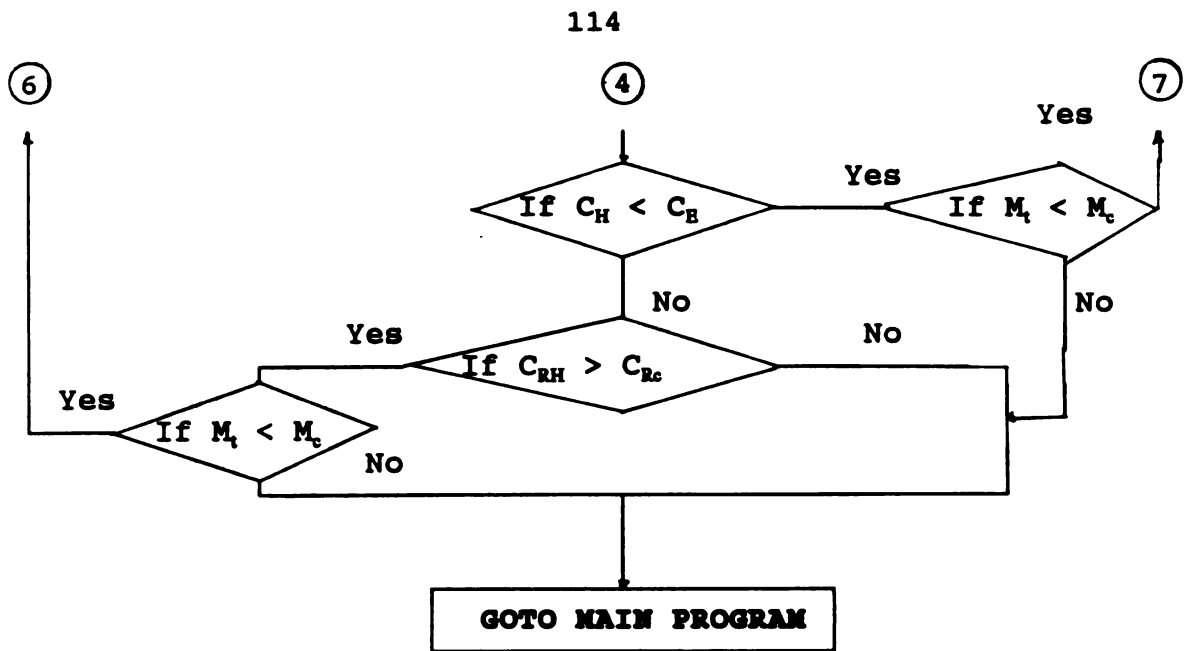
STEP 7

Calculation of Total Gain

$$M_t = (100/W) * A_R * \Delta R * (C_{RH} + C_{R1} + C_{R2} + \dots + C_{RU})$$

⑥

⑤





\*\*\*\*\*  
 \* PROGRAM TO CALCULATE SHELF-LIFE OF SPHERICAL SHAPE \*  
 \*\*\*\*\*

```

  DIMENSION C(201,120),AW(201),M(201),R(201),
+          A(201),TT(201),TM(201),SL(201)
  DOUBLE PRECISION M,R,A,C,AW,BL,B,AA,CC,BB
  INTEGER U,U1,U2,U3,N,I,J
  TT(1)=1
  DO 30 I=1,201,1
    AW(I)=0.0
    M(I)=0.0
    R(I)=0.0
    A(I)=0.0
    TT(I)=0.0
    TM(I)=0.0
    SL(I)=0.0
    DO 20 J=1,120,1
      C(I,J)=0.0
    20 CONTINUE
  30 CONTINUE

```

\*\*\*\*\*  
 \* INPUT DATA \*  
 \*

\* The data in need to run this program \*

-----\*

Component	Symbol	Name of symbol	unit
-----------	--------	----------------	------

=====\*

EXTERNAL	T	Temperature	C
ENVIRONMENT	RHE	Relative humidity	%
	AH	Absolute humidity	gH2O /g Air

-----\*

PACKAGE	DL	Diffusion coeff.	cm <sup>2</sup> /sec
		of water	
	HL	Henry's constant	(gH2O/cm <sup>3</sup> PKG) / (gH2O/cm <sup>3</sup> Air)
	BL	Thickness	cm
	AL	Surface Area	cm <sup>2</sup>
	VL	Volume	cm <sup>3</sup>

-----\*

PRODUCT	DR	Diffusion coeff.	cm <sup>2</sup> /sec
		of water	
	AMI	Initial moisture	(gH2O) / content (100g dry product)
	AMC	Critical moisture	"
		content	
	W	Dry weight	g
	RR	Radius	cm
	Rh	Thickness(plate)	cm
	AA,B,CC	G,A.B constant	

\*\*\*\*\*

```
*****
*      Enter the data      *
*****
```

```
100 PRINT*, 'Enter the temperature of storage environment',
    +'in celsius'
    READ(5,110)T
110  FORMAT(F10.5)
    PRINT*, 'Enter the relative humidity of storage',
    +'environment in %'
    READ(5,110)RHE
    PRINT *, 'Enter the absolute humidity of storage',
    +'environment in gH2O/gAir'
    READ(5,110)AH
    PRINT *, 'Enter the diffusion coefficient of',
    +'packaging material in 10^-7 cm^2/sec'
    READ(5,110)DL
    PRINT *, 'Enter the Henry constant of packaging',
    +'material in (gH2O/cm^3 PKG)/(gH2O/cm^3 Air)'
    READ(5,110)HL
    PRINT *, 'Enter the thickness of packaging material',
    +'in cm'
    READ(5,110)BL
    PRINT *, 'Enter the surface area of packaging',
    +'material in cm^2'
    READ(5,110)AL
    PRINT *, 'Enter the volume of packaging material in',
    +'cm^3'
    READ(5,110)VL
    PRINT *, 'Enter the diffusion coefficient of product',
    +'in 10^-5 cm^2/sec'
    READ(5,110)DR
    PRINT *, 'Enter the initial moisture content in',
    +'gH2O/100g dry product'
    READ(5,110)AMI
    PRINT *, 'Enter the critical moisture content in',
    +'gH2O/100g dry product'
    READ(5,110)AMC
    PRINT *, 'Enter the dry weight of product in g'
    READ(5,110)W
    PRINT *, 'Enter the G.A.B constant aa, b, cc'
    READ(5,110)AA,B,CC
    PRINT *, 'Enter the radius of product in cm'
    READ(5,110)RR
    PRINT *, 'Enter the thickness of product (Only Plate',
    +'shape product. But input 0 for spherical shape)',
    +'in cm'
    READ(5,110)TH
    N=5
    U=80
    NR=200
    PI=3.141592
```

```
*****
* ### CALCULATION OF OUTSIDE OF PACKAGE ###
*****
```

```
T1=9.0*T/5.0+32.0+460.0
CSAT=AH/(1.5829*T1)
CE=RHE*CSAT/100.0
CLE=HL*CE
```

```
*****
* ### CALCULATION OF INITIAL CONCENTRATIONS ###
*****
```

```
VR=(4*PI*RR**3)/3.0
AR=4*PI*RR**2
VH=VL-VR
CRH=AMI*W/(100.0*VR)
BB=(B-1/AMI)
AWI=-(BB+SQRT(BB**2-4*AA*CC))/(2*AA)
CH=AWI*CSAT
CLH=HL*CH
```

```
IF (CH.GT.CE) THEN
  PRINT *, 'There is no diffusion from outside',
+         'package into headspace because CH is'
  PRINT *, 'equal to CE.'
  STOP
ENDIF
```

```
*****
* ### CALCULATION OF DIMENTIONLESS CONSTANT ###
*
* This computer program has 4 dimensionless constants, *
* Q,G,A1,B1. Each constant has certain range of value*
* for stability, stability of each constant ia as *
* follows, *
*
* Spherical shape Plate shape *
*
* Q 0.3 - 0.0001 0.3 - 0.00001 *
* G < 0.3 < 0.3 *
* A1,B1 a1*CLH>1000*b1*CRH a1*CLH>1000*b1*CRH *
*****
```

```
EL=BL/N
ER=RR/U
200 Q=.3
```

```
S=10000000.0*(EL**2)*Q/DL
G=0.00001*(DR*S)/ER**2
```

```
IF(G.GT.0.3) THEN
```

```

      G=0.3
      S=100000.0*(ER**2)*G/DL
      Q=0.0000001*(DL*S)/ER**2
      IF(Q.GT.0.3) THEN
        GOTO 100
      ENDIF
    ENDIF

210 A1=0.0000001*S*DL*AL/(VH*EL)
    B1=0.00001*S*DR*AR/(VH*ER)

    X=B1*CRH/(A1*CLH)

    IF(X.GT.1000) THEN
      ER=RR/U
      EL=(9*DL*AL*ER*CLH)/(DR*AR*CRH)
      N=BL/EL
      N=INT(N)+1
      GOTO 200
    ENDIF

```

```

*****
*  DISPLAY OF ALL ENTERED DATA AND DIMISSIONLESS CONSTANT  *
*****

```

```

      PRINT *, 'All data are checked successfully !!!'
      PRINT *, 'Re-check all data entered'

      PRINT *, '-----',
+      '-----'
      WRITE(6,401)T
401 FORMAT('Temperature of storage environment in',
+      'celsius =',F5.2)
      WRITE(6,402)RHE
402 FORMAT('Relative humidity of storage environment in',
+      ' % =',F5.2)
      WRITE(6,403)AH
403 FORMAT('Absolute humidity of storage environment in',
+      'gH2O/gAir =',F5.4)
      WRITE(6,404)DL
404 FORMAT('Diffusion coefficient of packaging material',
+      'in 10^-7 cm^2/sec =',F5.3)
      WRITE(6,405)HL
405 FORMAT('Henry constant of packaging material in',
+      '(gH2O/cm^3 PKG)/(gH2O/cm^3 Air) =',F8.5)
      WRITE(6,406)BL
406 FORMAT('Thickness of packaging material in cm =',
+      F10.5)
      WRITE(6,407)AL
407 FORMAT('Surface area of packaging material in cm^2 =',
+      F10.5)
      WRITE(6,408)VL

```

```

408 FORMAT('Volume of packaging material in cm^3 =',F10.5)
    WRITE(6,409)DR
409 FORMAT('Diffusion coefficient of product in 10^-5',
+         'cm^2/sec =',F10.5)
    WRITE(6,410)AMI
410 FORMAT('Initial moisture content in gH2O/100g dry',
+         'product =',F4.2)
    WRITE(6,411)AMC
411 FORMAT('Critical moisture content in gH2O/100g dry',
+         'product =',F4.2)
    WRITE(6,412)W
412 FORMAT('Dry weight of product in g = ',F10.5)
    WRITE(6,415)AA,B,CC
415 FORMAT('Aw/M=',E10.4,1X,'Aw^2 +',1X,E10.4,1X,'Aw',
+         '+',1X,E10.4)
    WRITE(6,416)RR
416 FORMAT('Radius of product in cm = ',F10.5)
    WRITE(6,417)TH
417 FORMAT('Thickness of product (Only Plate shape) in',
+         'cm =',F10.5)

    PRINT *, '-----',
+         '-----'
    PRINT *, '                Hit any key to continue.....'

    PRINT *, '-----',
+         '-----'
    PRINT *, 'INITIAL CONCENTRATION'
    PRINT *, '-----',
+         '-----'

    WRITE (6,500)CE*1000
500 FORMAT('Concentration of outside environment (CE) =',
+         '1X,F8.5,2X,'g/L')
    WRITE(6,501)CLE*1000
501 FORMAT('Concentration of outside surface of PKG',
+         '(CLE) =',1X,F8.5,2X,'g/L')
    WRITE (6,502)CLH*1000
502 FORMAT('Concentration of inside surface of PKG',
+         '(CLH) =',1X,F8.5,2X,'g/L')
    WRITE(6,503)CH*1000
503 FORMAT('Concentration of headspace (CH) =',
+         '1X,F8.5,2X,'g/L')
    WRITE(6,504)CRH*1000
504 FORMAT('Concentration of outside surface of product',
+         '(CRH) =',1X,F8.5,2X,'g/L')

    PRINT *, '-----',
+         '-----'
    PRINT *, 'DIMENSSIONLESS CONSTANT'
    PRINT *, '-----',
+         '-----'

```

```

WRITE(6,505)Q,G,A1,B1,S,X
505 FORMAT('Q=',E10.4,/,
+'G=',E10.4,/, 'A1=',E10.4,/, 'B1=',E10.4,/, 'S=',E10.4,/,
+'X=',E10.4)

```

```

PRINT *, '-----',
+ '-----'

```

```

PRINT *, '          Hit any key to continue ..... '

```

```

*****
*      INPUT THE TIME STEP TO CALCULATE      *
*****

```

```

PRINT *, '-----',
+ '-----'

```

```

510 WRITE (6,508)
508 FORMAT(5X,'Enter the number of time to calculate',
+'concentrations at once.',//,10X,'<NOTICE !!! It',
+' must be over 200 and be times of 200>')

```

```

PRINT *, '-----',
+ '-----'

```

```

WRITE(6,550)
550 FORMAT(/////////)

```

```

511 READ(5,511)Z
FORMAT(F10.0)

```

```

Z1=Z/200
Z2=INT(Z1)
Z3=ABS(Z1-Z2)

```

```

IF((Z.LT.200).OR.(Z3.GT.0.0001)) THEN
PRINT *, 'Calculation error happened !!!'
PRINT *, 'Re-check no. of time step.'
GOTO 510

```

```

ELSE
ENDIF

```

```

Y=Z*S/3600

```

```

WRITE(6,512)

```

```

512 FORMAT(17X,'CONCENTRATION PROFILE IN PRODUCT')
PRINT *, '          (Spherical Shape)'
WRITE(6,513)Z,Y
513 FORMAT(14X,'Each step is',F10.0,1X,'steps', ' (',F7.4,
+'hrs)')
WRITE(6,514)U

```

```
514 FORMAT(14X,'<# of the divided shell of product is',
+         I10)
```

```
PRINT*, '-----',
+       '-----'
PRINT *, '      CLE      CL1      CL2      CL3      CL4',
+ '      CLH      CH      Meq '
PRINT *, '      CRH      CR1      CR2      CR3      CR4',
+ '      CRC      GAIN      TIME(hrs)'
PRINT*, '-----',
+       '-----'
```

```
U1=N+U+1
```

```
U2=U1+1
```

```
U3=U2+1
```

```
*****
* ### SET UP INITIAL CONCENTRATION ### *
*****
```

```
DO 600 J=1,N+1,1
      C(1,J)=CLH
600 CONTINUE
```

```
DO 610 J=N+3,U3,1
      C(1,J)=CRH
610 CONTINUE
```

```
      C(1,N+2)=CH
```

```
DO 620 I=1,NR+1,1
      C(I,1)=CLE
620 CONTINUE
```

```
*****
* ### CHOOSE THE SHAPE OF THE PRODUCT ### *
*****
```

```
PRINT*, 'Choose the item # of shape of the product'
PRINT*, ' 1. Spherical shape product'
PRINT*, ' 2. Circular plate shape product'
```

```
630 READ(5,630) ITEM
      FORMAT(F2.1)
      IF(ITEM.EQ.1) THEN
        CALL SPHERE
      ELSE
        CALL PLATE
      ENDIF
```

```
STOP
END
```

SUBROUTINE SPHERE(M,R,A,C,AW,B,AA,CC,U,U1,U2,U3,N,J,I)

\*\*\*\*\*  
 \* ### CALCULATION OF CONCENTRATION IN PKG MATERIAL (CL) \*  
 \*\*\*\*\*

DIMENSION C(201,120),AW(201),M(201),R(201),  
 + A(201),TT(201),TM(201),SL(201)  
 DOUBLE PRECISION M,R,A,C,AW,B,AA,CC  
 INTEGER U,U1,U2,U3,N,I,J  
 TT(1)=1  
 DO 30 I=1,201,1  
 AW(I)=0.0  
 M(I)=0.0  
 R(I)=0.0  
 A(I)=0.0  
 TT(I)=0.0  
 TM(I)=0.0  
 SL(I)=0.0  
 DO 20 J=1,120,1  
 C(I,J)=0.0  
 20 CONTINUE  
 30 CONTINUE

2000 DO 700 I=1,NR,1

DO 710 J=2,N,1  
 C(I+1,J)=Q\*(C(I,J-1)-2\*C(I,J)+C(I,J+1))+C(I,J)  
 710 CONTINUE

\*\*\*\*\*  
 \* ### CALCULATION OF CONCENTRATION IN INSIDE SURFACE \*  
 \* OF THE PACKAGING MATERIAL (CLH), THE HEADSPACE \*  
 \* (CH) AND THE OUTSIDE SURFACE OF PRODUCT (CRH) \*  
 \*\*\*\*\*

C(I+1,N+2)=A1\*C(I,N)-A1\*C(I,N+1)+C(I,N+2)  
 + -B1\*C(I,N+3)+B1\*C(I,N+4)  
 C(I+1,N+1)=HL\*C(I+1,N+2)  
 AW(I+1)=C(I+1,N+2)/CSAT  
 M(I+1)=AW(I+1)/(AA\*AW(I+1)\*\*2+B\*AW(I+1)+CC)  
 C(I+1,N+3)=M(I+1)\*W/(100\*VR)

\*\*\*\*\*  
 \* ### CALCULATION OF CONCENTRATION IN INSIDE PRODUCT ### \*  
 \*\*\*\*\*

DO 720 J=N+4,U1  
 C(I+1,J)=G\*(C(I,J-1)+(2/(U3-J))\*(C(I,J+1)-C(I,J))  
 + -2\*C(I,J)+C(I,J+1))+C(I,J)  
 720 CONTINUE  
 C(I+1,U2)=3\*G\*(C(I,U1)-C(I,U2))+C(I,U2)



```

      C(I+1,U3)=1*C(I+1,U2)
700 CONTINUE

```

```

*****
*   ### CALCULATION OF TOTAL WATER GAIN AND SHELF-LIFE ###   *
*****

```

```

      DO 800 I=1,NR,1
        A(I)=0
800 CONTINUE

```

```

      DO 810 I=1,NR,1
        DO 820 J=N+3,U2,1
          R(J)=RR-ER*(J-(N+3))
          A(I)=A(I)+(4*PI/3)*(R(J)**3-R(J+1)**3)*
+             (C(I+1,J+1)*(1+R(J+1)/ER)-C(I+1,J)*
+             R(J+1)/ER)+ PI*(R(J)**4-R(J+1)**4)*
+             (C(I+1,J)-C(I+1,J+1))/ER
820 CONTINUE
810 CONTINUE

```

```

      DO 900 I=1,NR,1
        TM(I+1)=100*A(I)/W
        TT(I+1)=1+TT(I)
        SL(I+1)=TT(I+1)*S/3600
900 CONTINUE

```

```

*****
*   ### PRINT THE CONCENTRATION PROFILE ###   *
*****

```

```

      F=TT(NR+1)/Z
      F1=INT(F)
      F2=ABS(F-F1)

      IF(F2.GT.1/Z) GOTO 3000

      WRITE (6,1000) (C(NR+1,J)*1000,J=1,N+2),M(NR+1)
      WRITE (6,1000) (C(NR+1,J)*1000,J=N+3,U3,U/5),
+             TM(201),SL(201)

```

```

1000 FORMAT (F8.4,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4,
+/,F8.4,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4)

```

```

*****
*   CALCULATION SHELF-LIFE   *
*****

```

```

3000 IF((C(NR+1,N+2).LT.CE).AND.(C(NR+1,N+2).NE.CE)) GOTO
+3100

```

```

      IF((C(NR+1,U3).LT.C(NR+1,N+3)).AND.(C(NR+1,U3).
+      NE.C(NR+1,N+3))) GOTO 4000

      IF(TM(NR+1).LT.AMC) THEN
        PRINT *, '      It has infinite shelf-life'
        STOP
      ELSE
        GOTO 6000
      ENDIF

3100 IF((TM(NR+1).LT.AMC).AND.(TM(NR+1).NE.AMC)) THEN
      TT(1)=TT(NR+1)
      DO 3200 J=1,U3,1
        C(1,J)=C(NR+1,J)
3200    CONTINUE
      GOTO 2000
    ELSE
      GOTO 6000
    ENDIF

4000 IF((TM(NR+1).LT.AMC).AND.(TM(NR+1).NE.AMC)) THEN
      TT(1)=TT(NR+1)
      DO 4100 J=N+2,U3,1
        C(1,J)=C(NR+1,J)
4100    CONTINUE
      GOTO 2000
    ELSE
      GOTO 6000
    ENDIF

*****
*      SHELF-LIFE      *
*****

6000 PRINT*, '-----',
+ '-----'
      WRITE(6,6100)SL(NR+1)
6100 FORMAT(10X,'SHELF-LIFE OF THIS PRODUCT IS',1X,F10.5,
+ 'hrs')

      PRINT*, '-----',
+ '-----'

      RETURN
      END

```

SUBROUTINE PLATE(M,R,A,C,AW,B,AA,CC,U,U1,U2,U3,N,I,J)

\*\*\*\*\*  
 \* ### CALCULATION OF CONCENTRATION IN PKG MATERIAL (CL) \*  
 \*\*\*\*\*

```

    DIMENSION C(201,120),AW(201),M(201),R(201),
+      A(201),TT(201),TM(201),SL(201),XL(201)
    DOUBLE PRECISION M,R,A,C,AW,B,AA,CC
    INTEGER U,U1,U2,U3,N,I,J
    TT(1)=1
    DO 30 I=1,201,1
      AW(I)=0.0
      M(I)=0.0
      R(I)=0.0
      A(I)=0.0
      TT(I)=0.0
      TM(I)=0.0
      SL(I)=0.0
      XL(I)=0.0
      DO 20 J=1,120,1
        C(I,J)=0.0
20    CONTINUE
30  CONTINUE

```

2000 DO 700 I=1,NR,1

```

      DO 710 J=2,N,1
        C(I+1,J)=Q*(C(I,J-1)-2*C(I,J)+C(I,J+1))+C(I,J)
710    CONTINUE

```

\*\*\*\*\*  
 \* ### CALCULATION OF CONCENTRATION IN INSIDE SURFACE \*  
 \* OF THE PACKAGING MATERIAL (CLH), THE HEADSPACE \*  
 \* (CH) AND THE OUTSIDE SURFACE OF PRODUCT (CRH) \*  
 \*\*\*\*\*

```

      C(I+1,N+2)=A1*C(I,N)-A1*C(I,N+1)+C(I,N+2)
+      -B1*C(I,N+3)+B1*C(I,N+4)
      C(I+1,N+1)=HL*C(I+1,N+2)
      AW(I+1)=C(I+1,N+2)/CSAT
      M(I+1)=AW(I+1)/(AA*AW(I+1)**2+B*AW(I+1)+CC)
      C(I+1,N+3)=M(I+1)*W/(100*VR)

```

\*\*\*\*\*  
 \* ### CALCULATION OF CONCENTRATION IN INSIDE PRODUCT ### \*  
 \*\*\*\*\*

```

    DO 720 J=N+4,U1
      C(I+1,J)=G*(C(I,J-1)-2*C(I,J)+C(I,J+1))

```

```

      +      +C(I,J)
720  CONTINUE
      C(I+1,U2)=G*(C(I,U1)-C(I,U2))+C(I,U2)
      C(I+1,U3)=1*C(I+1,U2)
700  CONTINUE

*****
*   ### CALCULATION OF TOTAL WATER GAIN AND SHELF-LIFE ###   *
*****

      DO 800 I=1,NR,1
        A(I)=0
800  CONTINUE

      DO 810 I=1,NR,1
        DO 820 J=N+4,U2,1
          A(I)=A(I)+C(I+1,J)
820  CONTINUE

          XL(I)=AR*ER*((C(I+1,N+3)+C(I+1,U3))/2+A(I))

810  CONTINUE

      DO 900 I=1,NR,1
        TM(I+1)=100*XL(I)/W .
        TT(I+1)=1+TT(I)
        SL(I+1)=TT(I+1)*S/3600
900  CONTINUE

*****
*   ### PRINT THE CONCENTRATION PROFILE ###   *
*****

      F=TT(NR+1)/Z
      F1=INT(F)
      F2=ABS(F-F1)

      IF(F2.GT.1/Z) GOTO 3000

      WRITE (6,1000) (C(NR+1,J)*1000,J=1,N+2),M(NR+1)
      WRITE (6,1000) (C(NR+1,J)*1000,J=N+3,U3,U/5),
+      TM(201),SL(201)

1000  FORMAT (F8.4,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4,
+/,F8.4,1X,F8.4,1X,F8.4,1X,F8.4,1X,F8.4)

*****
*   CALCULATION SHELF-LIFE   *
*****

3000  IF((C(NR+1,N+2).LT.CE).AND.(C(NR+1,N+2).NE.CE)) GOTO

```

```

+3100
  IF((C(NR+1,U3).LT.C(NR+1,N+3)).AND.(C(NR+1,U3).
+   NE.C(NR+1,N+3))) GOTO 4000

      IF(TM(NR+1).LT.AMC) THEN
          PRINT *, '          It has infinite shelf-life'
          STOP
      ELSE
          GOTO 6000
      ENDIF

3100 IF((TM(NR+1).LT.AMC).AND.(TM(NR+1).NE.AMC)) THEN
      TT(1)=TT(NR+1)
      DO 3200 J=1,U3,1
          C(1,J)=C(NR+1,J)
3200  CONTINUE
      GOTO 2000
  ELSE
      GOTO 6000
  ENDIF

4000 IF((TM(NR+1).LT.AMC).AND.(TM(NR+1).NE.AMC)) THEN
      TT(1)=TT(NR+1)
      DO 4100 J=N+2,U3,1
          C(1,J)=C(NR+1,J)
4100  CONTINUE
      GOTO 2000
  ELSE
      GOTO 6000
  ENDIF

*****
*      SHELF-LIFE      *
*****

6000 PRINT*, '-----',
+ '-----'
      WRITE(6,6100) SL(NR+1)
6100 FORMAT(10X, 'SHELF-LIFE OF THIS PRODUCT IS', 1X, F10.5,
+ 'hrs')

      PRINT*, '-----',
+ '-----'
      RETURN
      END

```

## **.LIST OF REFERENCES**

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