A FUNDAMENTAL ANALYSIS OF EQUILIBRIUM AND TRANSPORT PROCESSES IN THE DRYING OF VEGETABLE FOODSTUFFS

by

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ABSTRACT

A FUNDAMENTAL ANALYSIS OF EQUILIBRIUM AND TRANSPORT PROCESSES IN THE DRYING OF VEGETABLE FOODSTUFFS.

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The equilibrium and kinetics of the drying of vegetable foodstuffs are studied. To do this, the cellular membrane permeability is considered. Conflicting evidence and definitions are reconciled by referring them to a rigorous definition of permeability and taking into account the boundary layer resistances. On this basis the flux of water through the cellular membrane is predicted and compared with experimental data to determine that water permeation through the membrane is not the controlling step.

After reviewing existing correlations to predict the equilibrium of foodstuffs with moist air, it is found that they are not adequate. A new equilibrium expression is presented on the basis of equal chemical potentials in the external and internal phases. Existing data on transport properties are reviewed and new data reported. New expressions to predict transport properties are developed on the basis of a model for the porous tissue structure and the properties of the constituent materials.

The mass and energy transport equations are written for the case under consideration and they are coupled through use of the equilibrium expression. To do this a physical model of the process is outlined which takes into account the tissue structure and considers the outward flux of water as one of water vapour through stagnant air. Using the selected initial and boundary conditions the system of partial non-linear differential equations is solved numerically for vapour weight fraction and temperature. Through the equilibrium expression the resulting values of moisture content are obtained and averaged over the volume at each time step. The predicted change of moisture content as a function of time is compared with experimental data. Satisfactory agreement is observed.

TO MY PARENTS

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TABLE OF CONTENTS

REFERENCES

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

All symbols used are defined below, with the exception of some of occasional use which are defined in the text. When the same symbol designates different constants, the respective defining equation numbers are indicated.

$\hat{a}$ = activity of component in solution.

a' = constant, equations (52) and (53).

b = constant.

c = constant, equations (47) and (49).

c_p = specific heat, J/kgK.

d = non-sugar dry matter, kg.

d_i = generalized driving force.

g = acceleration, m/s^2

h = heat transfer coefficient, $J/m^2 s$ K.

k = thermal conductivity, N/sK.

k = mass transfer coefficient, m/s or $kg/m^2 s$.

ℓ = constant.

m = weight, kg.

n = vapour mass flux, $kg/m^2 s$.

n = moles.

n' = constant.

p = vapour pressure, at

p = pressure, at

q = number of cells.

q = heat flux $J/m^2 s$

r = radius, m

r' = constant

t = time, s
v = velocity, m/s
w = weight fraction
x = mole fraction, liquid phase
y = mole fraction, gas phase
z = coordinate axis

A = area, m^2
A = temperature dependent variable
B = constant, equations (48) and (51)
C = concentration, $kmol/m^3$
D = diffusion coefficient, m^2/s
D' = effective diffusivity, m^2/s
Đ = multicomponent mass diffusivity, m^2/s
E = constant
H = enthalpy, J
J = diffusional flux, $kmol/m^2s$ or m^3/m^2s
K = coefficient
L = length, m
L = Phenomenological coefficient
M = molecular weight, kg/kmol
N = molar flux with respect to a fixed point, mol/m^2s
P = constant
P = permeability, m/s or m/s at
P' = permeability, when convective flux is taken into account, m/s.
R = gas constant, m^3at/mol K.
S = stress, at
S = entropy, J
T = temperature, K
V = volume, m^3

W = water vapour weight fraction, kg/kg.

X = moisture content, kg water/kg dry matter.

Y = air humidity, kg moisture/kg dry air.

γ = activity coefficient

δ = internal boundary layer thickness, microns

ε = porosity, m^3/m^3

η = ratio available area/total area of a sphere

θ = water volumetric content, m^3/m^3

κ = constant, equations (50), (51) and (53)

λ = ratio cube edge/sphere diameter

ψ = water potential, at

μ = chemical potential, J/mol

ξ = constant

π = osmotic pressure, at

ρ = density, kg/m^3

σ = reflection coefficient

$\underline{\tau}$ = viscous stress tensor, kg/s^2m

ϕ = water vapour activity

χ = constant, J/m^3

ω = water vapour weight fraction, kg/kg.

Ω = relaxation coefficient

<u>Subscripts</u>

a = atmospheric

bulk = bulk property

c = cellular matter

c_1 = cellular matter of one cell

d = diffusional
da = dry air
ex = external
g = gas phase
i = a general component
j = a general solute
ℓ = characteristic value, equation (54)
l = liquid
m = membrane
mv = monolayer value
mx = solid matrix
o = full turgor
os = osmotic
ose = tissue matter other than water and sugars
out = external
p = hydraulic permeability
ps = porous solid
s = solute, solid constituent
soln = solution
sp = sorptional process
t = true
v = volumetric
w = water
up = water, due to a pressure effect
wv = water vapour
x = defined on the basis of mole fraction x

C = defined on the basis of molar concentration, C.

M = insoluble material (matric material)

S = surface

I = range of X defined by equation (53)

II = range of X defined by equation (54)

ω = mass transfer, ω driving force.

SUPERSCRIPTS.

in = internal

m = membrane

o = value when cellular pressure equals atmospheric pressure

out = external

sat = saturated

vac = vacuole

1 = single unit

* = guessed value

Overlines

^ = property per kg (unless specified)

– = partial molar property

CHAPTER I

INTRODUCTION

The drying of foodstuffs presents an interesting problem in chemical engineering modelling. The challenge in this case is to use the generalized transport phenomena approach and at the same time to take into account the peculiarities that characterize foodstuffs, making them different from the heterogeneous structures more frequently studied in chemical engineering.

When an analysis is made of the structure of cellular tissues of which foodstuffs are made, it is realized that the transport properties should depend on the constituents and the way they are organized. It then becomes apparent that the prediction of these properties is closely related to the ability to model the porous structure in question. Accordingly the drying behaviour will depend on these characteristics. In this sense it is hoped that the present work will suggest ways to systematize the study of the drying of different foodstuffs.

CHAPTER II

ON CELLULAR MEMBRANE PERMEABILITY

Experimental information

Two main types of experiments can be found in the literature. One is based on an osmotic driving force. The other is based on a purely diffusional driving force. In the first case, the permeability results from:

$$\frac{dV}{dt} = - P_{os} \mathcal{A}(\pi^{in} - \pi^{out}) \qquad (1)$$

as

$$\pi \simeq RT\ \Sigma C_j = RT\ (C - C_w)$$

$$\frac{dV}{dt} = P_{os}\ \mathcal{A}\ RT(C_w^{in} - C_w^{out})$$

In the second case, the diffusion is usually one of labelled water versus water:

$$\frac{\partial n_w}{\partial t} = - \frac{D\mathcal{A}(C_w^{out} - C_w^{in})}{Dx} = P_d\ A(C_w^{in} - C_w^{out}) \qquad (2)$$

Typical experimental arrangements

In the case of artificial bilayer lipid membranes (BLM), H. T. Tien (1974) describes typical experimental arrangements. For P_{os} a 10 ml Teflon beaker is the inner chamber, which is enclosed in an outer chamber. On the wall of the Teflon beaker there is a semipermeable membrane. To start the experiment, solute is added to the outer chamber and is thoroughly mixed. Water will then go through the membrane towards the outer chamber, causing an inward bulging of the membrane. The volume of water that has permeated is measured by adding liquid until the membrane is again in its original planar position. This is checked by reflecting a light over the membrane.

To determine P_d a 5 ml Teflon cup, which can be sealed gas-tight is placed inside a larger beaker. The membrane again occupies a section of the wall.

A known volume of THO is added to the inner chamber. Its passage to the outer chamber is recorded as a function of time.

It can be seen that bulk concentrations are used for calculation purposes. The membranes are very small (e.g., membrane diameter $\doteq$ 1 mm, Huang and Thompson (1966)). Usually there is stirring only at one side of the membrane or there is no stirring.

With actual cells many experimental approaches have been tried. They differ in type of cell, mode of isolation and way of measuring concentrations and or changes in volume. Some experiments have been made with whole pieces of tissue.

The experiments of Solomon (Sidel and Solomon, 1957, Paganelli and Solomon, 1957) are representative of experimental techniques involving single cells. The osmotic experiments were made by mixing blood with a variety of anisotonic media, using a recirculating mixing chamber. The change in volume was measured by light scattering. The tritiated water experiments were made by mixing blood and tritiated water in a similar mixing chamber. The extracellular water was sampled at definite time intervals and analyzed for its tritium content.

Kohn and Dainty (1966) used disks of beet and artichoke of different thickness, which were submerged into anisotonic solutions. Glinka and Reinhold (1972) made similar experiments with carrots of constant thickness. No stirring was used. The two above papers report data as half-times instead of permeabilities.

Apparently, all of the experiments have been done with liquid phases at both sides of the membrane.

The definitions of permeability

There is a certain degree of confusion as to the definition of permeability, which results from the driving forces chosen or from more general coefficients which have a restricted meaning when applied to water permeability through semipermeable membranes.

Stein (1967) and Nobel (1974) define several coefficients which are used throughout the literature. They are summarized and interrelated below.

In general $$J_w = L_{ww}\Delta\mu_w + L_{ws}\Delta\mu_s \qquad (3)$$

$$J_s = L_{sw}\Delta\mu_w + L_{ss}\Delta\mu_s$$

assuming the membrane is fully non-permeable to sugars

$$\sigma = 1$$

$$J_s = 0$$

$$L_{sw} = 0 = L_{ws}$$

$$L_{ss} = 0$$

$$J_w = L_{ww} \Delta\mu_w$$

where L_{ww} is the phenomenological coefficient for water flux due to water force.

$$\mu_w = \mu_w^o + RT\ \ln\gamma_w x_w + \bar{V}_w(p - p^o)$$

Thus

$$J_w = L_{ww}\left[RT\ \ln \frac{(\gamma_w x_w)^{in}}{(\gamma_w x_w)^{out}} + \bar{V}_w(p^{in} - p^{out})\right] \qquad (4)$$

This can be expressed in terms of osmotic pressure

$$RT\ \ln \hat{a}_w = RT\ \ln \gamma_w x_w = - \bar{V}_w \pi \qquad (5)$$

Or, using an approximation, in terms of molar concentration:

$$\ln \hat{a}_w \simeq \ln x_w = \ln\left(1 - \frac{n_s}{n_w + n_s}\right) \simeq - \frac{n_s}{n_w + n_s} \simeq - \frac{n_s}{n_w}$$

$$\frac{\ln \hat{a}_w}{\bar{V}_w} \simeq - \frac{n_s}{n_w \bar{V}_w} \simeq - C_s$$

Thus

$$RT \ln \frac{\hat{a}_w^{in}}{\hat{a}_w^{out}} = \bar{V}_w RT \left(\frac{\ln \hat{a}_w^{in}}{\bar{V}_w} - \frac{\ln \hat{a}_w^{out}}{\bar{V}_w} \right)$$

$$= \bar{V}_w RT \ (C_s^{out} - C_s^{in})$$

$$= RT \ \bar{V}_w (C_w^{in} - C_w^{out}) \qquad (6)$$

Equation (4) can be written in two different ways, taking into account eqns. (5) and (6):

$$J_w = L_{ww} \left[\bar{V}_w (\pi^{out} - \pi^{in}) + \bar{V}_w (p^{in} - p^{out}) \right]$$

$$J_w = L_{ww} \ \bar{V}_w (\Delta p - \Delta \pi) \qquad (7)$$

where Δ is an operator which means value in left hand side, or inside, minus value in right hand side or outside.

$$J_w = L_{ww} \left[RT \ \bar{V}_w (C_w^{in} - C_w^{out}) + \bar{V}_w (p^{in} - p^{out}) \right]$$

$$J_w = L_{ww} \ RT \ \bar{V}_w \left[\Delta C_w + \frac{\Delta p}{RT} \right] \qquad (8)$$

Note that (5) and (6) are identical if the phenomenon by which there is a water flux is osmotic and only osmotic. Otherwise they represent different problems.

An alternative definition is based on volumetric flux. The "hydraulic conductivity coefficient" or "hydraulic permeability" L_p is defined:

$$J_v = L_p(\Delta p - \sum_j \sigma_j \Delta\pi_j)$$

where $$J_v = J_w\bar{V}_w + J_s\bar{V}_s$$

For the case under consideration

$$J_v = J_w\bar{V}_w = L_p(\Delta p - \Delta\pi) \qquad (9)$$

For volumetric flux of water and "water potential" as the driving force the "water conductivity coefficient" is defined:

$$J_{v_w} = J_v = J_w\bar{V}_w = L_w(\psi^{in} - \psi^{out}) \qquad (10)$$

$$\psi = \frac{\mu}{\bar{V}_w}$$

Thus $$J_w\bar{V}_w = \frac{L_w}{\bar{V}_w}(\mu^{in} - \mu^{out}) = L_w\left(\frac{RT}{\bar{V}_w} \ln \frac{\hat{a}_w^{in}}{\hat{a}_w^{out}} + \Delta p\right) \qquad (11)$$

using (6)

$$J_w\bar{V}_w = L_w\left(\frac{RT}{\cancel{\bar{V}_w}} \cancel{\bar{V}_w}\, \Delta C + \Delta p\right)$$

for a purely diffusional phenomenon or an osmotic one, provided that the latter case be one of diffusional osmosis.

$$J_w\bar{V}_w = L_w(RT\Delta C + \Delta p)$$

$$J_w = L_w \frac{RT}{\bar{V}_w}\left(\Delta C + \frac{\Delta p}{RT}\right) \qquad (12)$$

or, with the above restriction, introducing (5) in (11)

$$J_w\bar{V}_w = L_w\left[-\bar{V}_w \frac{\Delta\pi}{\bar{V}_w} + \Delta p\right]$$

$$J_w = \frac{L_w}{\bar{V}_w}(\Delta p - \Delta\pi) \qquad (13)$$

A more rigorous definition

The above definitions fail to account for the convective contribution to water flux, since they describe only the diffusional flux.

Lightfoot (1974) has presented an approach in which the membrane is considered one of the species, to allow for the body forces term.

From the postulate that fluxes are linearly and homogeneously related to driving forces, defining previously a generalized mass transfer driving force $\vec{d}_i$, it follows:

$$CRT\,\vec{d}_i = \sum_{j=1}^{n} L_{ij}(\vec{v}_j - \vec{v}) + L_{io}\vec{\nabla}T$$

$$\vec{\nabla}\ln T = \sum_{j=1}^{n} L_{oj}(\vec{v}_j - \vec{v}) + L_{oo}\,\vec{q}$$

neglecting the contribution of thermal diffusion, which is normally unimportant in biological systems

$$\vec{d}_i = \sum_{\substack{j=1 \\ j \neq k}}^{n} \frac{L_{ij}}{CRT} (\vec{v}_j - \vec{v}_k) \qquad (14)$$

where v_k has been used as the reference velocity. Equation (14) is now a set of Stefan-Maxwell equations.

The phenomenological coefficient is re-defined in terms of the multicomponent mass diffusivities $\mathcal{D}_{ij}$.

$$\vec{d}_i = \sum_{\substack{j=1 \\ j \neq k}}^{n} \frac{x_i x_j}{\mathcal{D}_{ij}} (\vec{v}_j - \vec{v}_k)$$

From an entropy balance it can be shown that

$$CRT\,\vec{d}_i = C_i (\vec{\nabla}\mu_i)_{P,T} + (C_i \bar{V}_i - w_i)\vec{\nabla}p - \rho_i (\vec{g}_i - \sum_k w_k \vec{g}_k) \qquad (15)$$

Following the approach used by Scattergood and Lightfoot (1968) it is concluded that for a binary system composed of water and the membrane, the body forces are respectively

$$\vec{g}_m = \vec{g} + \frac{\vec{\nabla}p}{\rho_m}$$

for the membrane and, for water

$$\vec{g}_w = \vec{g}$$

Thus, the body forces term in equation (15) can be written

$$\vec{g} - w_w\vec{g} - w_m\vec{g} - w_m\frac{\vec{\nabla}p}{\rho_m} = -\frac{\vec{\nabla}p}{\rho}$$

Equation (15) becomes now

$$CRT\ \vec{d}_w = C_w(\vec{\nabla}\mu_w)_{P,T} + (C_w\bar{V}_w - w_w)\vec{\nabla}p + \rho_w\frac{\vec{\nabla}p}{\rho}$$

$$CRT\ \vec{d}_w = C_w(\vec{\nabla}\mu_w)_{P,T} + C_w\bar{V}_w\vec{\nabla}p$$

$$= C_w\ RT\ (\vec{\nabla}\ \ln\ a_w)_{P,T} + C_w\bar{V}_w\vec{\nabla}p$$

$$\vec{d}_w = x_w(\vec{\nabla}\ \ln\ a_w)_{P,T} + x_w\frac{\bar{V}_w}{RT}\vec{\nabla}p \qquad (16)$$

$$x_w\ \vec{\nabla}\ \ln\ a_w = x_w\ \vec{\nabla}\ \ln\ \gamma_w\ x_w = x_w(\vec{\nabla}\ \ln\ \gamma_w + \vec{\nabla}\ \ln\ x_w)$$

$$= x_w\ \vec{\nabla}\ \ln\ \gamma_w + \vec{\nabla}x_w$$

$$x_w\ \vec{\nabla}\ \ln\ \gamma_w = \frac{\partial \ln\ \gamma_w}{\partial \ln\ x_w}\ \vec{\nabla}x_w$$

thus

$$x_w\ \vec{\nabla}\ \ln\ a_w = \vec{\nabla}x_w\left(1 + \frac{\partial \ln\ \gamma_w}{\partial \ln\ x_w}\right) \qquad (17)$$

Fick's equation

$$N_w = J_w + x_w(N_w + N_m) \qquad (18)$$

can be used here, redefining the diffusional term

$$\vec{J}_w = - C \text{Ɖ}_{wm} \vec{d}_w \tag{19}$$

Taking into account (16), (17), (18) and (19)

$$N_w = - C \text{Ɖ}_{wm} \left[\left(1 + \frac{\partial \ln \gamma_w}{\partial \ln x_w}\right) \frac{\partial x_w}{\partial z} + \frac{x_w \bar{V}_w}{RT} \frac{\partial p}{\partial z}\right] + x_w N_w \tag{20}$$

Before proceeding further it is necessary to recall the physical description of the problem. The membrane is regarded mainly as a bimolecular lipid layer, hydrocarbon end pointing hydrocarbon end, polar ends pointing outwards either surrounded by or indented by proteins. It is assumed that they behave as a thin layer of oily material.

Both external phases are dilute solutions, eventually one of them may be pure water.

As the membrane interphase concentrations cannot be measured, a partition coefficient is defined

$$K_{dw} = \frac{C_w^m}{C_w} \tag{21}$$

The total molar concentration should be essentially constant and the same can be expected to be γ_w throughout the membrane. Therefore, equation (20) can be simplified

$$N_w = - \text{Đ}_{wm} \left(\frac{\partial C_w^m}{\partial z} + C_w^m \frac{\bar{V}_w}{RT} \frac{\partial p}{\partial z} \right) + x_w N_w \qquad (22)$$

It is interesting to note that in terms of mole fraction the contention of these solutions being dilute ones is not a heavy restriction. For typical vacuolar compositions of apple tissue, table 1 shows this fact.

Equation (22) can be integrated

$$N_w = - \text{Đ}_{wm} \left[\frac{C_{we}^{m,out} - C_{we}^{m,out}}{\Delta z} + \frac{C_w^m \bar{V}_w}{RT} \frac{(p^{out} - p^{in})}{\Delta z} \right] + (x_w)_{av} N_w \qquad (23)$$

where $(x_w)_{av}$ is the average water mole fraction in the membrane.

If the partition coefficient is the same at both sides, i.e. the relationship between external water concentration and local membrane composition is linear, and $C_w^m \bar{V}_w \approx 1$

$$N_w = \frac{\text{Đ}_{wm} K_{dw}}{\Delta z} \left[C_{we}^{in} - C_{we}^{out} + \frac{1}{RT} (p^{in} - p^{out}) \right] + (x_w)_{av} N_w \qquad (24)$$

The equilibrium external concentrations can be substituted by bulk external phase concentrations provided there is no significant mass transfer resistance across the boundary layer. Then

Table 1

Typical vacuolar water mole fraction as a function of moisture content

X g H_2O/g dry material	x_W
7	0.9905
1	0.9368
0.48	0.8768
0.32*	0.8259
0.16	0.7034

* commercial dehydration limit.

$$N_w = P'_w \left[C_w^{in} - C_w^{out} + \frac{1}{RT} (p^{in} - p^{out}) \right] + (x_w)_{av} N_w \tag{25}$$

Interrelationship among the permeability coefficients

Considering the above definitions, it can be seen that all but (25) neglect the convective contribution to the water flux. This is acceptable only when $(x_w)_{av}$, the membrane average water mole fraction, is close to zero. Then:

$$N_w \simeq P_w \left[C_w^{in} - C_w^{out} + \frac{1}{RT} (p^{in} - p^{out}) \right] \tag{26}$$

The coefficients defined on the basis of osmotic gradients can be equated to those defined on the basis of concentrations provided there is no parallel or alternate mechanism superimposed with the diffusional one.

Most of the experiments with BLM are set so as to ensure equal hydrostatic pressure at both sides of the membrane. This is not always true when cells are involved.

Taking into account these remarks, table 2 can be used to interrelate the different permeability coefficients.

Experimental data

The literature reports experimental values for the water permeability coefficient, usually naming it according to the driving force under consideration. Thus experiments using labelled water - water are reported in terms of a "diffusional permeability" while those

Table 2

Interrelationship among the permeability coefficients

Equation	Symbol	Driving Force	Units	$P_w =$
(26)	P_w	C and P	cm/sec	P_w
(25)	P'_w	C and P	cm/sec	$P'_w/(1 - x_w)$
(24)	$Đ_{wm}$	C and P	cm^2/sec	$Đ_{wm}\ K_{Dw}/\Delta z(1 - x_w)$
(10)	L_w	ψ	cm/sec at	$L_w\ RT/\bar{V}_w$
(9)	L_p	P and π	cm/sec at	$L_p RT/\bar{V}_w$
(3)	L_{ww}	μ	$mol^2/at\ sec\ cm^5$	$L_{ww} RT\bar{V}_w$
(1)	P_{os}	π	cm/sec at	$P_{os} RT/\bar{V}_w$
(2)	P_d	C	cm/sec	P_d

based on an osmotic gradient are reported as yielding a "hydraulic" or "osmotic" permeability. Moreover, there is a wide range of values for these permeabilities and while a few experiments confirm the equivalence indicated in table 2, many give different values for the permeability of the same membrane when a different driving force is used. Tables 3 to 6 give observed values of water permeabilities for different membranes.

The bulk of the available data is for single cell membranes, with or without the cellular wall, and for synthetic membranes. The latter are basically bilayer lipid membranes. The data for tissue sections in terms of permeability coefficients is scarce. Because of the difficulty involved in accurately establishing the geometrical relationships, authors report permeability data in terms of half-times (see Kohn and Dainty, 1966; Glinka and Reinhold, 1972).

The differences among permeability values

The studies conducted on cell membrane properties appear to point to a unique basic structure, a bimolecular lipid layer with proteins around or ingrained (Stein, 1967; Nobel, 1974). On this basis it should be expected that the water permeability of membranes from different origins would be similar in magnitude. If the theoretical description of the phenomenon underlying equation (25) or the similar equations above, is correct, there is no apparent reason why P_{os} and P_d should be different. Nevertheless it can be seen from table 3 that water permeability values for single cells go from 0.23 to 127 x 10^{-4} cm/sec and those found by using an osmotic gradient are approximately equal to those found using a labelled water gradient in a few cases but differ significantly

Table 3

Water Permeabilities of Animal Cells

Cell			$P_{os}RT/\bar{V}_w$ 10^4 cm/sec	P_d 10^4 cm/sec	References
Arbacia punctulata	Sea Urchin (Atlantic coast)	unfertilised	2.2	--	Lillie (1916,1917) Lucke et al (1931)
		fertilised	4.5 - 6.7	--	Lillie (1916,1917) McCutcheon & Lucke (1932)
Paracentrolus lividus	Sea Urchin (Mediterranean)	unfertilised	2.2	--	Maxia (1934)
		fertilised	4.5	--	Maxia (1934)
Stronglyocentrotus, Dendraster, Patiria Pisaster (unfertilised)	Sea Urchin, Sand Dollar, Starfish (Pacific coast) (temp. 17-22°C)		2.2 - 8.9	--	Leitch (1931)
Zoothanium sp.	Fresh water peritrich ciliate		2.7 - 5.6	--	Kitching (1938)
Gregarina			4.5	--	Adcock (1940)
Chaetopterus Pergamentaceus	Marine annelid (Atlantic coast)		8.9 -11.2	--	Lucke et.al (1939)
Cumingia tellenoides	Marine mollusc (Atlantic coast)		8.9 -11.2	--	Lucke et al (1939)
Mouse, rat, chick	fibroblasts		8.9 -22.3	--	Brues & Masters (1936)
Rabbit	leucocytes		6.7	--	Shapiro & Parpart (1937)
Human	leucocytes		29.0	--	Shapiro & Parpart (1937)
Ox	erythrocytes		55.8	--	Jacobs (1932)
Human	erythrocytes		67.0	--	Jacobs (1932)
	Amoeba		0.37	0.23	Prescott & Zeuthen (1953)
	Frog, ovarian egg		89.1	1.28	ibid
	Frog, body cavity egg		1.30	0.75	ibid
	Xenopus, body cavity egg		1.59	0.90	ibid
	Zebra fish, ovarian egg		29.30	0.68	ibid
	Zebra fish, shed egg		0.45	0.36	ibid
	Human (adult) erythrocyte		127.0	53.00	Sidel & Solomon (1957) Paganelli & Solomon (1957)
	Human (adult) erythrocyte		116.0	41.0	Sjolin (1954) Barton & Brown (1964)
	Human (fetal) erythrocyte		61.0	23.00	ibid

Table 4

Water Permeabilities of Cells in Tissues (Vegetable & Animal)

Tissue	$P_{os}RT/\bar{V}_w$ 10^4 cm/sec	P_d 10^4 cm/sec	References
Toad, bladder:			
no vasopressin	4.1	0.95	Hays & Leaf (1962)
with vasopressin	188.0	1.6	ibid
Rat:			
luminal surface of intestinal mucosal cells	83	-	Lindemann & Solomon (1962)
kidney, proximal tubule	2400.0	-	Ullrich et al. (1964)
kidney, distal tubule	1100.0	-	Ullrich et al. (1964)
Beet root:			
unplasmolyzed	0.3	-	Myers (1951)

Table 5

Water Permeability of Vegetable Cells

Cell	$P_{os}RT/\overline{V}_w$ 10^4 cm/sec	P_d 10^4 cm/sec	References
Chlorophyceae:			
Cladophora glomerata (pH = 7)	12.3	-	Seeman (1950a)
Rhizonium hieroglyphicum	6.4	-	Lenk (1956)
Oedogonium echinospermum	4.3	-	Lenk (1956)
Spyrogira affinis	3.1	-	Lenk (1956)
Spyrogira communis	3.8	-	Lenk (1956)
Spyrogira condensata	6.7	-	Lenk (1956)
Spyrogira gracilis	7.5	-	Lenk (1956)
Spyrogira porticalis	2.5	-	Lenk (1956)
Spyrogira pseudovarians	2.0	-	Lenk (1956)
Spyrogira singularis	11.2	-	Lenk (1956)
Spyrogira stictica	2.7	-	Lenk (1956)
Spyrogira varians	3.2	-	Lenk (1956)
Spyrogira sp.	4.6	-	Lenk (1956)
Spyrogira sp.	3.2	-	Huber & Höfler (1930)
Spyrogira sp.	2.2	-	Bochsler (1948)
Spyrogira H. (pH = 7)	15.3	-	Seeman (1950a)
Zygnema velox	16.8	-	Huber & Höfler (1930)
Zygnema sp.	5.3	-	Bochsler (1948)
Zygnema sp.	17.7	-	Hofmeister (1935)

Characeae:			
Mougeotia scalaris	0.9	-	Lenk (1956)
Nitella flexilis (Transcellular osmosis)	154.0-416.0	-	Kamiya & Tazawa (1956)
Nitella mucronata, live cell	-	13.7	Collander (1954)
dead cell	-	17.0	Collander (1954)
isolated protoplast	-	50.0	Collander (1954)
Chara australis (Transcellular osmosis)	123.0	-	Dainty & Hope (1959)
Tolypellopsis stelligera, live cell	-	5.6	Wartiovaara (1944)
dead cell	-	16.8	Wartiovaara (1944)
membrane	-	8.9	Wartiovaara (1944)
intact cell	24.0	-	Palva (1939)
Phaeophyceae:			
Fucus vesiculosus (egg cell of sea water alga)	3.6	-	Resuhr (1935)
Filicinae:			
Salvinia natans (glycerine)	1.8	-	Seeman (1950b)
Salvinia natans	3.6	-	Seeman (1953)
Salvinia auriculata (leaf cell of fresh-water fern)	12.3	-	Huber & Höfler (1930)
Dicotyledonae:			
Caltha palustrio	4.0	-	Hofmeister (1935)
Anemone hepatica	0.7	-	Hofmeister (1935)
Ramunculus repens	3.5	-	Heinrich (1962)
Beta vulgaris	4.8	-	Myers (1951)
Stachys annua	3.6	-	Huber & Höfler (1930)
Stachys recta	5.4	-	Heinrich (1962)
Lamium maculatum	5.1	-	Heinrich (1962)
Solanum tuberosum	14.4	-	Heinrich (1962)
Physalis alkekengi	2.3	-	Heinrich (1962)

Monocotyledonae:

Valisneria spiralis (pH = 7)	2.6	-	Seeman (1950a)
Allium cepa (cell of onion)	7.8	-	Levitt et al.(1936)
Majanthemum bifolium	1.2	-	Seeman (1950b)
Majanthemum bifolium	1.7	-	Höfler (1934)
Majanthemum bifolium	2.2	-	Höfler (1930)
Majanthemum bifolium	2.0	-	Heinrich (1962)

Table 6

Water Permeabilities of Synthetic Membranes

	$P_{os}RT/\overline{V}_w$ 10^4 cm/sec	P_d 10^4 cm/sec	References	
Bimolecular Lipid Membrane	8.3 -14.4	2.3	Hanai et al. (1965)	
Dialysis Tubing	230	-	Durbin (1960)	
Cellophane	870	-	ibid	
Wet gel	3400	-	ibid	
Dialysis tubing	380	10.9	Ginzburg & Katchalsky (1963)	
Wet gel	1200	19.2	ibid	
Brain lipids in chloroform:methanol	24.0	-	Mueller et al. (1964)	
Lecithin (egg) in chloroform:methanol	17-120	4.4	Huang & Thompson (1966)	
Lecithin (egg) + Cholesterol in decane, NaCl	18	-	Hanai et al. (1966)	
sucrose	18	-	ibid	
urea	21	-	ibid	
Brain lipids + cholesterol	7- 21	-	Finkelstein & Cass (1967)	T = 36°C
Lecithin (egg); THO	-	4-5	Vreeman (1966)	T = 20°C
Oxidized cholesterol in octane	8.5±0.5	-	Tieng & Ting (1968)	T = 22.5°C
Cholesterol and HTDAB	8.2±0.5	-	ibid	T = 22.5°C
Cholesterol and DAD	8.8±0.5	-	ibid	T = 22.5°C
Oxidized cholesterol + 2.5×10^{-5}M valinomycin	9.5	-	ibid	
Chloroplast extract	51.0	-	Ting et al. (1968)	
Lecithin + cholesterol	31.7	-	Prince & Thompson (1969)	T = 25°C
Lecithin (egg) + 1.7×10^{-9}M vasopressin	39.3	-	Graziani & Livne (1971)	T = 28°C
Monogalactosyl diglyceride	73.1	-	Graziani & Livne (1973)	T = 37°C
Lecithin (egg), phosphatidyl choline and cholesterol in n-decane	20.0*	19.7*	Everitt & Haydon (1969) Everitt et al. (1969)	

(* boundaries resistances discounted)

in other cases.

If synthetic membranes are considered it can be seen that they differ even if the scatter of data is not so wide, 2.3 to 73.0 x 10^{-4} cm/sec. There is still a lack of agreement among permeabilities found using the alternate driving forces.

The data for tissues offer the same discrepancies.

It is significant that there is also an important increase in permeability when the cells are dead. Glinka and Reinhold (1972) found that the half time for THO equilibration was three times longer for a living carrot cylinder than for a dead one, under the same experimental conditions. The tissue was killed either by exposure to chloroform vapour or by freezing and thawing.

Dick (1971) finds a correlation by plotting the osmotic water permeability of live and dissected cells as a function of the surface to volume ratio: permeability increases as the ratio increases and dissected cells show a higher permeability. Contending that only when cells are larger the diffusional resistance is important the author concludes that "true membrane permeabilities are of the order of 10^{-3} cm/sec". The lower values for tracer experiments were explained on the grounds of the existence of water pores or channels. These pores would allow a parallel hydraulic flow when there is an osmotic gradient.

The idea of pores has been considered by several authors (Dainty,1963, Stein, 1967, among others) and the pore radius calculated by considering the osmotic flow a pure Pouiseille flow and the tracer flow, a Fickian one. Nevertheless there is no agreement among authors on this theory, as will be seen below.

Davson and Danieli (1952) collected early data on osmotic permeabilities. Bennet-Clark (1959) reported experimental methods and data for the same type of permeabilities. When discussing the relative permeabilities of plasmolyzed and unplasmolyzed cells, he concluded that the cell wall is relatively large-pored and permeable and the protoplast increases in permeability when plasmolyzed.

Stein (1967) regards the experimental data obtained by Paganelli and Solomon (1957) and by Sidel and Solomon (1957) as particularly reliable (cf. table 3). They show a 2.4/1.0 ratio between the osmotic and the labelled water permeability.

Tien (1974) examined the evidence in favour of the bimolecular lipid leaflet as a suitable experimental model for the biological membrane. He also points out that under the electron microscope all membranes thus far examined are in the order of 100 Å in thickness. After noting the discrepancies between permeabilities obtained with the different driving forces (cf. table 6) and reviewing the aqueous pores idea, he mentions that recent papers attribute the difference to inadequate stirring giving rise to stagnant layers at the biface stating that "it is now generally agreed that the equality of the diffusion and osmotic coefficients, and the liquid crystalline property and its high electrical resistance ... argue strongly against the existence of aqueous pores in at least unmodified BLM". Moreover, "in view of the fact that the interior of the BLM is liquid hydrocarbon-like, as well as from the evidence resulting from recent studies, the possibility of the existence of pores in the BLM is untenable". The reference to recent studies seems to apply in particular to Andreoli and Troutman (1971) who found that in BLM modified by amphotericin B, the unstirred layers account for 84% of the total resistance to the diffusion of water (they measured P_d).

Dainty has emphasized the boundary layer effect, the "unstirred layer" as it is called, as a possible explanation for the discrepancies (Dainty, 1963, Kohn and Dainty, 1966). He estimates this layer as being between 20 μ and 500 μ thick, depending on sizes and rate of stirring and that it is significantly more important for labelled water diffusion although it exists in both types of experiments. The reason for this difference would be the sweeping effect of the bulk flow on the solute, which drives it away from the membrane. This in turn results in a diffusion of solute. The result is, for $\sigma = 1$ and at steady state

$$J_v C_j + D_{j,H_2O} \frac{dC_j}{dx} = 0$$

Thus, the boundary layer in the osmotic gradient experiments would be stirred by the flux. Dainty's statement (Dainty, 1963) is quite strong although they do not produce enough quantitative backing: "In most experiments only the external unstirred layer is important"; "I would like to make the point quite strongly here that in all the published comparisons of $L_pRT/\bar{V}_w$ with P_d, P_d has always been underestimated and therefore the difference between $L_p\ RT/\bar{V}_w$ and P_d is never as great as has been claimed". On the other hand, the above equation does not take into account natural convection.

Kohn and Dainty (1966) and Glinka and Reinhold (1972) have tried to measure membrane permeabilities to water in sections of whole tissue. Kohn and Dainty investigated beets and artichokes. The authors believe that the values for P_{os} of the largest cells are probably accurate, in particular when obtained by the transcellular osmosis technique. These are in the order of 10^{-2} cm/sec. The 0.26×10^{-4} cm/sec for unplasmolyzed beet parenchyma tissue (Myers, 1951) is regarded as much less reliable. Using an unsteady state approach, after Phillip (1958) the authors claim that if cell permeability were the single controlling variable the half time should be independent of the sample thickness, which is contrary to their experimental evidence.

Stadelman (1963) corroborates this finding stating that the rate of exchange of labelled and unlabelled water is controlled entirely by the dimensions of the tissue and not by the diffusional permeability of the cell membranes. Glinka and Reinhold (1972) in turn experimented with cylinders of carrot tissue subjected to labelled water exchange. They claim that the effect of the membrane is significant enough to result in different permeability values when the membrane is treated with different chemicals. Thus, if there is a significant boundary layer effect, it is not as high as to mask the true membrane permeability change thus obtained.

Some relevant equations

One of the simplest relevant equations to be considered is the one describing the series resistances involved.

$$\frac{1}{P} = \frac{1}{P_t^m} + \frac{1}{k^{out}} + \frac{1}{k^{in}} \tag{27}$$

It can be seen that if the diffusional boundary layer resistances were controlling

$$O(k) << O(P_t^m) \tag{28}$$

For the true membrane permeability to be at least influential

$$O(k) \simeq O(P_t^m) \tag{29}$$

If the diffusional boundary layer resistances were negligible

$$O(k) >> O(P_t^m) \ . \tag{30}$$

One approximation to the value of k^{out} when dealing with single spherical cells can be made using the classical heat/mass transfer correlations for a single sphere of diameter D in a large body of fluid. It is known that both the correlation for free convection and that for forced convection (Bird, Stewart and Lightfoot, 1960) yield for a motionless fluid

$$Nu_{AB} = \frac{kx}{C} \; \frac{D}{\mathcal{D}_{AB}} = k_C \frac{D}{\mathcal{D}_{AB}} = 2$$

Thus

$$k_C = 2\,\frac{\mathcal{D}_{AB}}{D} \tag{31}$$

This is valid for equimolar counterdiffusion only, which is an acceptable description of the heavy water experiments. The osmotic experiments can be thought as diffusion of one component, the other remaining stagnant. For this case equation (32) must be used instead of (31):

$$k_C = 2\,\frac{D_{AB}}{D}\;\frac{C}{(C_B)_{lm}} \qquad (32)$$

Typical experiments for the osmotic case, such as Zeeman (1950a) or Levitt et al (1936), show $C/(C_B)_{ln}$ relationships of an order of magnitude 10^2.

It can be seen that the outer boundary layer resistance is to be expected to be much more influential when labelled water experiments are considered. If the order of magnitude of vegetable cellular membranes is considered, the diameter for total external boundary layer control in the two alternative cases is shown in table 7.

Unfortunately there is not accurate experimental data available to recalculate the diffusional permeabilites. Nevertheless it is apparent that they are higher than the reported values. By defining

$$P^{in} = \frac{1}{1/P_m^t + 1/k_C^{in}} = \frac{1}{1/P - 1/k_C^{out}} \qquad (33)$$

a few tentative calculations are shown in table 8.

It can be expected that the difference between P^{in} and P_t^m be due to the internal boundary layer resistance. Poznansky et al (1976)

Table 7

Order of magnitude of cellular diameter for total external boundary layer control

$N_A = -N_B$	$N_B = 0$
130-2000 μ	13000-200000 μ

predicted internal boundary layers of about 200 μ for spherical BLM. The actual value depends of course on the sphere radius. If the inside of the cell is considered homogeneous and the diffusivity and total concentration is regarded as constant, the differential equation

$$\frac{d}{dr}\left(r^2\frac{dC_w}{dr}\right) = 0 \qquad (34)$$

describe the concentration profile.

Accepting the above estimation of P^{in}

$$C_w = \frac{G}{r} + H$$

$$C^{i}_{wm} = \frac{G}{R} + H$$

$$\mathcal{D}^{i}_{AB}\ \frac{G}{R} = P^{in}(C^{in}_{w} - C^{out}_{m}) = P^{m}_{t}\ (C^{in}_{m} - C^{out}_{m})$$

Thus

$$\frac{1}{P_t^{m}} = \frac{1}{P^{in}} - \frac{\delta}{\mathcal{D}^{in}_{AB}\ (1 - \delta/R)} \qquad (35)$$

Taking P^m_t as P_w from an osmotic experiment, it is possible to estimate δ. The results for a few cases are given in table 8. They show that the above indicated expectation is reasonable.

Moreover, from equations (35), (31) and (27), it can be seen that

$$\frac{1}{P} = \frac{1}{P^{m}_{t}} + \frac{\delta}{\mathcal{D}^{in}_{AB}\ (1 - \delta/R)} + \frac{R}{\mathcal{D}^{out}}$$

Table 8

Diffusional Permeabilities Excluding the Outer Boundary Layer Mass Transfer Coefficient

Cell	P_d (cm/sec)	P^{in} x 10^4	δ μ	Reference
Frog, ovarian egg	1.28	2.3	43.0	Prescott and Zeuthen (1953)
Frog, cavity egg	0.75	1.1	234	
Xenopus, body cavity egg	0.90	1.2	276	
Human (adult) erythrocyte	41	46	2.3	Barton and Brown (1964)
Human (fetal) erythrocyte	23	25	2.6	Barton and Brown (.964)

By considering the diffusivities at both sides of the membrane approximately equal

$$\frac{1}{P} \approx \frac{1}{P_t^m} + \frac{R}{D_{AB}}\left(\frac{1}{1 - \delta/R}\right)$$

This equation justifies Dick's contention that the boundary layer resistances become influential for larger cells. Provided $\delta/R < 0.5$, the inner boundary layer will be more influential than the outer one.

It is concluded that the reported differences between P_d and $P_{os}RT/\bar{V}_w$ may be accountable for the internal and external mass transfer coefficients. Since the transfer mechanism involved in drying is similar to the one considered for P_{os}, the latter is the relevant value for our case.

Recent evidence on BLM permeabilities seems to clarify quite definitely the issue of the different permeabilities and boundary layer resistances.

Corrected permeability values in BLM

The synthetic membranes having a more amenable geometry and being easier to use under controlled experimental conditions, have allowed to gain understanding on the issue of the difference between osmotic and diffusional permeabilities.

Everitt and Haydon (1969) noted that the build up or depletion of solute concentration (Dainty, 1963) involves a corresponding change in density and therefore natural convection. By using the approach suggested by Levich (1962) with suitable changes in the boundary conditions, non-nil membrane equilibrium concentration and non-nil normal velocity at the wall, the authors were able to calculate the membrane equilibrium concentration values. These values permit a direct calculation of the true membrane permeability. The results are shown in table 9. The mass transfer coefficients have been calculated from the author's data at the high concentration side. The concentration ratios (bulk and equilibrium values) is also calculated.

It can be seen that the influence of the mass transfer resistances in series with the membrane, is very low when osmotic experiments are conducted.

On the other hand, Everitt et al (1969) proved that the boundary layer resistances are significant when labelled water diffusion is under consideration. The authors corrected the P_d values by two methods. In one they estimated the thickness of the boundary layers using membranes of known permeability (glass or one and two layers of a known membrane (cellophane)). In the other they placed the problem membrane in a known linear velocity profile. The results are quoted in table 10, indicating again an estimation of the mass transfer coefficient calculated from the original data as above. A third method based on the apparent permeability and time lag proved impracticable within the limits of accuracy of the experiment.

The selection of a representative permeability value

From the above discussion it can be seen that equation (20) and its further developments seem to describe reasonably well the permeation of water through the cellular membrane.

Table 9

Osmotic permeabilities $P_{os}RT/\bar{V}_w$ in BLM

Solution	Nominal permeability cm/sec x 10^3	Concentrations Conctd. side	Depleted side	Corrected Permeability cm/sec x 10^3	Difference %	Mass Transfer Coefficient cm/sec x 10^3
NaCl	1.72	0.9998	0.9985	1.96	14.0	28.0
NaCl	1.77	0.9984	0.9978	2.01	13.6	29.7
Urea	2.05	1	0.9996	2.08	1.5	284.3
Urea	1.90	1	0.9985	1.95	2.6	148.2

Table 10

Diffusional Permeabilities, P_d, in BLM

Method of correction	Corrected P_d cm/sec x 10^3	Mass Transfer Coefficient cm/sec x 10^3
Glass mesh	1.99	1.80
Cellophane	2.09	0.60
Linear velocity field	1.83	

The difference between P_{os} and P_d can be explained in terms of the usually unaccounted for boundary layer diffusional resistances. These are important when determining P_d and are negligible or relatively unimportant in osmotic experiments, especially at smaller cell sizes.

Thus, values of P_{os} can be used to estimate the rate of permeation through the cellular membrane. Since the boundary layer resistances are unimportant, bulk concentrations can be used instead of equilibrium membrane concentrations.

Dick (1966) has shown that there is a correlation between permeability coefficients and surface/volume ratio of the cells. His data is reproduced in table 11, for the sake of clarity.

The surface/volume ratio for apple cells, as reported by Reeve (1953) from histological studies, is within the range of 0.0190 to 0.0299 μ^{-1}. This corresponds, in Dick's data, to an average value

$$P_w = 4 \times 10^{-4} \text{ cm/sec}$$

The value should be acceptable to depict a drying process on the grounds that, as discussed earlier, the osmotic permeabilities are very close to the true membrane permeabilities.

On the other hand, the collected data for plant cells (table 5) shows a wide range of values but if the frequency of values is considered (table 12) it appears reasonable to narrow the selection to 1 to 10 x 10^{-4} cm/sec. The average value within this range is

$$P_w = 4.04 \times 10^{-4} \text{ cm/sec}$$

TABLE 11

OSMOTIC WATER PERMEABILITY COEFFICIENTS OF ANIMAL CELLS

Cell No.	Permeability Coefficient μ/sec	Surface/Volume Ratio μ^2/μ^3	Reference
A. Free Living Cells			
Amphibian and Fish Eggs			
1	1.3	0.003	Prescott & Zeuthen, *Acta physiol. scand.* 28, 77 (1953).
2	1.6	0.004	
3	0.45	0.009	
Protozoa			
4	0.37	0.017	Prescott & Zeuthen, *Acta physiol. scand.* 28, 77 (1953).
5	1.2	0.04	Mast & Fowler, *J. cell. comp. Physiol.* 6, 151 (1935).
6	3.6	0.23	Kitching, *J. exp. Biol.* 15, 143 (1938).
Marine invertebrate eggs			
7	8.4	0.035	Leitch, *J. cell. comp. Physiol.* 4, 457 (1934).
8	2.9	0.047	
9	1.9	0.072	
10	4.8	0.049	
11	1.2	0.078	
12	9.8	0.057	Lucké, Hartline & Ricca, *J. cell. comp. Physiol.* 14, 237, (1939).
13	2.7	0.078	
14	10	0.092	
15	11	0.060	Shapiro, *J. cell. comp. Physiol.* 18, 143 (1941).
16	3.8	0.079	Lucke, Ricca & Parpart, *J. natn. Cancer Inst.* 11, 1007 (1951).
17	13	0.12	Lucké & Ricca, *J. gen. Physiol.* 25, 215 (1941).
Mammalian leukocytes and ascites tumor cells			
18	11	0.56	Lucké, Hempling & Makler, *J. cell. comp. Physiol.* 47, 107 (1956). (Corrected results calculated by Dr. H. G. Hempling and published by his kind permission).
19	11	0.62	
20	14	0.66	
21	9.1	0.86	
22	13	0.88	
23	11	0.90	
24	89	0.38	Hempling, *J. gen. Physiol.* 44, 565 (1960).
25	6	0.71	Shapiro & Parpart, *J. cell. comp. Physiol.* 10, 147 (1937).
26	30	0.75	
Chick heart fibroblasts			
27	16	0.55	Brues & Masters, *Am. J. Cancer* 28, 324 (1936).
28	63	1.37	Dick, *Proc. Roy. Soc. B* 150, 43 (1959).
Mammalian erythrocytes			
29	49	1.75	Jacobs, *Biol. Bull mar. biol. Lab., Woods Hole* 62, 178 (1932).
30	67	1.88	
31	127	1.88	Sidel & Solomon, *J. gen. Physiol.* 41, 243 (1957).
32	221	1.88	Sjolin, *Acta paediat., Stockh.,* 43, suppl. 98
33	117	1.76	
34	400	1.82	Villegas, Barton & Solomon, *J. gen. Physiol.* 42, 355 (1958).
35	156	1.59	
B. Dissected Cells			
Cephalopod Axons			
36	11	0.011	Villegas & Villegas, *J. gen. Physiol.* 43, Suppl. 1, 73 (1960).
37	49	0.01	Hill, *J. Physiol., Lond.,* 111, 304 (1950).
38	16	0.02	
Amphibian and Fish Eggs			
39	89	0.004	Prescott & Zeuthen, *Acta physiol. scand.,* 28, 77 (1953).
40	29	0.009	
Frog muscle Fibers			
41	223	0.033	Hodgkin & Horowicz, *J. Physiol., Lond.,* 148, 127 (1959).
42	128	0.033	Zadunaisky *et al.*, *Nature, Lond.,* 200, 365 (1963).
43	67	0.016	Reuben *et al.*, *J. gen. Physiol.,* 47, 1141 (1964).

Table 12

Frequency of measured values of permeability for plant cells

(all values x 10^4 cm/s)

< 1	1 to 10	11 to 20	21 to 30	31 to 40	41 to 50	> 51
4	62	12	1	0	1	3

Most of the quoted data corresponds to sugar solutions outside and/or inside the cells. There is no specific data for apple cells, but a certain similarity could be claimed for Beta vulgaris.

On the other hand, some evidence like the transcellular osmosis experiments and the BLM data seem to indicate that the true membrane permeability is higher. Nobel (1974) states that a good estimate for the water permeability is 10^{-2} cm/sec(1). This is a very much alive issue in the field of biophysics and the experimental techniques involved are not easy. It is to be expected that through better experiments and a more refined analysis the issue will be eventually clarified. The above values can nevertheless be used for an order of magnitude analysis and they can be regarded as conservative figures, i.e., they may be lower than the actual values thus exaggerating the influence of the cellular permeability on the drying process.

The use of water permeability data to predict flux

The physical situation when drying is different from that for which the permeability was defined and experimentally determined (see figure 1 and equations (20) and (22)).

The main difference is that the intercellular space is the outside (or "right" side) and it is filled with moist air.

Going back to equation (23) it will yield

$$N_w = P'_w \left[C_w^{vac} + \frac{1}{RT} (p^{in} - p^{out}) \right] + (x_w)_{av} N_w \qquad (36)$$

---

(1) Kohn and Dainty (1966) shared this view, as pointed out earlier.

provided that, for the usual drying experimental conditions

$$0 \leqslant \frac{K_{wD}^{air,m}}{K_{wD}} \leqslant 100$$

which appears to be a restriction easily met.

A further simplification can be made considering the pressure term. According to Nobel (1974) the tonoplast is slack, not taut. Thus, there is no pressure drop. When stressed, two cases can be considered as representative: spherical cells and cylindrical cells. In the first case the stress would be

$$S = \frac{\Delta p \times r}{2\delta m}$$

In the second case

$$S = \frac{\Delta p \times r}{\delta m}$$

A higher limit at which most membranes rupture is (Nobel, 1971) S = 1 at.

Thus, the maximum contribution to the water flux due to the pressure term can be calculated by equation (37). The result is $N_{wP} = 2.7 \times 10^{-12}$ g moles/cm^{2}sec considering spherical cells with a representative membrane thickness of 100 $\overset{o}{A}$ and a cellular radius of 125 μ, the average value for apple tissue cells (Reeve, 1953).

$$N_{wP} = \frac{P_w}{RT} \frac{2S\delta^m}{r} \tag{37}$$

The pressure term is thus negligible and equation (38) can be regarded as suitable to calculate N_w

$$N_w = P'_w \frac{C_w^{vac}}{1 - (x_w)_{av}} \tag{38}$$

To be able to predict the water permeation flux, $(x_w)_{av}$ needs to be known. This is not easily available information, but two cases can be considered:

a) $(x_w)_{av} = x_w^{vac}$

b) Assuming very slight water solubility in the membrane, as would be the case if it were a pure lipid, $(x_w)_{av} \simeq 0$.

Experimental drying water fluxes

In previous work carried out by the author, Granny Smith apples were selected, washed, peeled and cut into parallelepipeds of 2.4 cm x 2.4 cm x 1.2 cm. They were sulfited by exposure to SO_2 and air dried on a weighing tray. The air was filtered and heated through a heat exchanger. To secure the desired air moisture, steam was injected. The steam injection was countercurrent to insure good mixing. The air velocity was measured by a hot wire anemometer. Dry and wet bulb temperatures were continuously recorded and controlled. Air velocity was 10 cm per sec, dry bulb temperature 76°C, and relative humidity of air, 10%. The weight of the drying sample was recorded as a function of time.

To translate this data in terms comparable to permeation fluxes it is needed to know the effective amount of cellular wall, i.e., the fraction of total cellular wall abutting on the intercellular air space. According to Slatyer (1967) practically all cells have part of their surface open to these spaces.

A geometrical model for the intercellular spaces

Reeve (1953) reported the total cell wall area per unit volume of apple flesh parenchyma, for several varieties. To calculate the experimental rates of drying in terms comparable to the permeation fluxes it is needed to know the effective amount of cellular area i.e., the fraction of total cellular wall area abutting on the intercellular spaces. Reeve (1953), Lee et al. (1967), published histological studies that give some insight into the geometry of the system. On this basis a simple geometrical model is proposed.

The cells do not behave as perfect spheres with only point contact among them. It is suggested that they appear as cubically truncated spheres, i.e., they occupy the common volume of a cube and a sphere intersecting in such a way, that they have a common center, the cube diameter being $2 \lambda r$. The portions of sphere outside the cube are melted into the adjacent sphere (Figure 1).

The values of λ must be

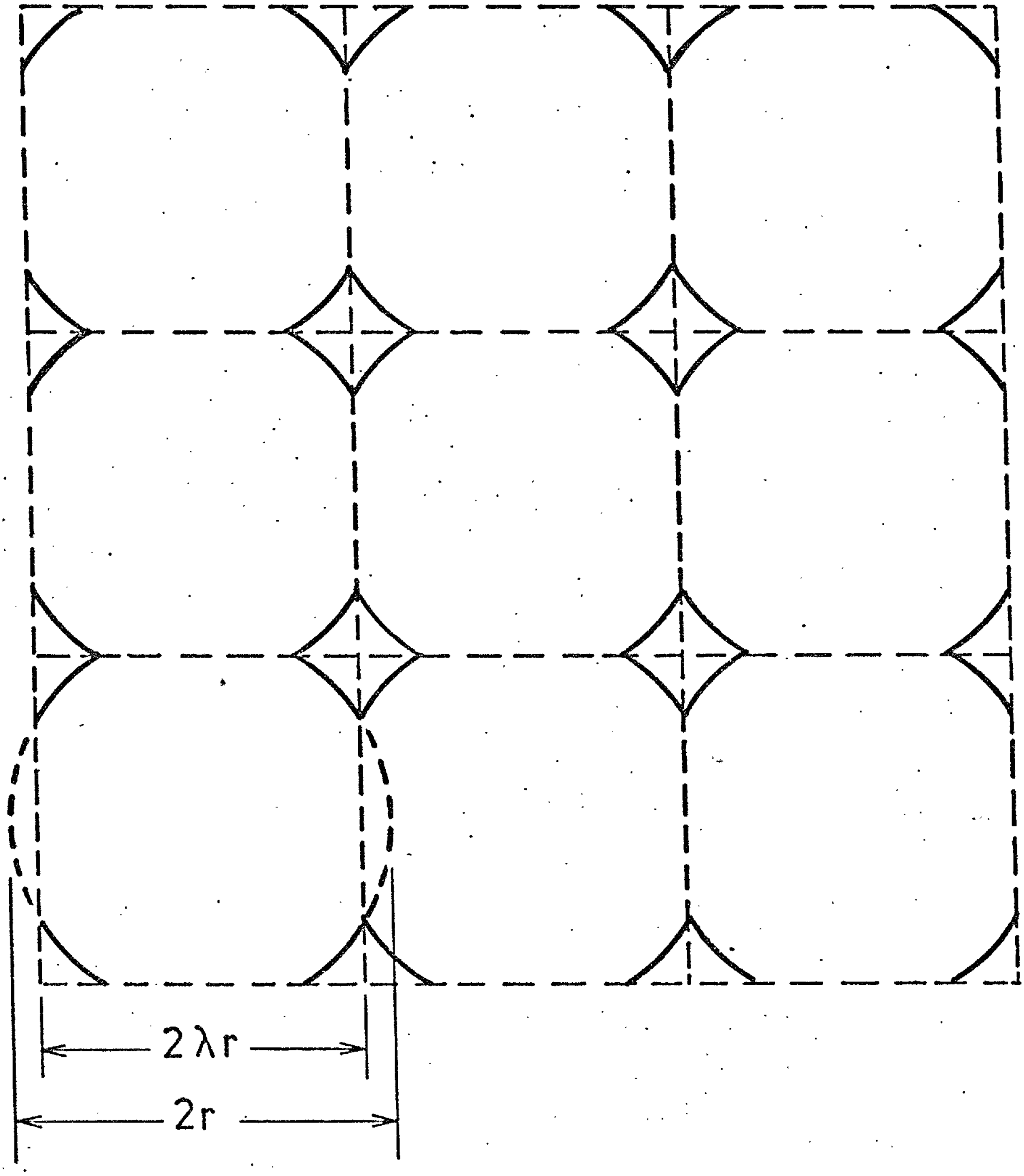
$$.7071 < \lambda < 1 \tag{39}$$

for the two limit situations would be all the cube inside the sphere and all the sphere inside the cube.

The value of λ can be calculated from porosity data using equation (40).

Figure 1

The modelled porous structure



$$\lambda = \left(\frac{4\pi}{4(1-\varepsilon)+\pi}\right)^{\frac{1}{2}} \cos\left\{\frac{1}{3}\cos^{-1}\left[-\frac{\left(\frac{4(1-\varepsilon)}{\pi}+1\right)^{\frac{1}{2}}}{1.5}\right] + \frac{2\pi f}{3}\right\} \tag{40}$$

where f = 0, 1, 2.

Porosity

Smock and Neubert (1950) estimated that 25% of the volume of the apple parenchymatic tissue is occupied by intercellular spaces. Czerski (1964) used a gasometric method to measure porosity of leaves of several species, obtaining a range of values between 7.4% and 57.7%. Hardy (1949) found that the porosity of fresh samples of Cox Orange Pippin was 33.3% . The more comprehensive determination of porosity were made by Smith (1938) and by Reeve (1953). Both covered seven different apple varieties.

On the basis of the above, a value of $\varepsilon = 0.225$ appears to be representative. This range of value is confirmed by Skene (1966).

Effective cell wall area

The total area of a sphere is related to that of the above collapsed sphere by equation (41)

$$\eta = -2 + 3\lambda \tag{41}$$

For $\varepsilon = 0.225$ and the average value of point-contacting sphere area reported by Reeve, equation (40) yields three roots of λ of which two can be disregarded on account of equation (39). This results in

$$\lambda = 0.8473$$

$$\eta = 0.5419$$

which in turn result in a rounded figure of 1000 cm^2 for a sample of tissue of the dimensions used in the experiments.

Comparison of experimental and permeation fluxes

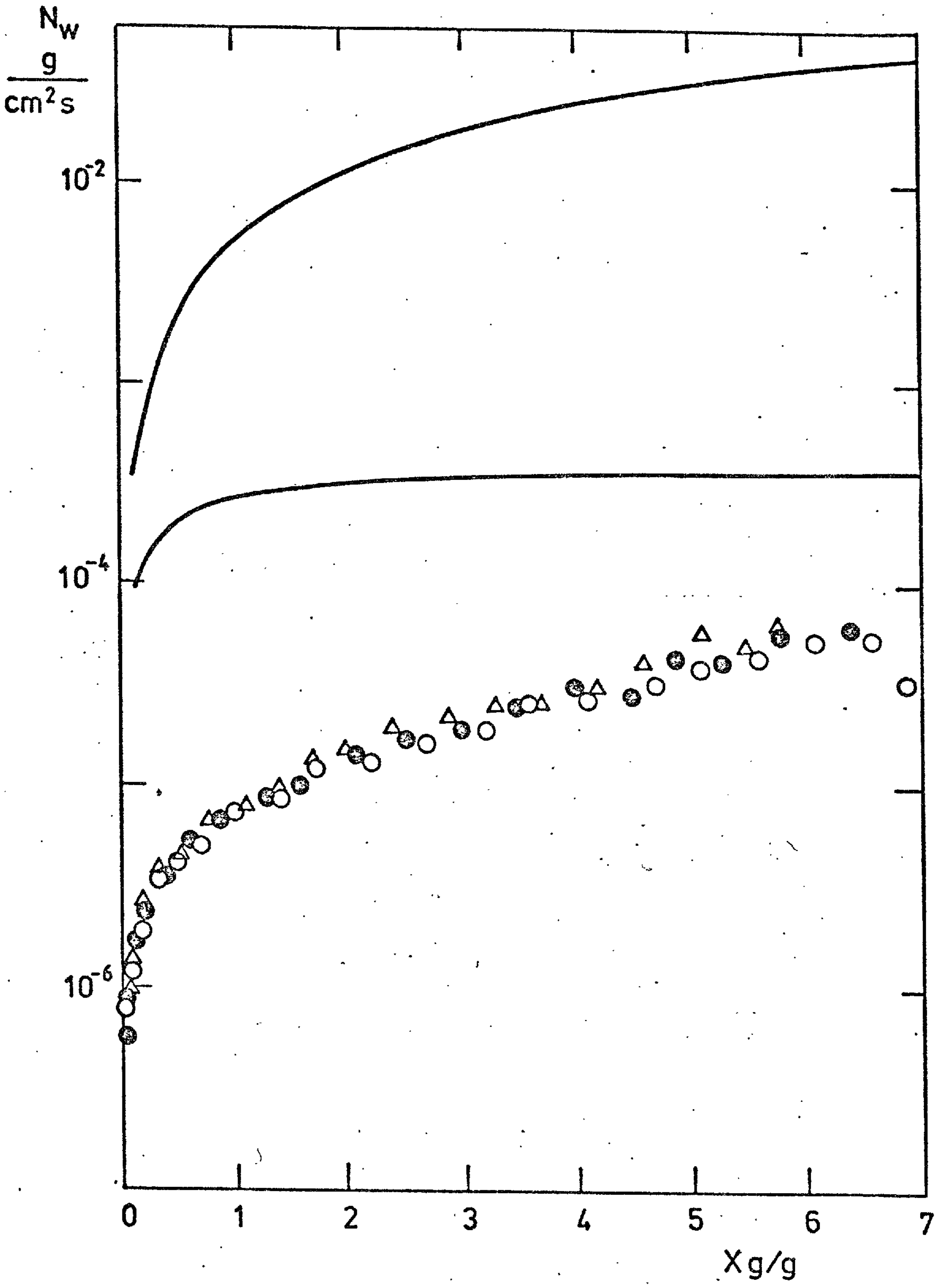
Figure 2 indicates the experimental water fluxes and permeation water fluxes calculated on the basis of hypothesis (a) and (b) above.

It can be seen that the predicted permeation fluxes are between one and three orders of magnitude higher than the actual fluxes. Thus there is a strong indication that the drying process is controlled by resistances external to the cell.

In the case of hypothesis (a), for the closer starting values to meet it would be necessary to accept that either the permeability is one order of magnitude lower or the effective cellular wall area is 1/20th of the total area or there is a suitable compromise between both extremes. In the case of hypothesis (b) it would be necessary to accept even larger departures from the selected values.

Figure 2

Apple drying fluxes



From top to bottom: Hypothesis (b), Hypothesis (a),
experimental results (3 runs).

CHAPTER III

PREDICTION OF THE SORPTIONAL EQUILIBRIUM RELATIONSHIP

The drying of foodstuffs is a problem of coupled heat and mass transfer. Mathematical modelling results in a set of coupled partial differential equations. The coupling equation, equation (42), is the equilibrium relationship which, at the prevailing temperature, relates the water content of the food to the moisture content of the surrounding air.

$$X = X(\phi, T) \tag{42}$$

In addition, the following derivatives of equation (42) are required:

$$\left(\frac{\partial X}{\partial T}\right)_{\phi} = f_T(\phi, T) \tag{43}$$

$$\left(\frac{\partial X}{\partial \phi}\right)_{T} = f_{\phi}(\phi, T) \tag{44}$$

The applications of equations (42) to (44) extend beyond the drying process to packaging, room temperature storage, cold storage, controlled atmosphere storage, as well as to alternative dehydration processes. The differences lie in the magnitudes of the variables X, ϕ, T, considered as well as in the extent of changes in the variables. In the case of controlled atmosphere storage, moisture becomes one of the contributing composition variables but not the only one.

Attempts to obtain equations of the form of (42), (43) and (44) have followed two main directions. In the first use has been made of theoretical expressions developed for the adsorption of gas molecules onto non-volatile solid surfaces, while in the second empirical equations have been fitted to experimental data.

In order to assess the applicability of the various expressions that have been obtained it is necessary to test them against experimental data. This has been done for the specific case of apples.

Sorption equilibrium data by desorption starting from fresh food are rather scarce for vegetable foodstuffs including apples.

Wolf et al. used vacuum dried apple samples and obtained desorption data for rehydrated samples. Taylor (1961) used freeze dried samples which were ground and re-hydrated. Gane (1950) also used freeze dried samples. Saravacos (1967) used air-dried samples. All of the above authors reported data at room temperature only. Filonenko and Chuprin (1967) reported equilibrium data starting from fresh apples at 20°, 40°, 60° and 80°C.

In the ensuing discussion the term relative humidity or water vapour activity, is defined as follows:

$$\phi = \frac{p_W}{p_W^{sat}} \qquad (45)$$

Langmuir isotherm

Langmuir (1916, 1918) described the case of adsorption of a monomolecular layer, by considering equilibrium between molecules reaching and leaving

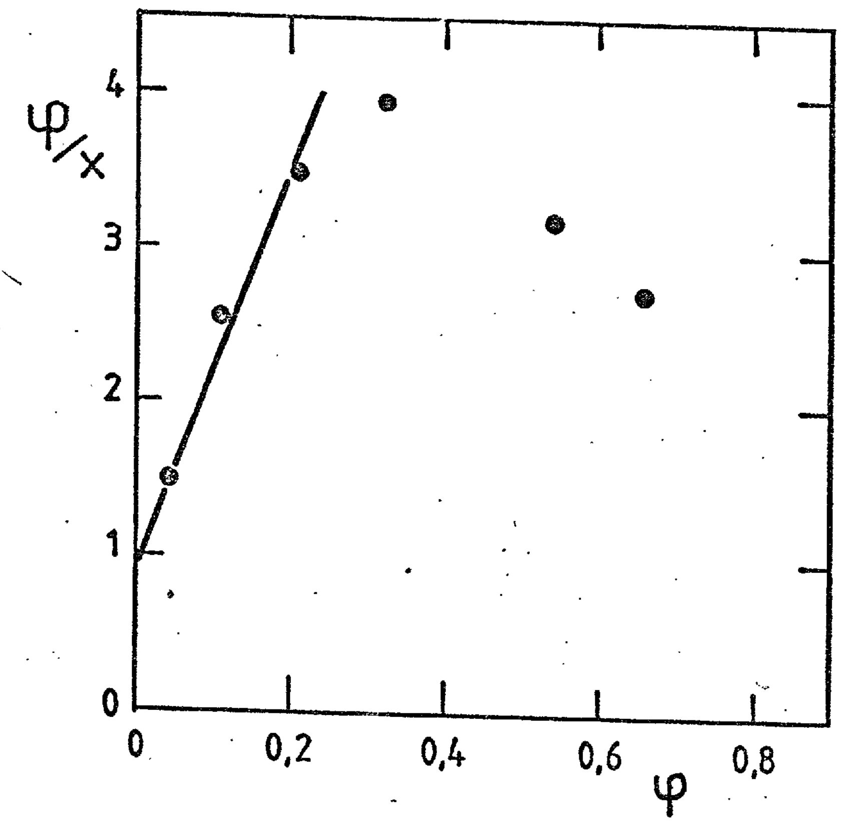


Figure 3

Langmuir equation

the surface. His expression can be written

$$X = \frac{k_1 k_2 \phi}{1 + k_2 \phi} \tag{46}$$

A plot of ϕ/X vs ϕ (Figure 3) shows that the experimental data for apples at 20°C follow Langmuir behaviour only below $\phi = 0.3$. At higher relative humidities the calculated values of ϕ/X go through a maximum and then decrease, indicating that the actual moisture content is significantly higher than expected. Below $\phi = 0.3$ a least square linear regression procedure yields:

$$k_1 = 0.076$$

$$k_2 = 14.293$$

Equation (46) satisfies Henry's law as $\phi \to 0$, but predicts a low moisture content when $\phi = 1$:

$$X\Big|_{\phi=1} = 0.071 \text{ kg/kg dry matter}$$

This value may be compared with experimental values of the order of 7 kg/kg dry matter.

The B.E.T. isotherm

The adsorption model of Brunauer, Emmet and Teller allows for multilayer adsorption (Brunauer et al., 1938). It is usually acceptable for the prediction of equilibrium moisture contents of foodstuffs when the water vapor activity is between 0 and 0.3 to 0.5 (Labuza, 1974). Equation (47) is one representation of this isotherm.

$$\frac{\phi}{X(1 - \phi)} = \frac{1}{X_{mv}c} + \frac{(c - 1)}{X_{mv}c} \phi \qquad (47)$$

When experimental data for apples at 20°C are plotted as $\frac{\phi}{X(1 - \phi)}$ vs ϕ (Figure 4), it can be seen that for $\phi > 0.30$ the experimentally measured moisture content are much higher than those predicted by equation (47). For $\phi \leqslant 0.30$ a least square linear regression procedure yielded:

$X_{mv} = 0.05094$ kg/kg dry matter

$c = 31.15873$

Equation (47) satisfies Henry's law when $\phi \rightarrow 0$. It is an improvement over Langmuir's equation for the present purpose because it predicts increasing values of X when ϕ is high. On the other hand, it predicts infinite moisture contents when $\phi \rightarrow 1$, a clearly unrealistic prediction.

Rounsley

The Rounsley equation (Rounsley, 1961) is related to the B.E.T. equation The main difference is that it is based on the assumption that the distribution of molecules among the different layers builds up during adsorption in an efficient, orderly manner. This results in equation (48)

$$\frac{\phi(1 - \phi^{n})}{X(1 - \phi)} = \frac{1}{Bc} + \frac{(c - 1)}{Bc} \phi \qquad (48)$$

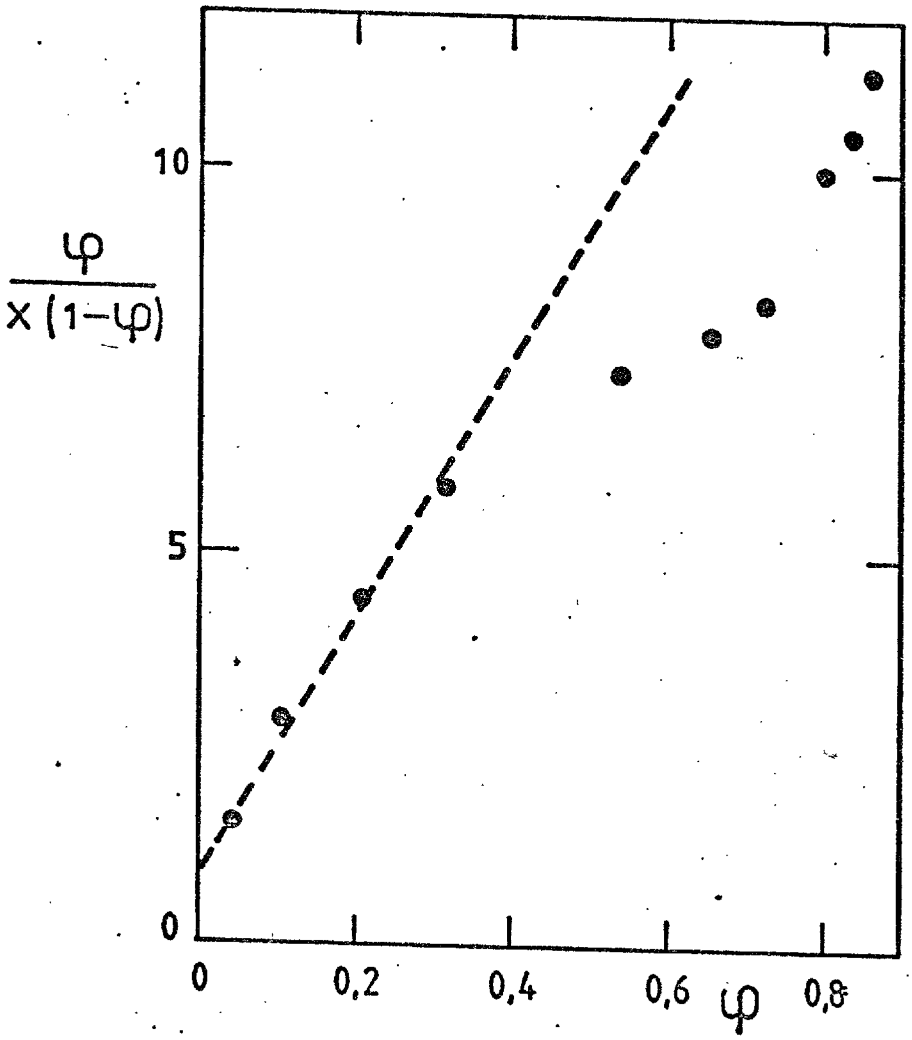


Figure 4

B.E.T. Equation

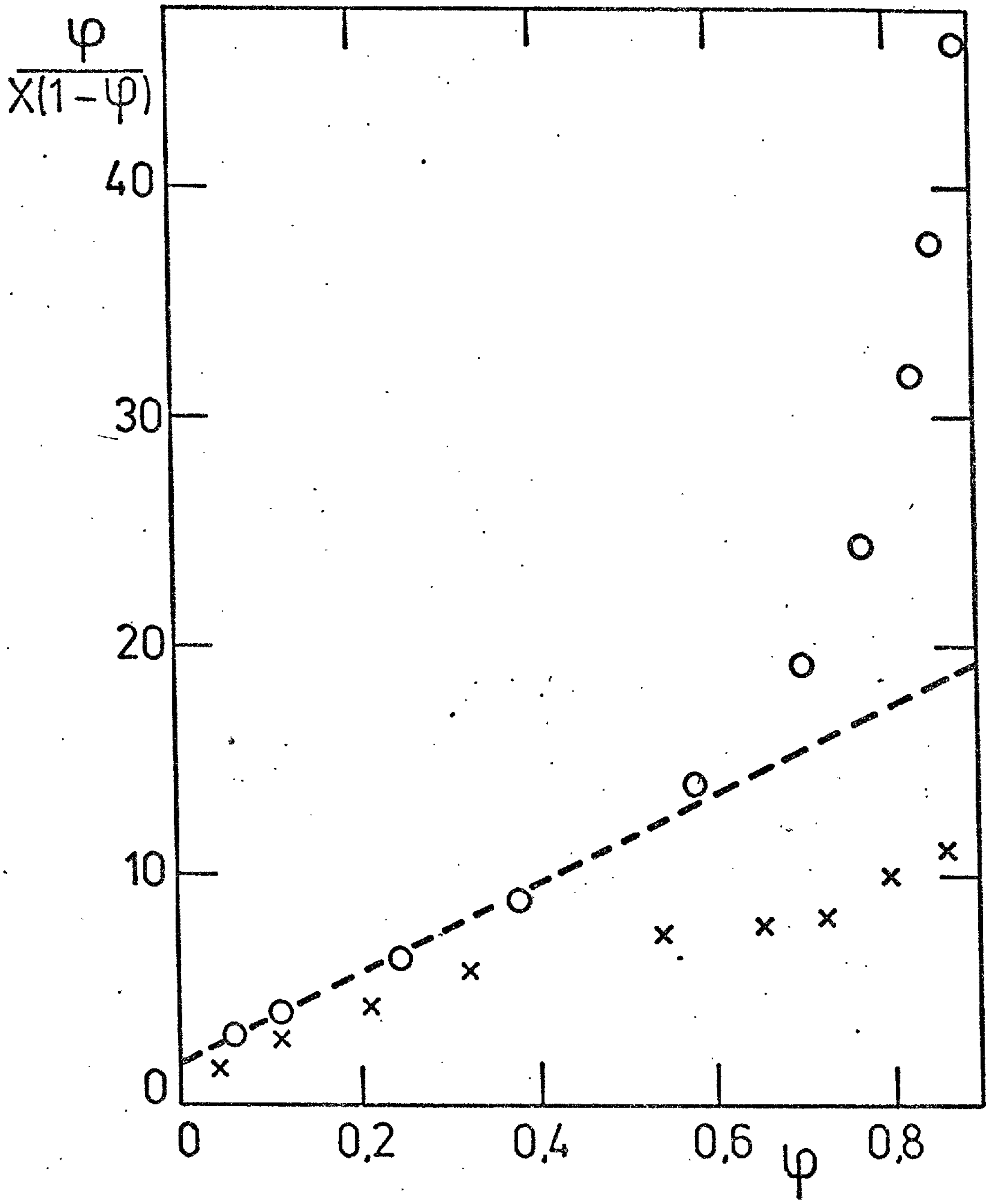


Figure 5

Rounsley Equation

Rounsley suggested a method of obtaining n by plotting $\phi/X(1 - \phi)$ as a function of ϕ, and taking advantage of the fact that as $\phi \rightarrow 0$, $(1 - \phi^n) \rightarrow 1$. This should result in the experimental data for higher water vapor activities falling above the extrapolated line drawn through the values obtained for low activities. The value of n can be obtained from the ratio of the experimental values to the extrapolated line. As shown in Figure 5, this procedure was followed for cellulose, using Rounsley's data (op.cit.) and those for apples at 20°C. It can be seen that the data for apples are anomalous in that at high water vapour activities they have much higher water contents than predicted by the theory.

It is interesting to note that the behaviour of the data for apples approaches those of cellulose at low water vapor activities although the values of $\phi/X(1 - \phi)$ are too high. This suggests that conventional adsorption is taking place at low activities but is not confined to cellulose surfaces alone.

Harkins and Jura

The isotherm of Harkins and Jura (Harkins and Jura, 1947) is related to the Gibbs adsorption isotherm.

$$\ln \phi = E - \frac{c}{X^2} \qquad (49)$$

Figure 6 is a semilogarithmic plot of ϕ vs. X^{-2}. It also includes results for water vapor adsorption on cellulose (Jeffries, 1960). It can be seen that equation (49) does not represent the behaviour of either of the systems, except for narrow ranges of water vapor activities.

Henderson

Henderson (1952) presented a semi-empirical correlation for foodstuffs (Equation (50)) based on the thermodynamic relationip between surface tension and osmotic pressure. He also used convenient empirical relationships to relate the amount of adsorbed moisture per unit wetted area to that for totally wetted area, and to relate changes in the amount of adsorbed moisture to changes in surface energy.

$$- \ln (1 - \phi) = \kappa T_R (100 X)^{n'} \tag{50}$$

A non-linear reqression procedure, incorporating temperature as a variable, yields:

$$\kappa = 1.3949 \times 10^{-4}$$

$$n' = 0.86532$$

Figure 7 shows experimental and predicted equilibrium values. Equation (50) fits the experimental values with an error of less than 15% when $\phi \geqslant 0.2$. It represents an improvement over the equations described previously in that it gives reasonable results over the entire range of experimental values of water vapor activity. Unfortunately, it predicts $X \to \infty$ as $\phi \to 1$.

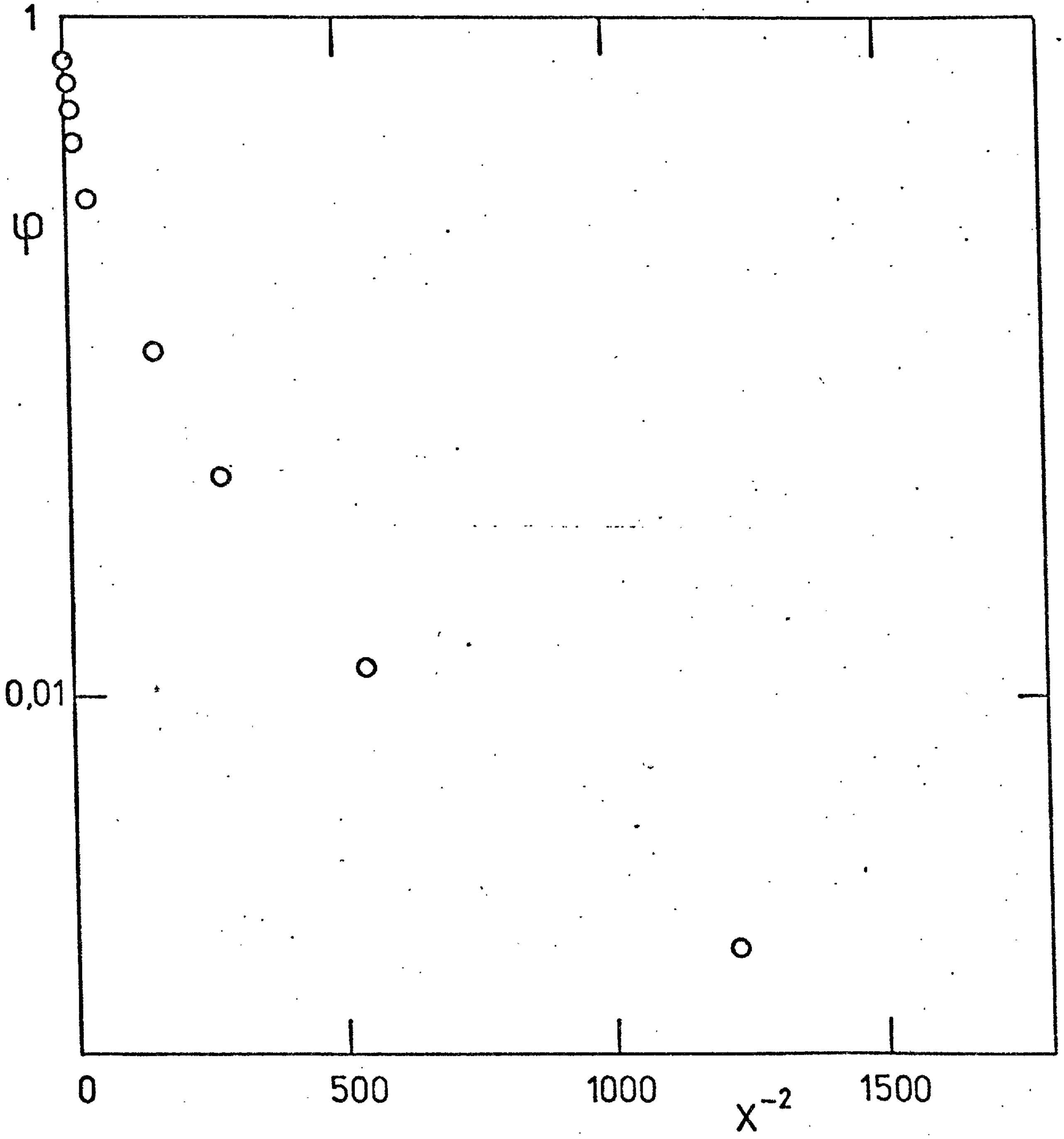


Figure 6

Harkins and Jura equation

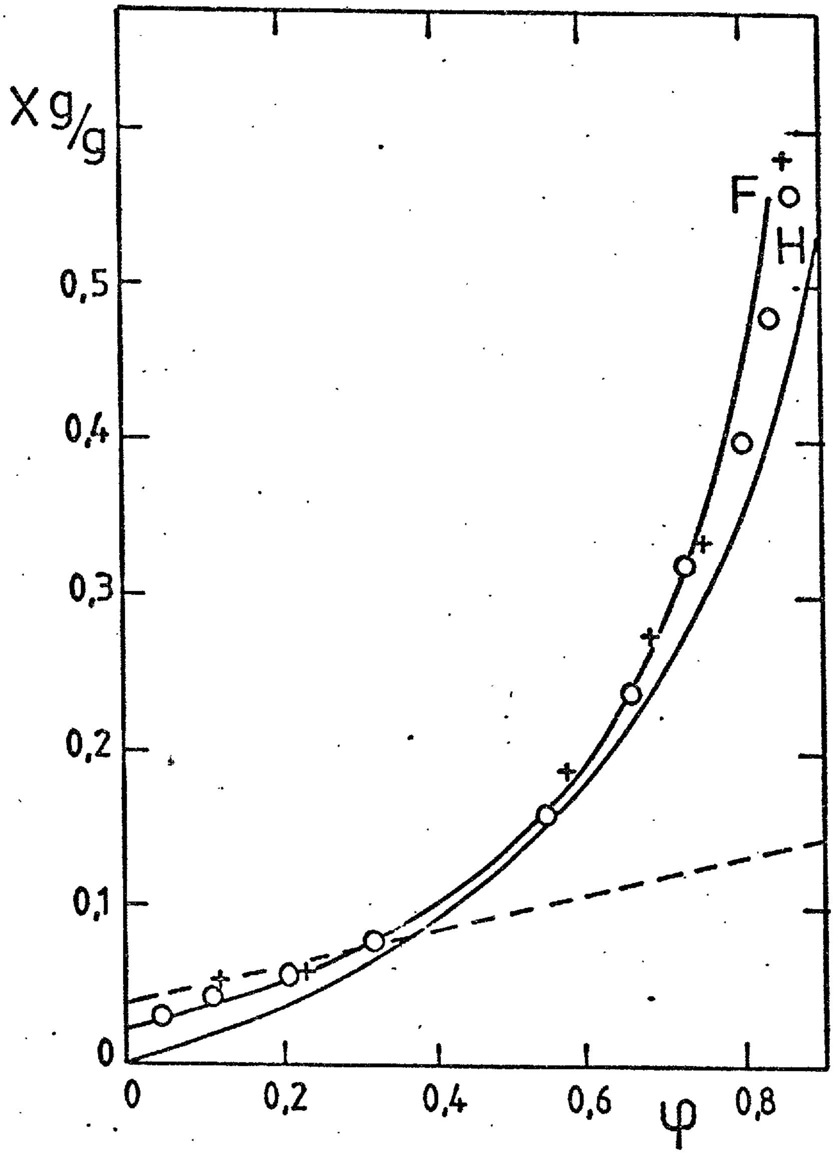


Figure 7

Filonenko and Chuprin's (F) and
Henderson's (H) equations

Kuhn

Kuhn (1964) presented an equation which allows for capillary condensation and uses a potential distribution function to compute the contribution of groups of different size particles in the pores. For correlation purposes Kuhn's equation can be written as follows:

$$X = \kappa \frac{1}{(-\ln \phi)^{\xi}} - B \qquad (51)$$

For apples at 20°C,

$\xi = 0.9971$

$B = 0.0003$

$\kappa = 0.0971$

The predicted and experimental values can be seen in Figure 8. The fit is fairly good and represents an improvement over that obtained using Henderson's correlation although, once again, the equation predicts $X \to \infty$ as $\phi \to 1.0$.

Halsey

Halsey (1948) developed a theoretical treatment of co-operative multilayer adsorption over a non-uniform surface. The resulting equation is:

$$\ln \phi = -\frac{a}{RT} \left(\frac{X}{X_{mv}}\right)^{-r'} \qquad (52)$$

The ability of this equation to correlate sorptional equilibrium data

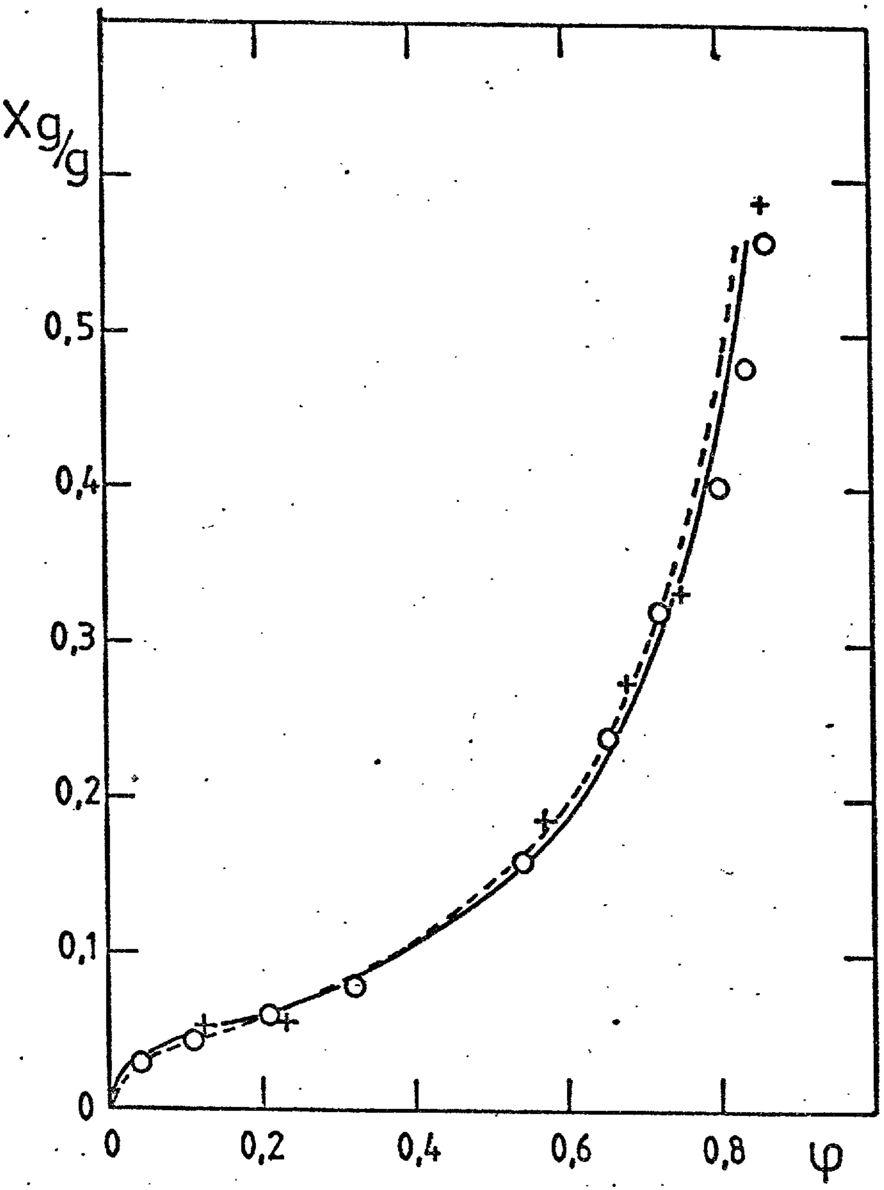


Figure 8

Kuhn's (---) and Halsey's (——) isotherms

+ Experimental data

o Filonenko and Chuprin (1967)

at constant temperature has been tested for several foodstuffs (Iglesias et al., 1975). It was found that it is applicable within the range $0.10 < \phi < 0.80$, which for apples at 20°C corresponds to moisture contents between 0.04 and 0.40. For apples, a least squares linear regression procedure yielded:

$$\frac{a'}{RT} = 2.3858$$

$$r' = 0.9530$$

The above values correspond to a value of X_{mv} of 0.05094 kg/kg dry material and do not agree with those of Iglesias el al. (1975), (1.7100 and 0.76432 respectively, for $X_{mv} = 0.0417$). The differences may be because Iglesias et al. used data obtained by Taylor (1961) who, as reported above, used freeze dried samples. From a theoretical standpoint a value of $r' = 3.0$ should be expected (Young and Crowell, 1962). On the other hand, a value of $r' = 2.0$ is typical of many systems. Halsey (1948) concluded that large values of r' characterize systems in which the vapor-solid attraction is very specific and does not extend far from the surface. Small values of r' characterize typical van der Waals forces.

The predicted values (Figure 8) compare well with the experimental data although the limit at $\phi = 1.0$ is again that of infinite adsorption.

Filonenko and Chuprin

Filonenko and Chuprin (1967) disregard the region $X \leqslant X_{mv}$ as being of little practical importance. They proposed equation (53) for the region $X_{mv} < X \leqslant X_{\ell}$ and equation (54) for $X > X_{\ell}$. Equations (53) and (54) are empirical.

$$X_I = \frac{a' + \phi}{\kappa} \tag{53}$$

$$X_{II} = \frac{B(\phi - \phi_{\ell})}{b - (\phi - \phi_{\ell})} + X_{\ell} \tag{54}$$

where:

$a' = 0.32$

$\kappa = 8.2 + 0.00075\ T_c^2$

$B = 0.18 - 0.000125\ T_c^2\ /100$

$X_{\ell} = 0.08 - 0.004\ T_c$

$b = 0.75$

$\phi_{\ell} = X_{\ell}\kappa - a'$

For apples at 20°C, equation (54) covers the entire range of moisture contents and provides a reasonable fit of the experimental data (Figure 7). Nevertheless, in the high moisture region it under-estimates the moisture content yielding for $\phi = 1$ $X = 3.0979$ kg/kg, as compared with $X = 7$ kg/kg.

The derivative $(\partial X/\partial \phi)_T$

As pointed out earlier, there is a need not only for equilibrium data but also for the derivatives of moisture content with respect to temperature and water vapour activity.

Langmuir's expression yields equation (55) for $(\partial X/\partial\phi)_T$ and equation (56) is obtained from the B.E.T. equation.

$$\left(\frac{\partial X}{\partial \phi}\right)_T = \frac{k_1 k_2}{(1 + k_2\phi)^2} \tag{55}$$

$$\left(\frac{\partial X}{\partial \phi}\right)_T = X_{mv}c \frac{[1 + (c - 1)\phi^2]}{[1 + (c - 2)\phi - (c - 1)\phi^2]^2} \tag{56}$$

The Rounsley equation and that of Harkins and Jura cannot be used, as explained above. The derivative of Henderson's expression is

$$\left(\frac{\partial X}{\partial \phi}\right)_T = \frac{0.01[- \ln(1 - \phi)]^{\frac{1}{n'} - 1}}{(\kappa T_R)^{1/n} \cdot n'(1 - \phi)} \tag{57}$$

The Kuhn isotherm yields:

$$\left(\frac{\partial X}{\partial \phi}\right)_T = \frac{\kappa\,\xi}{\phi(- \ln \phi)^{1+\xi}} \tag{58}$$

The use of Filonenko and Chuprin's equation for $X > X_1$ and of Halsey's equation results in equations (59) and (60), respectively.

$$\left(\frac{\partial X}{\partial \phi}\right)_T = \frac{bB}{[b - (\phi - \phi_\ell)]^2} \tag{59}$$

$$\left(\frac{\partial X}{\partial \phi}\right)_T = \left(\frac{a}{RT}\right)^{1/r} \frac{X_{mv}}{r'} \frac{1}{\phi(- \ln \phi)^{1+\frac{1}{r'}}} \tag{60}$$

Table 13

The derivative $(\partial X/\partial \phi)_T$

ϕ	Langmuir	BET	Experimental	Henderson	Kuhn	Filonenko	Halsey	$\phi = \gamma_w x_w$
0.01	0.832	0.9588		0.1163	0.4579	0.1264	0.4389	0.3084
0.10	0.184	0.1581	0.220	0.1845	0.1831	0.1517	0.1817	0.1889
0.20	0.073	0.1107	0.160	0.2332	0.1874	0.1889	0.1892	0.1852
0.30	0.039	L.1192	0.200	0.2867	0.2233	0.2445	0.2287	0.2102
0.40	0.024	0.1505	0.320	0.2988	0.2891	0.3266	0.3001	0.2595
0.50	0.016	0.2097	0.370	0.4452	0.4042	0.4583	0.4254	0.3468
0.60	0.012	0.3226	0.580	0.5812	0.6202	0.6891	0.6626	0.5107
0.70	0.009	0.5691	0.970	0.8085	10904	1.1510	1.1858	0.8654
0.80	0.007	1.2759	2.100	1.2689	2.4376	2.2988	2.7129	1.8774
1.00	0.005	∞		∞	∞	76.5306		629.2271

The results obtained using equations (55) to (60) are given in table 13, together with experimental results for apples at $20^{o}C$. It can be seen that, with the obvious exception of Langmuir's correlation, all of the correlations provide acceptable predictions up to $\phi = 0.6$. As the water vapour activity increases further, the equations of Halsey, Kuhn, and Filonenko and Chuprin increasingly overestimate the value of the derivative while the Henderson and BET correlations under-estimate it. Moreover, when the air becomes saturated, a situation equivalent to fresh fruit at full turgor, all but the Filonenko and Chuprin correlation predict an infinite value for the derivative. This presents a difficulty because the derivative is required at various moisture contents as the moisture content is reduced from that of full turgor. Moreover, if the problem to be considered is one of storage of fresh fruit, the analysis is entirely dependent on reliable results for conditions of full turgor.

The derivative $(\partial X/\partial T)_{\phi}$

Most of the above correlations have been developed in order to describe isothermal situations and temperature has not been included as a variable but has been implicitly incorporated into the correlating constants. The exceptions are the Henderson and the Filonenko and Chuprin correlations.

Clearly it is possbile to express the constants as functions of temperature and to correlate experimental data in order to obtain equations in which temperature is an explicit variable. At present, insufficient data are available for this purpose.

The derivative of moisture content with respect to temperature at constant water vapour activity can be obtained analytically for only two of the correlations previously considered; those of Henderson and Filonenko and

and Chuprin.

For the Henderson correlation:

$$\left(\frac{\partial X}{\partial T}\right)_\phi = -\frac{X}{nT} \qquad (61)$$

For the Filonenko and Chuprin correlation:

$$\left(\frac{\partial X}{\partial T}\right)_\phi = \frac{[b - (\phi - \phi_\ell)]\,[BZ_1 + (\phi - \phi_\ell)Z_2] - B(\phi - \phi_\ell)Z_1}{[b - (\phi - \phi_\ell)]^2} - 0.0004 \qquad (62)$$

where $Z_1 = 10^{-4}(1.2\ T_c - 0.006\ T_c^2 - 4\kappa)$

$$Z_2 = -\ 2.5 \times 10^{-6}\ T_c$$

The results are shown in table 14 for the case of apples at 30°C. It can be seen that the Henderson correlation yields reasonable estimates up to a water vapour activity of about 0.7, i.e. a moisture content X = 0.255 g/g dry matter. Beyond this range the value of the derivative grows too quickly. This is clearly undesirable for applications to the drying of foodstuffs because the starting point for the calculation procedure is the 'as fresh' moisture content. The Filonenko and Chuprin correlation is only acceptable at low water vapour activities. Beyond ϕ = 0.5 the derivative decreases too rapidly and finally changes sign.

Application of the chemical potential

To describe the equilibrium content of water in vegetable tissues it is

Table 14

The derivative $(\partial X/\partial T)_{\phi}$

Results for apples at 30°C

ϕ	Experimental	Correlation		
		Henderson	Filonenko & Chuprin	$\phi = \gamma_w x_w$
0.989		−0.02668	+0.02767	−0.00114
0.857	−0.00120	−0.00213	+0.00047	−0.00076
0.800	−0.00015	−0.00153	−0.00011	−0.00067
0.7	−0.00155	−0.00097	−0.00043	−0.00057
0.6	−0.00105	−0.00071	−0.00051	−0.00047
0.5	−0.00040	−0.00052	−0.00053	−0.00041
0.4	−0.00065	−0.00039	−0.00053	−0.00035
0.3	−0.00046	−0.00029	−0.00052	−0.00030
0.2	−0.00035	−0.00019	−0.00051	−0.00025
0.1	−0.00028	−0.00011	−0.00050	−0.00019

convenient to establish a model. In this case the model is a simplified description of tissues and its components, the cells. (Reeve, 1953, Slatyer, 1960, Nobel, 1974).

Tissues are regarded as assemblages of cells. Practically all cells have part of their surface abutting on intercellular air spaces. The generalized plant cell has an outside wall consisting of a mesh of cellulose microfibrils. Inside the outer wall there is cytoplasm, which consists mainly of proteins and water but which also contains lipids, salts and other compounds. At the inner wall-cytoplasm interface there is a membrane, plasmalemma, inside of which there is a large central aqueous phase which can occupy up to 90% of the volume of a mature cell: the vacuole. It is separated from the cytoplasm by a membrane.known as the tonoplast.

Most of the water content of the cell resides in the vacuole and frequently reaches levels of about 98% of the vacuole volume (Slatyer, 1960, Stocking 1956). The volumetric water content of the walls of turgid cells may be around 50% of the wall volume. The water is adsorbed on the solid surface and is retained in the interfibrillar spaces. The cytoplasm is even richer in water content. In the cytoplasm, water is bound to proteins and other hydrophilic colloids and also exists as free water. Most of the sugar in sugar-based foodstuffs, to which the following analysis is confined, is contained within the vacuole.. The vacuolar sap may be regarded as a solution (Slatyer, 1960).

Water equilibrium

When there is a change in water content, the solutes concentration as well as the sorptional force field resulting from the presence of the solid matrix and insoluble materials will be changed. The geometrical arrangement may also be altered.

This problem has some points of similarity with water-soil relationships. This was recognized by Slatyer (1960), who suggested that the thermodynamic approach used by Babcock (1963) would be applied to the above case.

If it is accepted that unique relationships can be established for the chemical potential of water as a function of volumetric water content then a general expression for a differential change in chemical potential of water is as follows:

$$d\mu_w = -\bar{S}_w dT + \bar{V}_w dp + \left(\frac{\partial \mu_w}{\partial C_s}\right)_{T,P,n_j,n_w} dC_s + \left(\frac{\partial \mu_w}{\partial \theta}\right)_{T,P,n_s} d\theta \qquad (63)$$

From a different standpoint, the number of moles of solute, of insoluble materials and of water may be considered to be the relevant variables (Noy-Meir and Ginzburg, 1967):

$$d\mu_w = \bar{S}_w dT + \bar{V}_w dp + \left(\frac{\partial \mu_w}{\partial n_s}\right)_{n_j,P,T} dn_s + \left(\frac{\partial \mu_w}{\partial n_M}\right)_{P,n_j,T} dn_M$$

$$+ \left(\frac{\partial \mu_w}{\partial n_w}\right)_{P,n_j,T} dn_w \qquad (64)$$

Equation (64) can be integrated from the reference state of pure water at atmospheric pressure as expressed by the following set of initial conditions

$$p = p_o \; ; \; n_s = 0 \; ; \; n_M = 0$$

where the water amount can be any non-null quantity. If the temperature is taken to be constant, then in order to obtain an expression for the change in chemical potential the term $(\partial\mu_w/\partial n_w)dn_m$ may be integrated at $\bar{p}_o$, $n_s = 0$, n_w, the term $(\partial\mu_w/\partial n_s)dn_s$ at p_o, n_m and n_w, and the $\bar{V}_w p$ term at n_s, n_m, n_w, between the reference state and the final state. Noy-Meir and Ginzburg (1967) discussed alternative partitions. While the pressure and solute terms of equations (63) and (64) are readily integrable, the sorptional force field terms are not. For the purpose of the present discussion the integrated effect of these terms will be lumped into a variable ψ_M. (Slatyer, 1960, Nobel, 1974, Shepherd, 1975). Then, for constant $\bar{V}_w$

$$\mu_w - \mu_w^o = \bar{V}_w(p - p_o) + RT \ln \hat{a}_w + \bar{V}_w\psi_M \qquad (65)$$

The problem under examination is that of equilibrium between tissue and humid air. Thus, the equilibrium isotherm is:

$$RT \ln \phi = \bar{V}_w(p - p_o) + RT \ln \hat{a}_w + \bar{V}_w \psi_M \qquad (66)$$

where the gas phase is considered to be ideal, an acceptable assumption at atmospheric pressure. Equilibrium implies that the chemical potential has the same value in each of the phases in the cell as in the surroundings. The use of equation (65) is not straightforward because of the complexity of the structure involved. The relative contributions of the terms to the value of the chemical potential value will be different for each of the phases; also the values to be used will, of necessity, be spatial averages since no techniques are available for the determination of cell properties on a micro-scale (Hellkvist et al. 1974).

The matric potential and the hydrostatic pressure terms

The matric potential term accounts for the capillarity, adsorption and hydration forces. The water held by matric forces roughly corresponds to bound water (Wilson and Rose, 1967). Wiebe and Al-Saadi (1976) measured matric water contents for tissues of several vegetable foodstuffs. From their data it can be seen that the matric water content is only of importance when the total water content is very low.

If the cell is regarded as being enclosed within ideally elastic walls, a linear relationship can be established between gauge pressure and relative change of volume from full turgor to zero gauge pressure (Noy-Meir and Ginzburg, 1967):

$$\bar{V}_w(p - p_o) = \bar{V}_w \chi \left(\frac{X - X^o}{X^o} \right) \qquad (67)$$

Sorption equilibrium prediction

A full description of the equilibrium relationships for apples should be for the full moisture content range, $0 \leqslant X \leqslant 7$ g/g (Figure 9) rather than for the restricted ranges covered by the existing equations. For the purposes of design or simulation of conventional drying processes, the process starts at full turgor. Fresh fruit are usually packaged and stored under conditions close to those of full turgor. Comercial hot air drying terminates at a standard moisture content X = 0.32 kg/kg while freeze drying or air drying followed by vacuum drying extends to a moisture content of almost zero.

Solubility

In the case of apples, a representative composition is shown in table 15 (Rotstein et al., 1969, Voho and Varo, 1975). The vacuolar solution is a sugar solution made primarily of glucose and fuctose, with some sucrose. Studies made on honeys by Bates et al. (1972) showed that sucrose could be treated as if it were fructose, from the standpoint of the solubility properties of the system. A characteristic feature of these solutions is their ability to remain in an oversaturated condition for a long period of time. Figure 10 is a plot of the solubility relationships for the system water - sucrose - invert sugar. If the glucose and fructose mixture is considered as if it were invert sugar the line WP shows the evolution of a typical apple as its moisture content changes.

The activity coefficient of glucose solutions

Taylor and Rowlinson (1955) correlated the activity coefficient of glucose as follows:

$$\gamma_w = 10^{A(1 - x_w)^2} \qquad (68)$$

Changes from one temperature to another can be made using the following equation:

$$\left(\frac{\partial \ln \gamma_w}{\partial T}\right)_{P,x} = - \frac{\overline{\Delta H}_w}{RT^2} \qquad (69)$$

If the partial molar enthalpy change of mixing of water is regarded as being practically constant within the temperature range under consideration then $\gamma_w(T)$ can be represented by equation (70).

$$\ln \gamma_w = \ell + P/T \qquad (70)$$

where $\ell = 1.274$ and $P = -635.840$ for $r^2 = 0.992$.

Relative contributions of the chemical potential terms

Figure 11 allows a comparison to be made of the values of the water vapor and osmotic chemical potential terms at successive sets of moisture content and activity values. The calculations were made on the assumption that the solutions reached oversaturation and that the thermodynamic relationships for the solution could be extrapolated into the oversaturated region. The test of the validity of this and other assumptions will be the ability of the method to predict equilibrium relationships. x_w was calculated using equation (71).

$$x_w = \frac{X}{X + \sum_j \left(\frac{m_j}{d + \Sigma m_j} \cdot \frac{M_w}{M_j} \right)} \qquad (71)$$

It can be seen that through most of the range of moisture contents under consideration, the contribution of the osmotic term is a close approximation to the total chemical potential of the system. Departures from this statement are noted mainly at extreme moisture contents both high and low. As bound, or matric, water is the last to leave the solid, it seems reasonable to conjecture that as water content is reduced it eventually becomes equal to the amount of bound water located mainly at the cell wall and cellular

Table 15

Typical composition of fresh apple

(Basis: 1 kg dry matter)

Water	6.50 - 7.00 kg/kg
Glucose and fructose	0.58 kg/kg
Sucrose	0.18 kg/kg

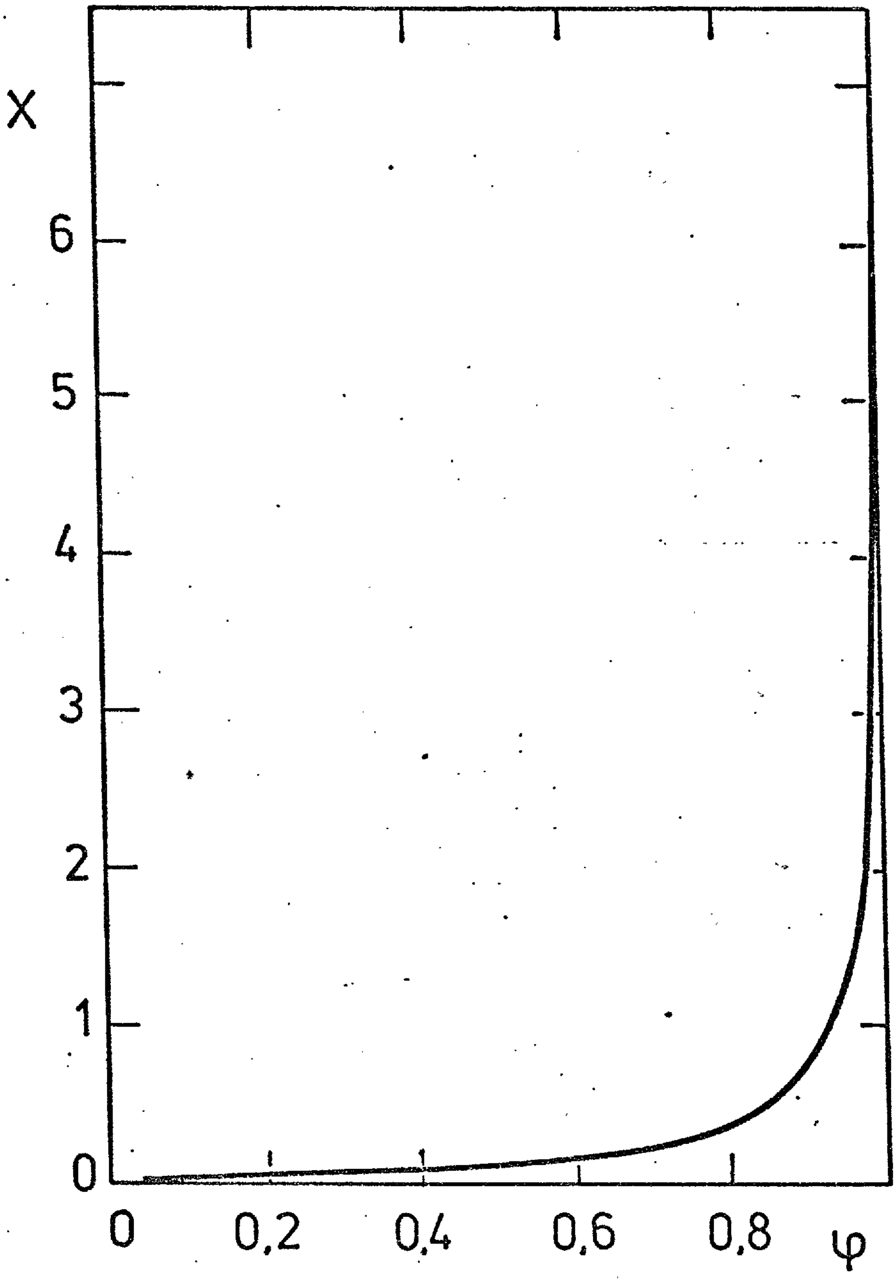


Figure 9

Apples. A complete isotherm

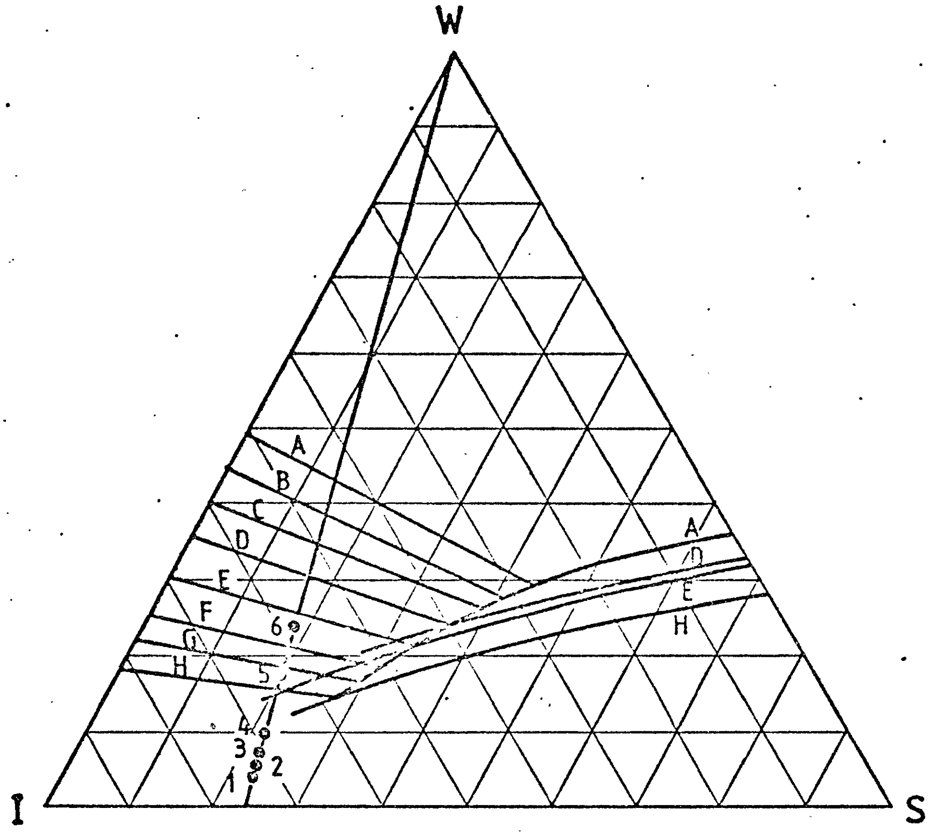


Figure 10

Solubility of the Sucrose - Invert Sugar - Water System

1,2,3,4,5,6 are moisture contents 0.03, 0.06, 0.08, 0.16 and 0.24 Kg/kg, respectively.

A,B,C,D,E,F,G,H = 0, 10, 15, 23.15, 30, 40, 45, 50°C, respectively.

W, I, S = 100% water, invert sugar and sucrose vertices respectively.

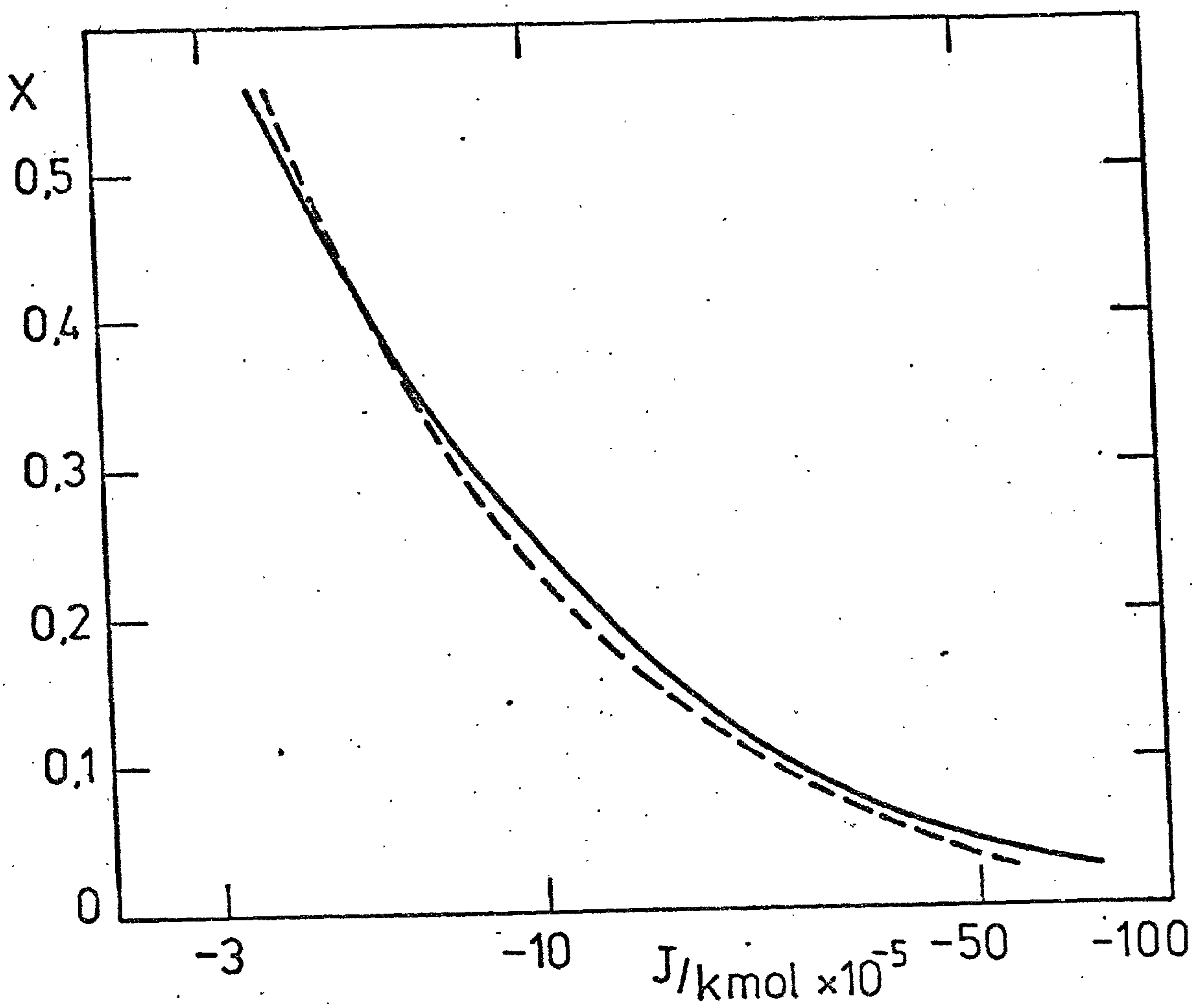


Figure 11

Total and osmotic chemical potential

--- RT ln ϕ

___ RT ln $\hat{a}_w$

membrane. Throughout this process the water apportioned to the osmotic term decreases and the matric chemical potential becomes the dominant term. Obviously the point at which all of the remaining water is bound water is ill-defined.

At high moisture content, it is to be noted that the difference between water vapor chemical potential and osmotic potential is not as large as it is at low moisture contents. At full turgor, the difference for apples is about -25100 J/kmol. As an approximation it seems reasonable to consider that at full turgor the water accountability can be restricted to the vacuole. In that case the significant contributions in equation (66) are the swelling pressure and osmotic terms. The difference between the osmotic term and the water vapour chemical potential is due to the pressure term. This is consistent with the pressure term being positive.

Regions in the equilibrium isotherm.

Three regions can be identified:

1 - The high moisture region

2 - The intermediate moisture region

3 - The bound water region.

The high moisture region

This region can be considered as extending from full turgor down to the moisture content at which the vacuolar pressure is equal to the external pressure. In terms of the foregoing analysis of the chemical potential, when attention is focused on the vacuole and matric potential is neglected, the moisture content at the lower limit of the high moisture region is located at the intersection of the curves RT ln ϕ and RT ln $\hat{a}_w$ (cf. Figure 11).

A simple correlation can be presented for the pressure term by making use of equation (67) and by noting that at full turgor the fruit can be considered to be in equilibrium with saturated moist air. Then, from equations (66) and (67)

$$0 = \bar{V}_w \chi \left(\frac{X - X^o}{X}\right) + RT \ln (\hat{a}_w)_{\phi=1} \qquad (72)$$

For the case of apples at 20°C, this results in

$$\chi = 1.54912 \times 10^6 \frac{J}{m^3}$$

The equilibrium relationship for the high moisture region then results:

$$RT \ln \phi = \bar{V}_w \chi \left(\frac{X - X^o}{X}\right) + RT \ln \hat{a}_w \qquad (73)$$

The actual significance of the pressure term is low, from the standpoint of the order of magnitude of its contribution to the moisture equilibrium content prediction. Figure 12 shows that there is little change in the predicted value if the pressure term in equation (73) is dropped. In the case under consideration this results in a maximum difference of 1% for moisture contents in the range $2 < X < 7$ kg/kg dry matter and progressively even less as the moisture content decreases further.

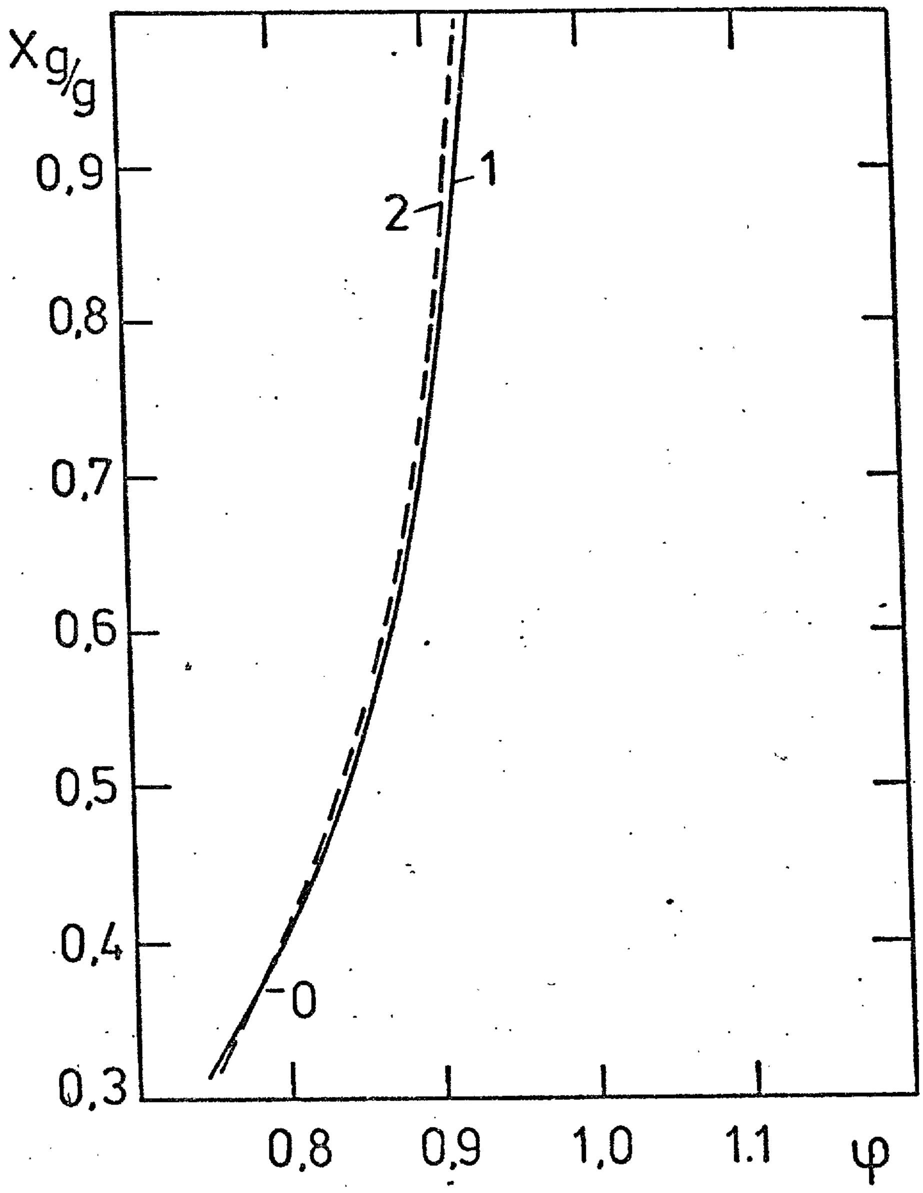


Figure 12

Hydrostatic pressure contribution

1 - equation (80)

2 - equation (81)

The low moisture region

The low moisture region refers to the bound water content of the foodstuff. It has been seen that at low moisture contents the B.E.T. equation predicts accurately the equilibrium values, probably because the actual situation is close to the concepts on which the Brunauer, Emmet and Teller theory is based.

The lower bound of this region is the zero moisture content point. The upper bound is defined as the intersection of the B.E.T. line and the line drawn for the intermediate moisture region.

The intermediate moisture region

As stated earlier, this region and that of low moisture content are the regions usually described in the literature. The upper bound of this region is the point of zero gauge vacuolar pressure. It is to be noted that the literature is conflicting as to whether or not negative pressures exist inside the cell. (Slatyer, 1960). The ability of a cell to retain a vacuum has been related to the cell wall capillaries, which it has been suggested (Nobel, 1974) operate as hydraulic seals. If the predictions of figure 11 are correct, by the time the vacuolar gauge pressure becomes zero a substantial amount of water has left the cell. If it were to keep its volume constant, this would mean that only about 10% of this volume would be liquid. Under this circumstances it is hard to visualize the build up of a substantial vacuum.

It is possible that depending on the vegetable under consideration partial vacuum could be built up which would then collapse.

On the other hand, and from a practical standpoint it has been pointed out above that the pressure term contribution can be neglected for the purposes of equilibrium moisture content prediction.

Thus the equilibrium relationship for the intermediate region is:

$$\phi = \hat{a}_w \tag{74}$$

In practice the use of this equation can be extended to the high moisture region. Figure 13 indicates the equilibrium values predicted by the above expression for apples at 20°C.

The $(\partial X/\partial \phi)_T$ derivative

For the intermediate and high moisture content regions the derivative $(\partial X/\partial \phi)_T$ can be calculated using the following expression obtained from equations (68), (71) and (74).

$$\left(\frac{\partial X}{\partial \phi}\right)_T = \frac{\alpha}{(1 - x_w)^2 \; \phi\left[\frac{1}{x_w} - 2\beta A(1 - x_w)\right]} \tag{75}$$

where

$$\alpha = \sum_j \frac{m_j}{(\sum_j m_j + d)} \cdot \frac{M_w}{M_j} \tag{76}$$

and $\beta = 2.30258 \ldots.$

The results for apples at 20°C using the above equations are shown in table 13 together with values calculated from several of the correlations described previously. It can be seen that several of the correlations yield good predictions for the intermediate moisture region. As moisture content increases, the best predictions are provided by the Filonenko and the Halsey correlations as well as by equation (75). The Filonenko and Halsey correlations tend to over-estimate the effect of a change in water vapor activity whereas equation (75) tends to under-estimate it.

The prediction of isotherms at different temperatures

Equations (68) and (64) enable sorptional equilibrium values to be predicted at any temperature. As an example values have been predicted for apples at 40°C (Figure 14).

The derivative $(\partial X/\partial T)_\phi$ in the proposed correlation

Using equation (74) to describe the whole range of moisture contents, the derivative is

$$\left(\frac{\partial X}{\partial T}\right)_\phi = - \frac{\alpha b P\,(1 - x_w)}{T^2\{2\ \ln\left(\frac{\phi}{x_w}\right) - \frac{(1 - x_w)}{x_w}\}} \qquad (77)$$

Representative values were calculated for apples at 30°C and are shown in Table 14. If can be seen that the predicted values are a reasonable representation of the measured values and that they extend into the high moisture content region in a satisfactory manner.

Application of the proposed correlation to other foodstuffs

The proposed correlation procedure was applied to other foods and the results compared with experimental data. Typical compositional data were used to predict equilibrium data for all but the low moisture content region, where a B.E.T. equation was used, as described earlier. As some of the foodstuffs to be considered are sucrose-based instead of glucose-based, there is need for data on the water activity of sucrose solutions.

The activity coefficient of sucrose solutions

Stokes and Robinson (1966) presented experimental data for the activity of sucrose solutions as well as a correlation which relates molalities to the activity coefficient of water.

The use of their correlation presents difficulties when carried beyond the scope for which it was developed ($m < 6$) and at high sugar concentrations it is not adequate. Instead, the experimental data obtained by the above authors, together with data obtained by Scatchard et al. (1938), were fitted by a least square linear regression procedure in the form of equation (68). As a result, the following value was obtained:

$$A = -\ 2.789326$$

which fits the experimental data to within 0.8%. Norris (1966) suggested a value of $A = -\ 2.60$, which results in maximum errors of 3.6%.

Beetroot

Cerny (1941), Dahlberg (1952) and Owens et al. (1955), have published data on typical compositions of beetroots from several origins. It is

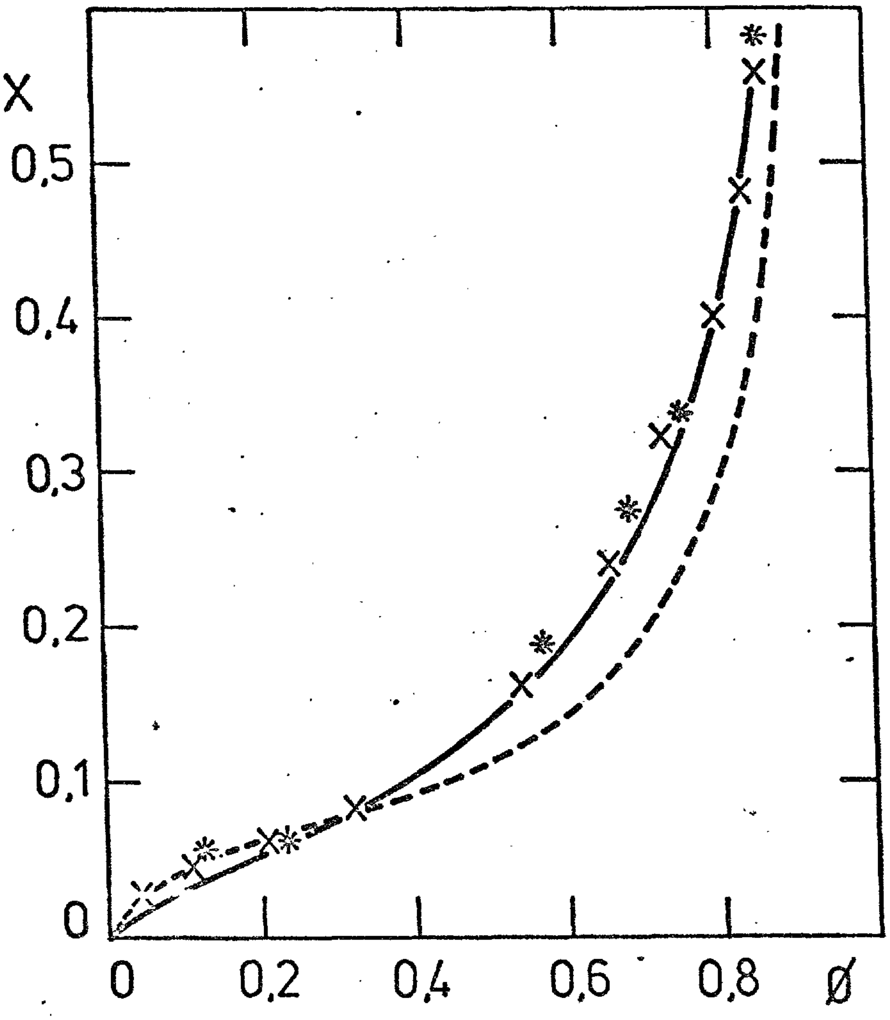


Figure 13

Predicted equilibrium data (Apples, 293°K)

___ equation (81)

--- BET equation

* experimental data

x Filonenko and Chuprin (1967)

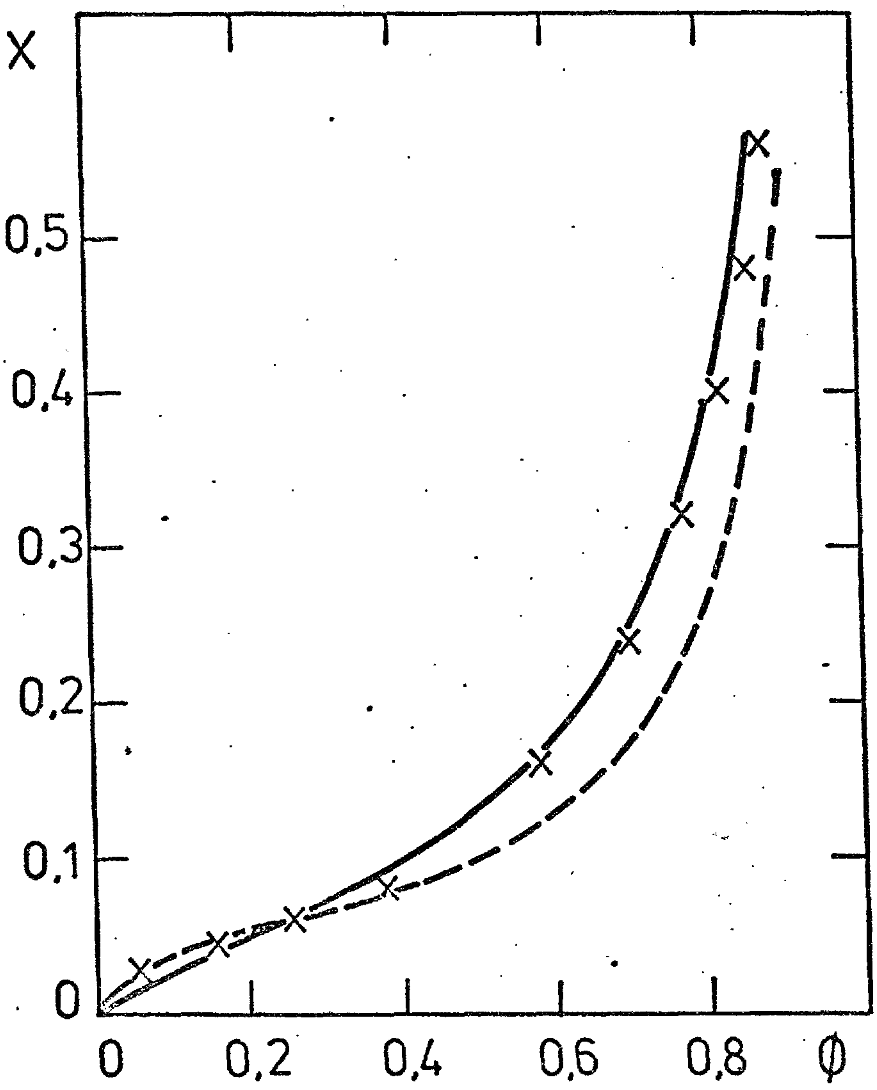


Figure 14

Predicted equilibrium data (Apples, 313°K)

___ equations (75) and (81)

--- BET equation

x . Filonenko and Chuprin (1967)

interesting to note that the sugar content of beetroot corresponds mainly to sucrose, instead of glucose. Equation (74) was used to predict the sorption equilibrium data in the intermediate moisture region, for beetroot at 25°C, using a representative value of α of 0.8061.

A least square linear regression procedure yielded $X_{mv} = 0.0518$ and $c = 16.16$ for the B.E.T. equation (equation (47)). The results are plotted in figure 15 and compared with experimental data (Iglesias et al., 1975). It can be seen that the predicted values fit the experimental results adequately.

Prunes

The chemical composition of prunes has been thoroughly reviewed by Strachan et al. (1951). Further reports were made by Kalasek and Blaha (1963) and by Chernovalova and Avetisyan (1969). It is concluded that about 70% of the sugar is sucrose. Figure 16 shows a prediction curve obtained by plotting the B.E.T. expression up to X_{mv} and then continuing with equation (74). In this case $X_{mv} = 0.0977$ g/g dry matter; $c = 11.7476$ as obtained by a least squares regression procedure, and $\alpha = 0.59$. It is interesting to note that the values predicted by equation (74) for $X < X_{mv}$ are almost the same as those predicted by equation (47). The results are compared with experimental data obtained by Filonenko and Chuprin (1967) and, as shown in figure 16, the theoretical prediction is satisfactory.

Apricots

The composition of apricots was reviewd thoroughly by Strachan et al. (1951). Additional data were reported by Minicone (1962-3). Figure 16 shows a prediction curve obtained by matching the B.E.T. line up to X_m with equation (74) from X_{mv} upwards.

Again the values predicted by the B.E.T. equation ($X_{mv} = 0.1092$ g/g, c = 0.1092) are almost identical with those predicted by equation (74). The predicted values compare well with the experimental data obtained by Filonenko and Chuprin (1967).

General comments on the proposed approach

The above discussion shows that equation (74) can be used over most of the range of moisture contents of sugar-based foodstuffs including the high moisture region, a feature not provided by any of the known correlations although high moisture content is the starting point for the study of the drying, packaging and storage problems considered earlier. Equation (74) has been found to provide simple analytical expression for $(\partial X/\partial T)_\phi$ and $(\partial X/\partial \phi)_T$ and to be well behaved at all moisture contents.

When the water content is close to the monolayer water content, the data are best represented by the B.E.T. equation. For some foodstuffs the values thus predicted agree with those predicted by equation (74), although there is no obvious thermodynamic justification for this.

The correlation is based on a simplified description of the composition of the food, so that it is sensitive to varietal or other composition differences.

The correlation may be useful in two distinct situations. First, it provides a means of predicting the equilibrium behaviour of sugar-based foodstuffs, when no data are available other than a knowledge of the average representative ratio of sugar to non-sugar dry matter together with the activity coefficient data reported above. Secondly, if experimental equilibrium data are available, they provide a simple model on which to base a correlation. In that case, α and A become the correlation parameters.

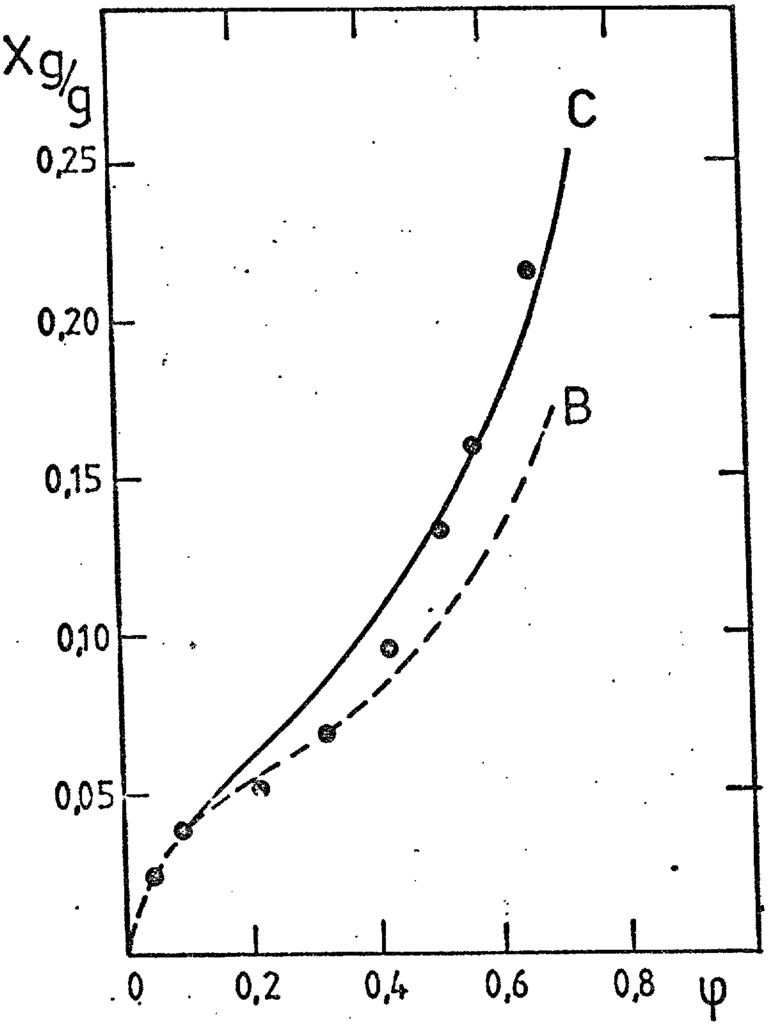


Figure 15

Beetroot, 298°K

C, equation (81)

B, BET equation

• Iglesias et al. (1975)

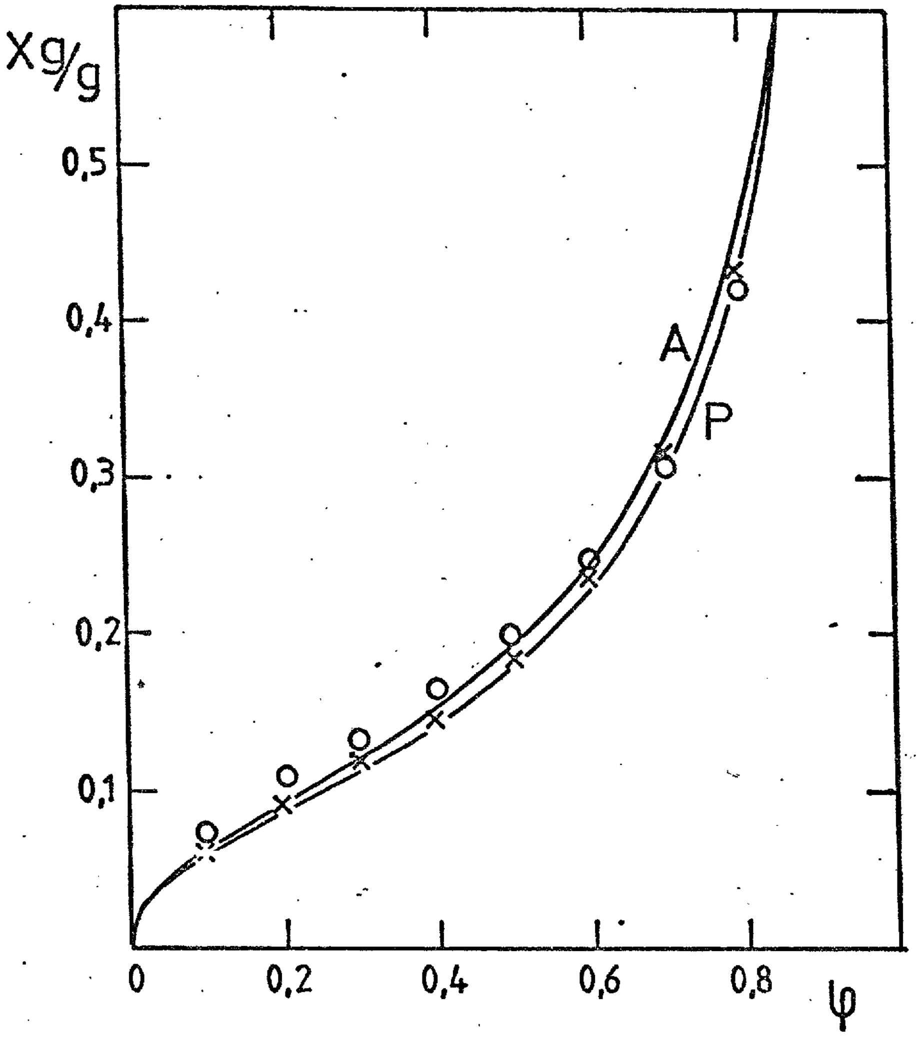


Figure 16

Apricots (A) and Plums (P), 293°K

o Apricots data (Filonenko and Chuprin, 1967)

x Plums data (Filonenko and Chuprin, 1967)

CHAPTER IV

TRANSPORT PROPERTIES

Changes in porosity as dehydration proceeds. Geometrical considerations.

The modelled porous structure described in Figure 1 can be extended to the situation in which the cell shrinks in size within the solid matrix. From a purely geometrical standpoint it is suggested that shrinkage can be described by considering the cells to remain spherical. Two regions of shrinkage can be recognized. The first describes a shrinkage of the sphere and a corresponding increase in λ, from the situation in which the cube is circumscribed by the sphere ($\varepsilon = 0$, $\lambda \simeq 0.7071$) to that in which the cube circumscribes the sphere ($\varepsilon = 0.476$, $\lambda \doteq 1$). The second describes further sphere shrinkage.

It is to be realized that the true lower bound should correspond to values of λ for $\varepsilon > 0$, since there are physiological needs for open intercellular air spaces (Smock and Neubert, 1950).

For $\lambda \leqslant 1$ equation (40) yields $\lambda(\varepsilon)$ and conversely:

$$\varepsilon = 1 - \frac{\pi\alpha}{6\lambda^3} \tag{78}$$

where $$\alpha = -2 + 4.5\lambda - 1.5\lambda^3 \tag{79}$$

For the second region of shrinkage, $\lambda \geqslant 1$, the cells are regarded as conserving basically their spherical shape. This would mean a loss of physical contact between individual cells but in practice they will be tied together by strands of matter, small enough to make the above description an acceptable approximation. In this case equation (80) describes the change in porosity as a function of λ .

$$\varepsilon = 1 - \frac{\pi}{6\lambda^3} \tag{80}$$

<u>The porosity equations as a function of moisture content.</u>

The porosity at any moisture content can be expressed as

$$\varepsilon = \frac{qV^1_{mx} - V_c}{q\, V^1_{mx}} \tag{81}$$

at full turgor

$$\varepsilon = \frac{q\, V^1_{mx,o} - V_{c,o}}{q\, V^1_{mx,o}} \tag{82}$$

The number of cells results from :

$$q = \frac{V_{c,o}}{V_{cl,o}} \tag{83}$$

By means of a material balance it is possible to estimate the volume of cellular matter per gram of dry matter at any time:

$$V_c = \frac{X + \dfrac{\Sigma m_j}{\Sigma m_j + d}}{\rho_{soln}} + \frac{\dfrac{d}{\Sigma m_j + d}}{\rho_{ose}} \tag{84}$$

The variable porosity can thus be expressed as:

$$\varepsilon = 1 - \frac{V_c}{\dfrac{V_{c,o}}{V_{cl,o}} \; V^1_{mx}} \qquad (85)$$

If the solid matrix volume remains unchanged:

$$\varepsilon = 1 - \frac{\alpha\pi_o}{6\ \lambda_o^{\,3}} \quad \frac{V_c}{V_{c,o}} \quad , \qquad (86)$$

If there is a contraction of this volume, i.e. shrinkage, equation (87) applies:

$$\varepsilon = 1 - \frac{\pi\alpha_o}{6\ \lambda_o^{\,3}} \quad \frac{V_c}{V_{c,o} \quad V^1_{mx}} \qquad (87)$$

where V^1_{mx} becomes a variable volume.

Experimental determination of porosity as a function of moisture content.

As reviewed earlier, there is meager information on porosity and it refers to the full turgor situation. Harper (1962) reports one value for freeze dried apples.

Most of the conventional methods for porosity determination cannot be applied in this case because of the lack of mechanical strength of the sample. A separate determination of bulk volume and intercellular space volume was found to be satisfactory.

The intercellular space volume was determined by measuring the true sample volume, using the apparatus sketched in figure 17. The volume V_2 of the expansion bulb from the stopcock to a fixed level mark is known. The volume V_1 of the empty sample chamber is also known. With the cover plate carefully closed to insure a good seal, H is read and the true volume of the sample is calculated from equation (88), taking into account the value of the atmospheric pressure at the time of the experiment

$$V_5 = V_1 - V_2 \frac{(P_a - H)}{H} \tag{88}$$

The bulk volume was found by mercury displacement.

Samples of different moisture content of Granny Smith apples were obtained by partial drying in an air-circulating oven at 76°C, followed by multiple wrapping in "cling film" and overnight storage to allow for moisture content homogenization. The moisture content was evaluated by a gravimetric technique (Rotstein et al., 1969). The results are plotted in figure 18. Although there have been no results reported in terms of $\varepsilon(x)$, some earlier data can be used to evaluate the results obtained.

Chirife (1969) measured the change in bulk volume of Granny Smith apples, as a function of moisture content. His experimental data can be represented by the correlation:

$$\frac{V_{bulk}}{V_{bulk,o}} = 0.15 + 0.85 \frac{X}{X_o} \tag{89}$$

By taking into account equation (90),

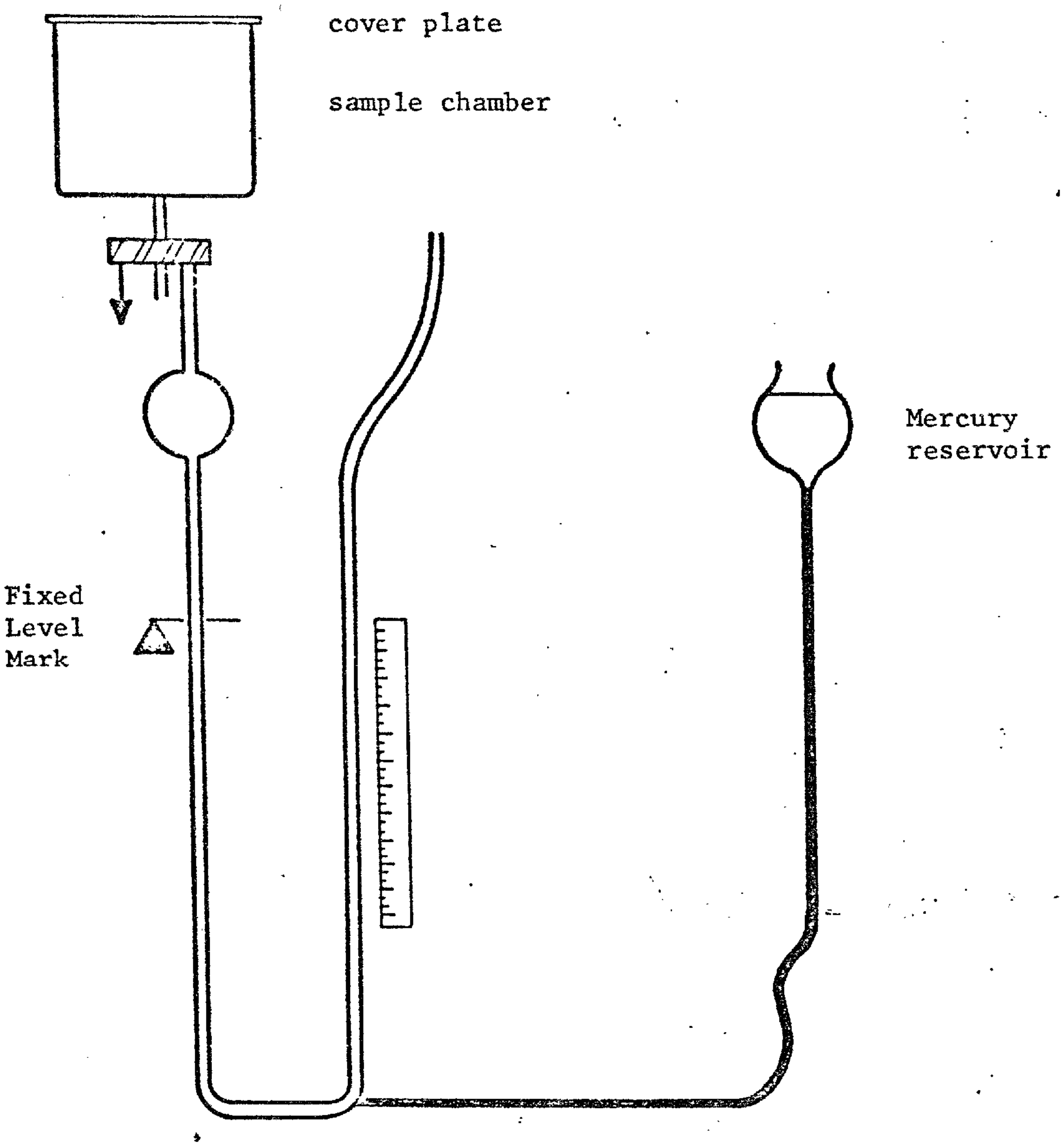
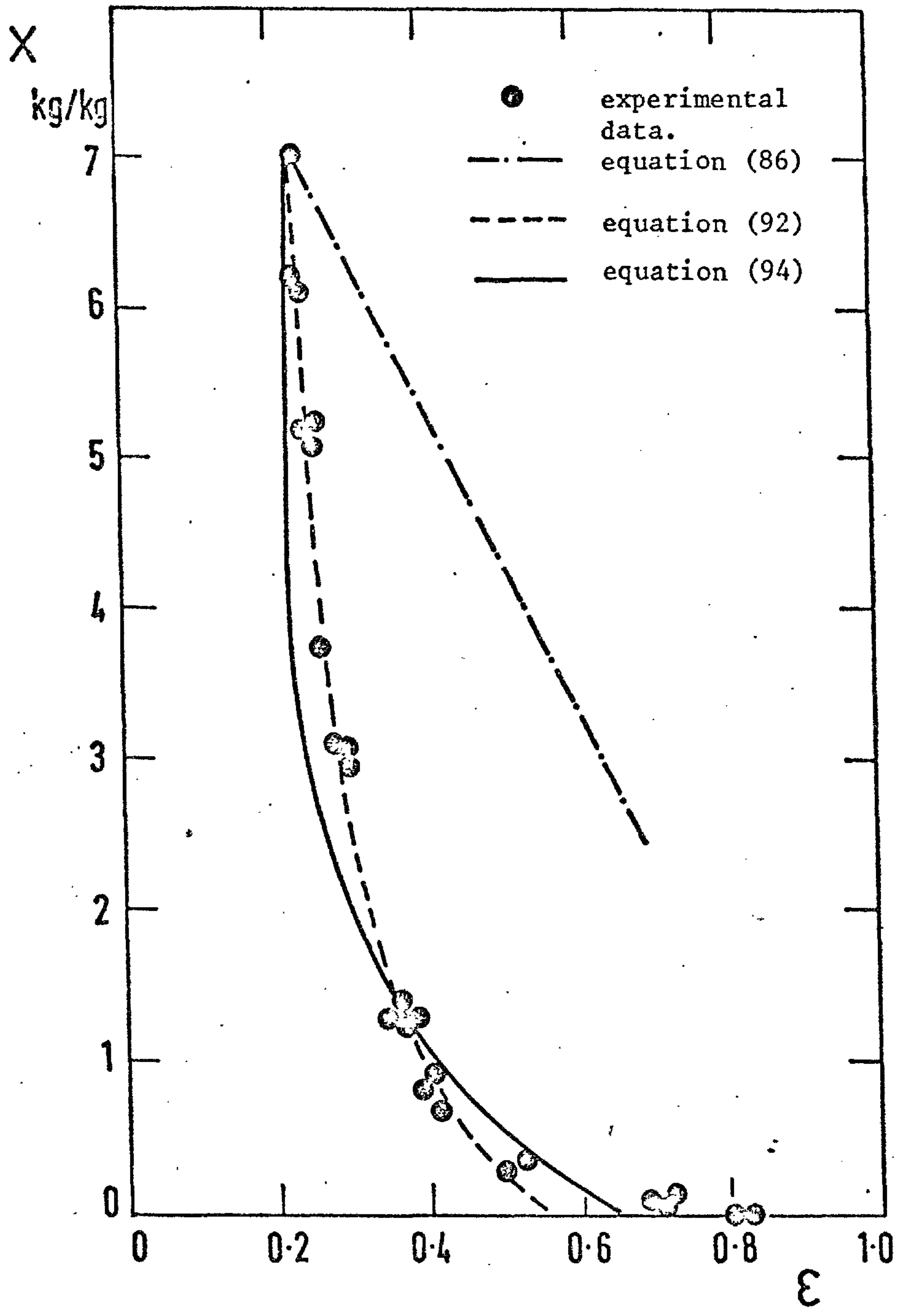


FIGURE 17

Apparatus for porosity determination.

FIGURE 18.

Porosity as a function of moisture content.



$$\frac{V_{bulk}}{V_{bulk,o}} = \frac{qV^{1}_{mx}}{qV^{l}_{mx,o}} \qquad (90)$$

correlation (89) can be used in equation (87) to yield:

$$\varepsilon = 1 - \frac{\pi\alpha_o}{6\ \lambda_o^3} \quad \frac{V_c}{V_{c,o}\ (0.15 + 0.85\ \frac{X}{X_o})} \qquad (92)$$

Values of (X) calculated using equation (92) are shown in Figure 18.

Aruanno (1971) studied the relationship between lateral area of sample and moisture content. By re-working his experimental data the following correlation of bulk volume as a function of moisture content can be obtained:

$$\frac{V_{bulk}}{V_{bulk,o}} = (0.24 + 0.76\ \frac{1+X}{1+X_o})^{3/2} \qquad (93)$$

In this case equation (87) can be written:

$$\varepsilon = 1 - \frac{\pi\alpha_o}{6\lambda_o^{3}} \quad \frac{V_c}{V_{c,o}(0.24 + 0.76\ \frac{1+X}{1+X_o})^{3/2}} \qquad (94)$$

Equation (94) has been used to predict values of $\varepsilon(X)$. The results are plotted in Figure 18.

A comparison of experimental data and values predicted by equations (92) and (94) indicates that the second equation is the better representation of the data over most of the moisture content range. The experimental results differ from the predicted values at very low moisture contents.

It can be seen that the change in porosity is not too large over most of the moisture content range. A simulation of the process down to the commercial dehydration moisture contents (X = 0.32 kg/kg) can be based, in principle, on an average constant porosity.

Thermal Conductivity.

Very little experimental information on the thermal conductivity of foodstuffs is available. Two comprehensive reviews (Qashou et. al., 1972, Rha, 1975) summarize all the available data. It can be concluded that some data are available for fresh and freeze-dried foods but that almost none exists for the thermal conductivity of foods as a function of moisture content.

In the particular case of apples, table 16 shows the available data. It is surprising to note that the porosity of the food has not been considered to be one of the parameters that should be recorded.

The prediction of the thermal conductivity of composite materials has been the subject of research for a long time, some of the pioneering work being carried out by Maxwell (1881) and Lord Rayleigh (1892). The studies have been addressed either to the problem of thermal conductivity or to analogous problems of electrical conductance, magnetic permeability, permitivity and diffusivity.

Five approaches have been examined for the purpose of predicting the thermal conductivity of foodstuffs: Maxwell's analysis of the case of a single sphere in a continuum (Maxwell, 1881), Lord Rayleigh's treatment of the case of spheres of uniform size in

TABLE 16

Data on thermal conductivity of apples.

Sample description	k (N/s ^{o}K)	Source.
Freeze dried apple at 1 at.	0.04216	Harper (1962)
Apple,green. Water content 88.5%, bulk density 0.79 g/cm^3	0.422	Sweat (1974)
Apple, red. Water content 84.9%, bulk density 0.84 g/cm^3	0.513	Sweat (1974)
Fresh apple (continuous heating). Bulk density 0.89 g/cm^3.	0.670	Häckel (1976)
Fresh apple. Bramley's seedling	0.418-0.591	Mann and Forsyth (1956)

cubical lattice position (Lord Rayleigh, 1892) which was eventually expanded by Jeffrey (1973), Bruggeman's study of the conductivity of mixtures of particles of different sizes (Bruggeman, 1935), the so-called 'Self-consistent scheme' discussed by Hashin (1968) and Tsao's collecting of resistances (Tsao, 1961).

Maxwell (1881) considered spheres at distances of each other large enough so that it could be assumed that there was no interaction between them. His assumptions require that the solution be rigorously valid only for very dilute dispersions. According to Meredith and Tobias (1962) Maxwell's equation represents accurately conductivity data of random or ordered dispersions of spheres only when the porosity is very high ($\varepsilon = 0.9$ or more). This is too high a value to be useful in the case of foodstuffs (see for instance Figure 18).

Lord Rayleigh (1892) considered the effect of a large number of spheres of uniform size surrounding any particular sphere of interest. There is in principle no reason to restrict the application of his conclusions to high porosity, but there is an explicit limit which corresponds to spheres of the same diameter as the cube length. This provides a limiting value of $\varepsilon = 0.476$ below which the equation loses physical significance. Moreover, Turner (1976) reports experimental evidence of poor results from Lord Rayleigh's equation when the porosity is below 0.400. For the same physical situation as that studied by Lord Rayleigh, Meredith and Tobias (1962) derived a further equation. They used a different function for the potential and considered higher terms in the series expression for the potential in the continuous phase. Although they expected better behaviour from their equation, the same restriction on porosity at $\varepsilon \leqslant 0.476$ applies and they found that their equation is accurate for $\varepsilon > 0.500$.

Bruggeman (1935) recognized that in concentrated mixtures the field adjacent to particles will be more accurately represented by using the effective conductance of the mixture as a whole, rather than that of the continuum. Bruggeman's equation is not limited to high values of porosity but is suited to represent dispersions where a large range of particle sizes are present. By changing the particle size distribution, the porosity can be made as low in value as is wished. On the other hand, the predictions obtained are good only when the particle-size range is broad. According to Meredith and Tobias (1962), the representation is unsatisfactory when the system consists of spheres of uniform size or of a narrow range of sizes. As apple tissue is visualized as consisting of cells of nearly uniform size, Bruggeman's equation would not be an adequate theoretical expression to use.

The "self consistent scheme" is a method of approximation based on considering a typical basic element of a heterogeneous medium and regarding it as being embedded in an equivalent homogeneous medium whose properties are the unknowns to be calculated. Several approaches can be tried to define the basic element, as reviewed by Hashin (1968). The case which appears closest to cellular tissue is that of a particulate composite. Here the approach is to consider a spherical inclusion surrounded by a concentric spherical shell of conductivity equal to that of the continuous phase. The composite sphere thus obtained is embedded in a homogeneous and isotropic medium whose conductivity is the unknown effective conductivity of the composite. Although the method lends itself to a theoretical analysis, in order to obtain results, a value must be found for the ratio between the radii of the two concentric spheres. In practice this becomes a correlating parameter, thus losing the predictive advantages expected from a theoretical approach. Two extreme cases (a) when the ratio of particle to shell radius is unity (no shell) and (b) when the ratio of particle volume to shell volume is equal to the volume fraction of particles, represent lower and upper bounds for the possible values.

Buyevich (1974) has given a treatment somewhat similar to Hashin. Turner (1976) found that Buyevhich's treatment predicted values of thermal conductivity higher than those predicted by Maxwell (1881) for different ratios of conductivities of the two phases.

Tsao (1961) suggested the approach of collecting the dispersed material into a strip so as to deal with homogeneous phases. This approach and some fallacies involved were reviewed by Turner (1976).

Thorough critical reviews of the different theoretical methods have been made by De Vries (1952, 1957) and by Meredith and Tobias (1962). Hashin (1968) and Turner (1976) included significant revisions of prior work.

From the above it is clear that there is no existing theoretical expression which could describe the behaviour of the foodstuff tissue as modelled earlier. (See figure 23 for a practical test of the theoretical expressions). An adaptation of earlier work such as that of Buyevich (1974) could be attempted or a new model could be proposed.

Theoretical expressions for thermal conductivity: an approximate theory.

The above review emphasizes the necessity of basing the theoretical model on a satisfactory model of the cellular tissue. Such a model must account for shrinkage and relate the moisture content to changing porosity. An attempt to devise such a model has been described at the beginning of this Chapter.

On considering this model, it is clear that the problem is essentially three-dimensional. It is expected that some degree of convection in the pores will exist and that the heat flux will be greatest at the contact surfaces between cells. Although such a problem could be solved numerically the effort required would not be warranted.

In consequence, a simplified theory is proposed on the basis of the following assumptions. One, the behaviour of the cellular structure is adequately described throughout the entire drying process by the model proposed earlier. Two, the temperature profiles are one-dimensional so that at any distance from the surface of the slab the temperature within the cellular material is the same as that within the intercellular air spaces. Three, convection in the pores can be neglected.

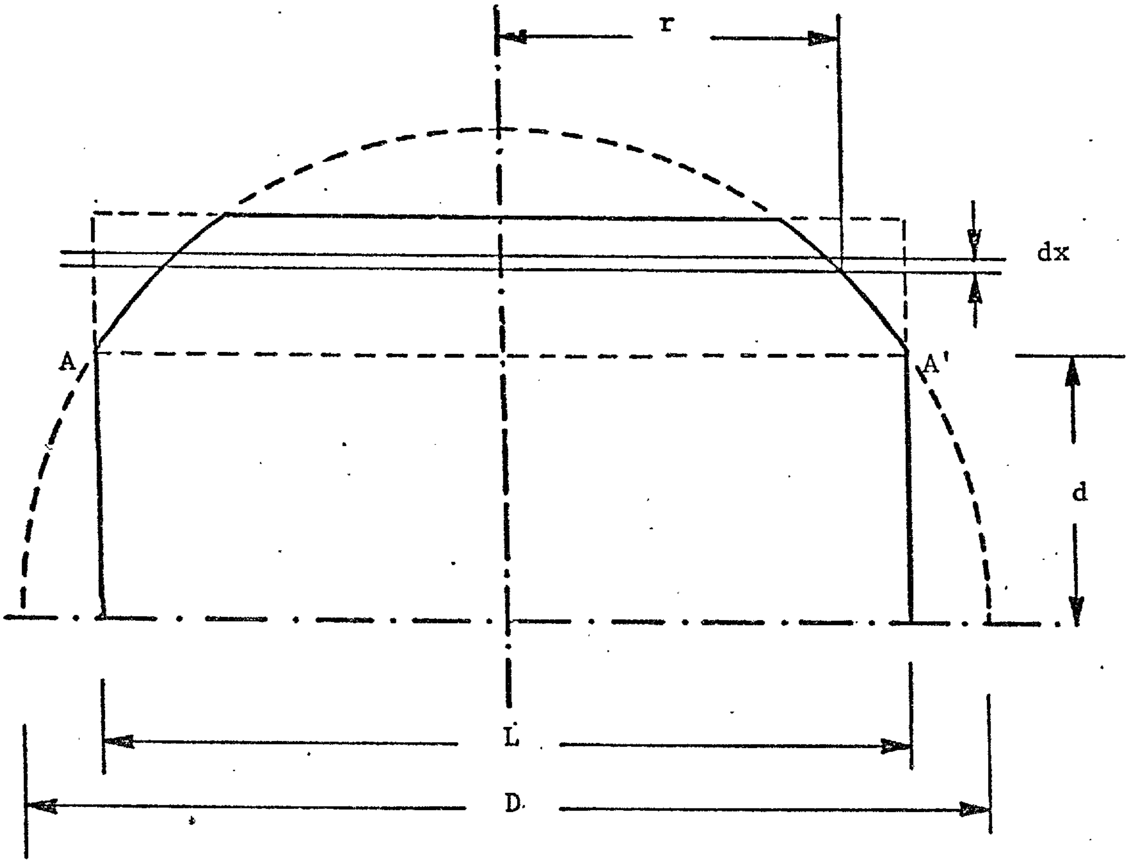
It should be emphasized that the theory involves several approximations and is in itself based on an approximate description at the tissue.

As in the case of porosity it is necessary to consider two successive cases; first when $1 \geq \lambda \geq \lambda_0$. (Figure 19) and secondly when $\lambda > 1$ (Figure 20).

In the first case the unit for calculation purposes can be considered as one half of the solid matrix cube (Figure 19). The conductivity of the composite is made up by the coupled resistances of cellular matter alone, up to AA', plus that of air and cellular matter

Figure 19

The case $1 \geq \lambda \geq \lambda_o$



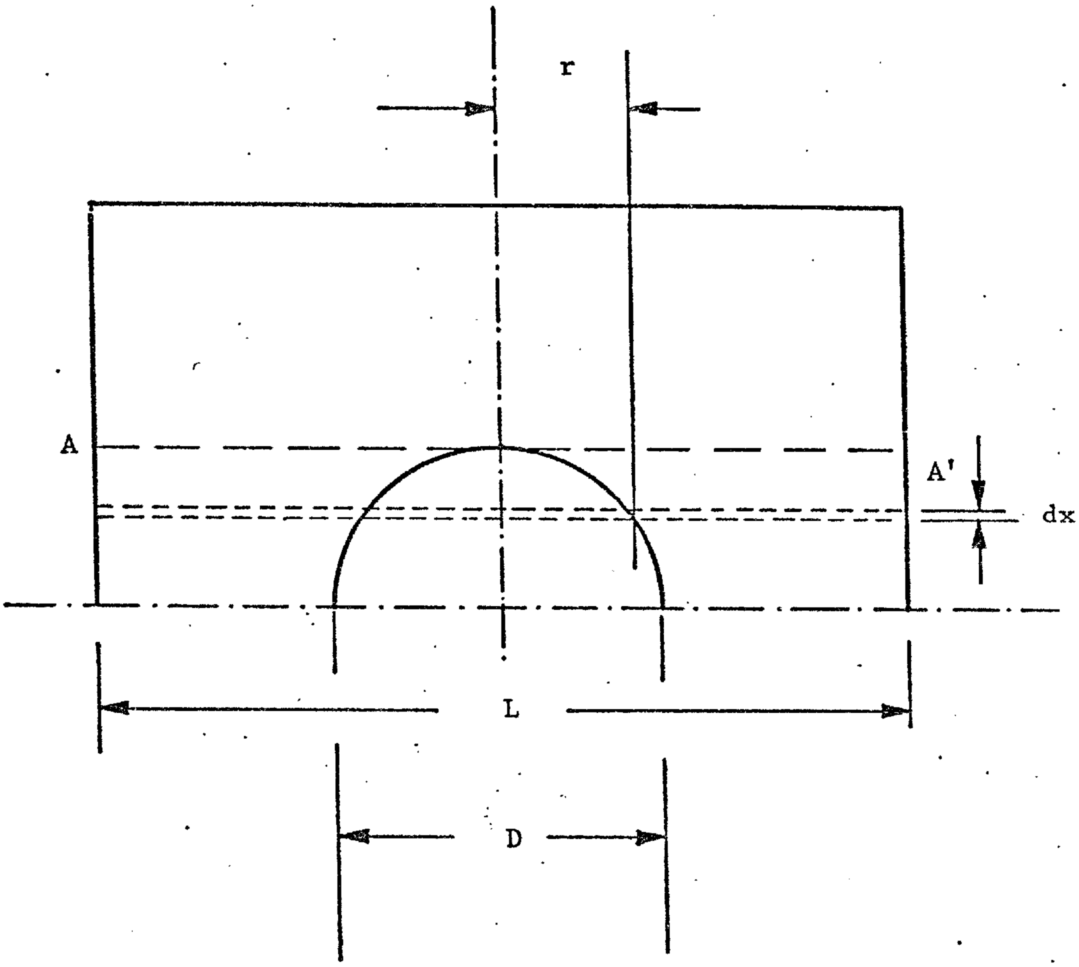


Figure 20

The case $\lambda \geqslant 1$

from AA' to the upper end of the cell. The latter can be calculated from:

$$- Q = k_c \pi r^2 \frac{dT}{dx} + k_g (L^2 - \pi r^2) \frac{dT}{dx} = k L^2 \frac{dT}{dx} \qquad (95)$$

Equation (95) assumes one dimensional conduction as stated earlier. From it:

$$\int_d^{L/2} \frac{dx}{(k/k_g)} = \int_d^{L/2} \frac{dx}{1 - \pi(r/L)^2 + (k_c/k_g)\pi(r/L)^2} \qquad (96)$$

Series addition of the resulting expression for the cellular matter thermal resistance results in

$$k = k_g \left[L_1 \frac{k_g}{k_c} + \frac{1}{2\tau M} \ln \frac{(M+1)(M-L_1)}{(M-1)(M+L_1)} \right]^{-1} \qquad (97)$$

where L_1 is a geometrical variable:

$$L_1 = \frac{\sqrt{1-\lambda^2}}{\lambda} \qquad (98)$$

τ is a thermal conductivity variable:

$$\tau = \frac{\pi}{4} \left(\frac{k_c}{k_g} - 1 \right)$$

and M is a mixed thermal conductivity and geometrical variable:

$$M = \sqrt{\frac{1}{\tau} + \frac{1}{\lambda^2}} \qquad (100)$$

As moisture content decreases, λ increases until the structure is represented by the case $\lambda \geqslant 1$ (Figure 20). By a similar reasoning when $\lambda \geqslant 1$

$$k = k_g \left[L_2 + \frac{1}{2\tau M} \ell n \frac{(\lambda M+1)}{(\lambda M-1)} \right]^{-1} \tag{101}$$

where L_2 is a geometrical variable:

$$L_2 = \frac{\lambda-1}{\lambda} \tag{102}$$

and τ and M are as defined previously.

Experimental work.

Experimental determinations of thermal conductivity as a function of moisture content have been reported by Urbicain and Rotstein (1977). The experimental equipment was basically of the type of the heated wire probe, i.e. a line-source technique. The method was originally proposed by Schleiermacher (1888) and the first result for foodstuffs were reported by Mann and Forsyth (1956). Particulars of the equipment used and the improvements on earlier versions were reported by Urbicain and Rotstein (1977). The experimental results for apples are indicated in figure 23, together with the theoretically predicted values.

Theoretical predictions of thermal conductivity.

To relate the thermal conductivity values to moisture content it is necessary to obtain λ. This is accomplished by simultaneous solution of equations (89), (90), (87) and (78) for $\lambda \leqslant 1$ and (89), (90),

(87) and (80) for $\lambda \geq 1$.

In order to use these equations, the values of several physical properties must be specified. In the case of equation (87) it is necessary to know the average chemical composition of the fruit, the density of the sugars solution as well as the density of the tissue matters other than water and sugars (ρ_{ose}). A representative composition was indicated in Table 15, from which it can be seen that the following values can be used in equation (84):

$$\frac{\Sigma m_j}{\Sigma m_j + d} = 0.76 \text{ kg/kg}$$

$$\frac{d}{\Sigma m_j + d} = 0.24 \text{ kg/kg}$$

The density of tissue matters other than water and sugars represents mainly fibrous material, most of it of cellulosic nature. Thus, for ρ_{ose} it is suggested to use as a representative value the density of cotton fiber. Kirk and Othmer (1964) reported extensively the density of native cotton in different displacement mediums as well as those of ramie, mercerized ramie, sulfite wood pulp and regenerated cellulose fibers. It can be concluded that an acceptable representative value is

$$\rho_{ose} = 1.550 \text{ kg/m}^3$$

The density of the solution depends on the concentration, i.e., on the foodstuff moisture content. The values for glucose solutions of different concentrations in terms of moisture content are plotted in figure 21, indicating also the density of solid glucose. The data (Taylor and Rowlinson, 1955) were correlated by a least square curve fitting procedure resulting in equation (103):

$$\rho_{soln} = 1 + \left(\frac{a}{X + 0.76} \right)^{m} \qquad (103)$$

where

a = 0.40973

M = 1.12414

The correlation predicts ρ_{soln} within a ± 1% precision, except at very low moisture contents. When X ≐ 0 , the value predicted is 4.2% lower than the density of solid glucose. Thus, it can be used safely over the entire moisture content range.

Equations (97) and (101) require values of the thermal conductivity of air occupying the intercellular spaces and of the cell itself. The first can be approximated by the conductivity of dry air at the local temperature and pressure in the intercellular spaces. Since the sugar solutions make up most of the cellular matter (on weight basis) over most of the moisture content range, the thermal conductivity of cells can be approximated to that of glucose solutions.

Popov and Zhura (1957) studied the thermal conductivity of glucose solutions at different concentrations, between 323^{o} and 368 ^{o}K. Figure 22 shows the thermal conductivities of water (Weast, 1969) and of glucose solutions equivalent to moisture contents of X = 0.34 kg/kg

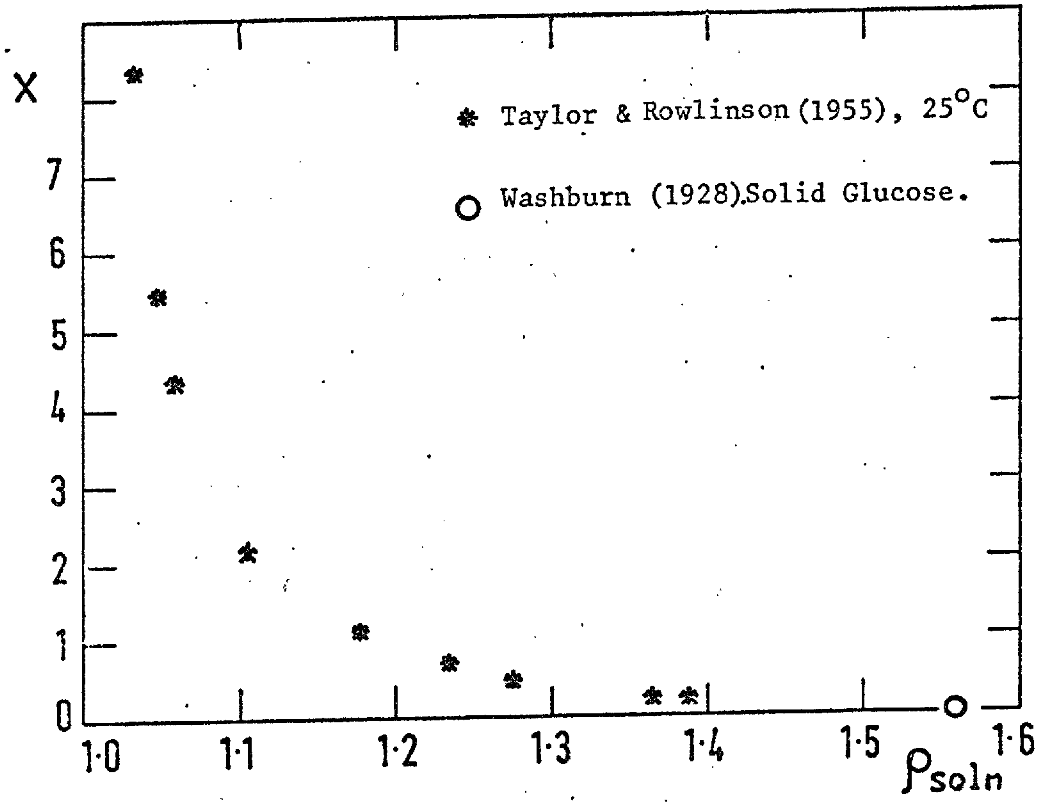
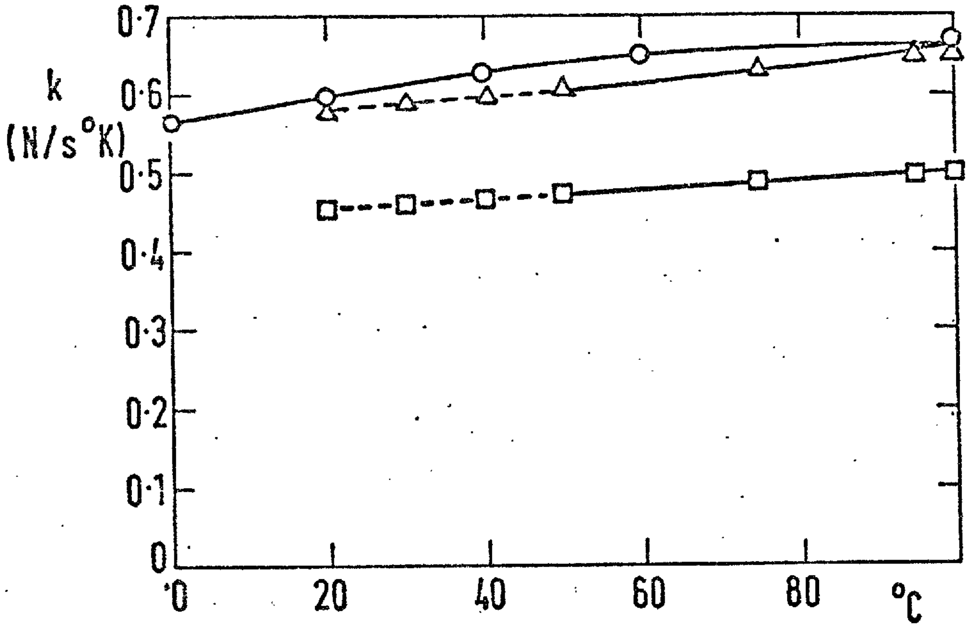


Figure 21
Density of glucose solutions in terms of moisture content.

Figure 22

Thermal conductivity of water and glucose solutions.



○ Water

△ Glucose solution equivalent to X = 3.04 kg/kg

□ Glucose solution equivalent to X = 0.51 kg/kg and X = 0.51 kg/kg, over the temperature range 273 - 373 ^{o}K. From figure 22 it can be seen that the data at 313^{o}K is an acceptable approximation to the values of the thermal conductivity within the drying temperature range : 293 - 343^{o}K.

The Popov and Zhura correlation was recalculated at this temperature by expressing the glucose concentration in terms of moisture content and the result used as a representation of the cellular thermal conductivity (equation (104)).

$$k_c = 0.6655 - \frac{0.2510}{0.76 + X} \quad \text{N/s}\ ^{o}\text{K} \qquad (104)$$

At low moisture contents, the value of thermal conductivity from equation (104) is k_c = 0.3352 N/s ^{o}K, an intermediate value between that of sugar cane and that of wood across grain (0.5820 N/s ^{o}K and 0.1586 N/s^{o}K respectively) it appears that equation (104) can be used down to low values of X.

With the use of the above selected physical property values, equations (97) and (101) were solved to predict the values of the thermal conductivity of apples for $0 < X \leqslant 7$ kg/kg. The results are plotted in figure 23 for two extreme cases of calculation of porosity : no shrinkage and shrinkage. The former case involves the use of equation (93) and the latter the relationship $(\lambda D/\lambda_o D_o)^3 = 1$. Clearly the predicted values fail to reproduce the experimental data, which fall between the two alternative predictions. The reasons for this can be traced to the original assumptions used in developing equations (97) and (101). Of these, the most important seems to be the description of the change in porosity that occurs throughout the drying process. The model established earlier lumped all the changes in porosity into shrinkage of the spheres while assuming that the distances between spheres remained unchanged. This is equivalent to stating that there is no change in the overall dimensions of the sample. This model should be improved so that changes in porosity can be described by changes in the distances between the sphere centres as well as in the sphere radii. To do this, there is need for experimental data on the change in bulk volume as a function of moisture content.

Using an analogous approach to calculate porosity and the cell thermal conductivity, the earlier statements as to the unapplicability of the Maxwell, Lord Rayleigh and Bruggeman expressions, were tested.

The expressions used were the following. The Maxwell correlation (Maxwell, 1881) :

$$k = k_g \left[\frac{H_c + 2 - 2\,(1 - \varepsilon)(1 - H_c)}{H_c + 2 + (1 - \varepsilon)\,(1 - H_c)} \right] \qquad (105)$$

The Lord Rayleigh expression (Lord Rayleigh, 1892) :

$$k = k_g \left[1 - \frac{3(1 - \varepsilon)}{\left\{ \frac{2+H_c}{1 - H_c} + (1-\varepsilon) - 0.525\, \frac{(1-H_c)(1-\varepsilon)^{10/3}}{\frac{4}{3} + H_c} \quad \ldots \right\}} \right] \qquad (106)$$

Bruggeman's equation (Bruggeman, 1935) :

$$k = k_g\left[\left\{-\frac{H_c}{2}+\left(\frac{H_c^2}{4}-\frac{\varepsilon^3(1-H_c)^3}{27}\right)^{\frac{1}{2}}\right\}^{\frac{1}{3}}+\left\{-\frac{H_c}{2}-\left(\frac{H_c^2}{4}-\frac{\varepsilon^3(1-H_c)^3}{27}\right)^{\frac{1}{2}}\right\}^{\frac{1}{3}}\right]^3 \qquad (107)$$

where

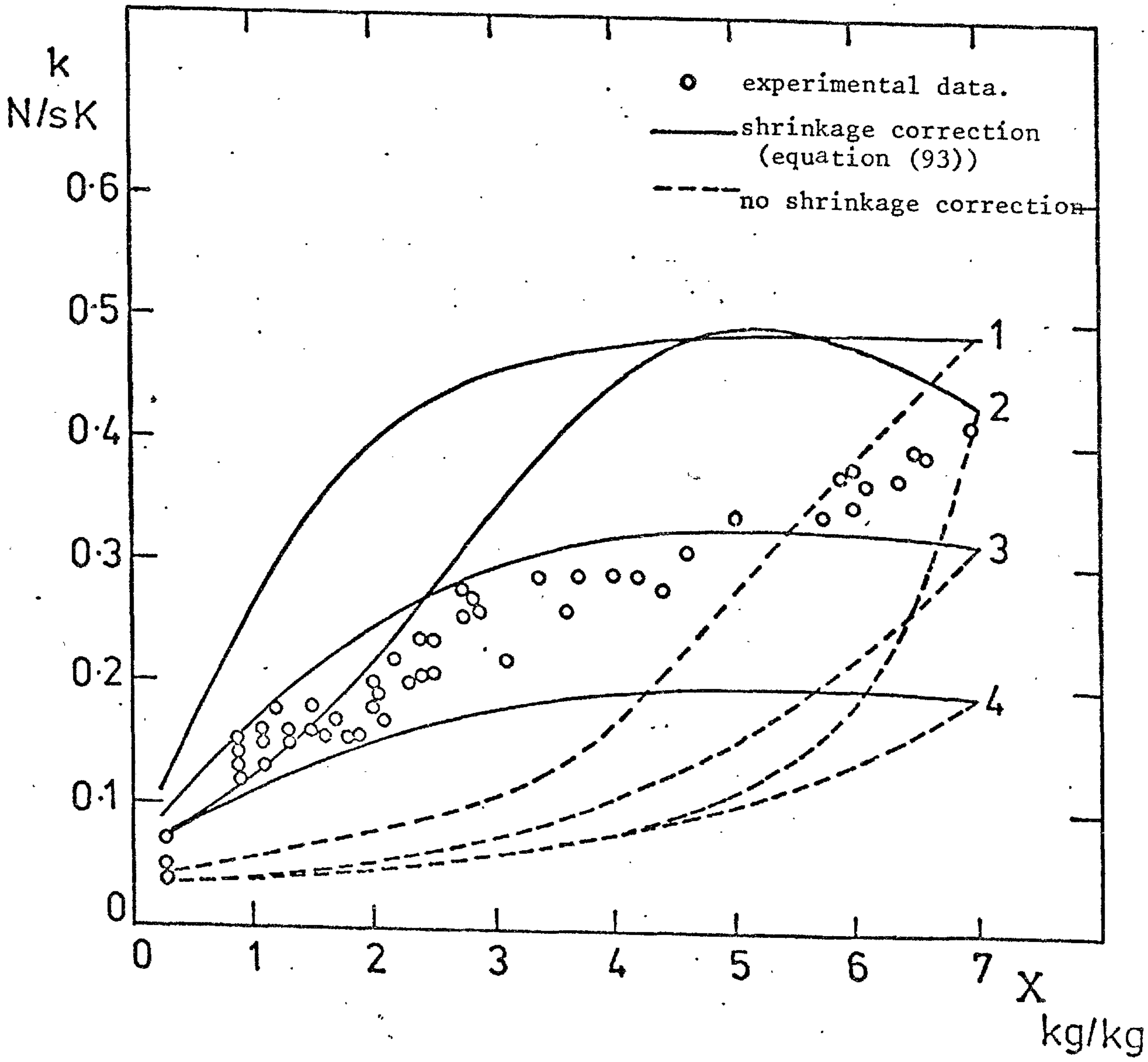
$$H_c = \frac{k_c}{k_g} \qquad (108)$$

For the purposes of the present work, it was decided to use an empirical correlation of the experimental data obtained by Urbicain and Rotstein (1977). This correlation is equation (109), with a coefficient of determination $r^2 = 0.965$.

$$k = 2.902184 \times 10^{-4} \quad X^{0.643165} \qquad (109)$$

Figure 23

Thermal conductivity. Experimental data and values predicted by: this work (1), Lord Rayleigh's (2) Bruggeman's (3) and Maxwell's (4) equations.



OTHER TRANSPORT PROPERTIES

Specific heat

The specific heat of liquid water, water vapour and air are available in the literature. The difference in values when the temperature changes within the range used in conventional drying of foodstuff processes, namely between 293° and $333^\circ K$, is slight so that average values can be used (Table 17). The specific heat of liquid water and that of apple juice are very close together. That of juice concentrate is only 28% lower than at the original dilution (Cho Kyun Rha, 1975).

The specific heat appears in the energy equation in the product $\rho_i(\hat{c}_p)_i$. In the case of the solid matter the product can be estimated by the following reasoning.

For the entire food, the product $\rho\hat{c}_p$ can be written as :

TABLE 17

Specific Heat of water and air at 293 and 333°K

	$\hat{c}_p$ cal/ g°C	
Constituent	293°K	333°K
liquid water	0.9988	0.9994
water vapour	0.4452	0.4507
dry air	0.2402	0.2425

$$\varepsilon\,\rho_v(\hat{c}_p)_v + \varepsilon\,\rho_a\,(\hat{c}_p)_a + \rho_{ps}\,(\hat{c}_p)_s + \rho_{ps}\,X(\hat{c}_p)_\ell = \rho\,\hat{c}_p \qquad (110)$$

At full turgor the value of the right hand side in equation (110) can be calculated from the data provided by Chokyun Rha (1975). As all the other constituents properties other than those of the solid matter are known, then:

$$\rho_{ps}(\hat{c}_p)_s = 0.92 \quad \text{cal/g}\ ^{o}\text{C}$$

Heat and Mass transfer coefficients.

Treybal (1955) reported correlations for the estimation of heat and mass transfer coefficients when drying.

For the mass transfer coefficient, in the case of flow of gas parallel to the drying surface, the following correlation can be used:

$$\frac{h}{\hat{c}_p G}\ \mathrm{Pr}^{2/3} = 0.581\ (\mathrm{Re}''')^{-0.48} \qquad (111)$$

or, alternatively figure 3.11 in Treybal (1955).

For the experimental set of conditions

$\mathrm{Re}''' = 11548.4$

$\mathrm{Pr} = 0.7213$

$G = 10.1114\ \text{kg/m}^2\text{s}$

Thus

$h = 81.298\ \text{kg/s}^3\ {}^{o}\text{K}$

Peck and Wasan (1974) reviewed the existing correlations for the case of drying of porous materials in the form of slabs or sheets. They suggest, for a case analogous to the present case, the use of equation (112).

$$\frac{hL}{k} = 0.0356\ (Re''')^{0.8}\ Pr \qquad (112)$$

this correlation leads to analogous if slightly lower (22%) values of h. Correlation (111) is preferred on account of its widespread use.

For the calculation of the mass transfer coefficient, equation (111) is used by taking into account the transport phenomena analogy. Thus,

$$\frac{k_y}{G_a}\ S_c^{2/3} = 0.581\ (Re''')^{-0.48} \qquad (113)$$

This mass transfer coefficient is defined by Treybal (1955) in terms of

$$n = k_y \left[(Y)_S - (Y)_{bulk} \right] \qquad (114)$$

The present solution is based on vapour weight fraction

$$\omega = \frac{Y}{Y + 1} \qquad (115)$$

Thus, equation (114) can be written :

$$\omega = k_y \left[\left(\frac{\omega}{1 - \omega} \right)_S - \left(\frac{\omega}{1 - \omega} \right)_{bulk} \right] \qquad (116)$$

Since the vapour weight fractions involved are low, it can be concluded that :

$$K \simeq k_y \tag{117}$$

From equation (113), for $S_c = 0.6814$:

$$K = 8.512 \times 10^{-2}\ \mathrm{kg/m^2s}$$

Effective Diffusivity.

The effective diffusivity is defined as

$$D' = D_{H_2O,Air} \frac{\varepsilon}{t} \tag{118}$$

This definition is valid provided Knudsen flow and surface diffusion can be dis-regarded (Rotstein, 1974, 1975).

There is very little experimental data available on this property. Harper (1962) measured the effective diffusivity for the system toluene-air in freeze dried apple tissue. Equation (118) yields, using a value $D_{H_2O,Air} = 0.260\ \mathrm{cm^2/sec}$ (Satterfield, 1970) and correcting for porosity using an average value $\varepsilon = 0.3$:

$$D' = 0.115 \times 10^{-5}\ \mathrm{m^2/sec.}$$

CHAPTER V

A TRANSPORT PHENOMENA APPROACH TO THE DRYING PROCESS.

Early work on drying of foodstuffs was carried out along two lines of thought: one a purely phenomenological description and the other based on a description of foodstuff tissue as a homogeneous solid through which water diffuses. Van Arsdel and Copley (1963) summarized the latter approach.

Actually, no satisfactory model can be proposed which does not take into account the heterogeneous nature of the cellular tissue structure. This in turn should lead to a description of the mechanism and kinetics of water migration as the fundamental step in the mathematical description of the process.

Rotstein et. al. (1974) and Peck and Wasan (1974) have reviewed alternative mechanisms of water migration and literature contribution based on the different approaches. In general the work is related to drying of inert solids and only recently has attention been focused onto the drying of foodstuffs.

The non-gravitational migration of water in a porous solid can be the result of one or more of the following driving forces :

1) Moisture concentration gradient: liquid diffusional flow.
2) Capillary forces: liquid capillary flow.
3) Vapor concentration gradient: vapor diffusional flow.
4) Pressure difference: liquid or vapor flow.

As indicated by Harmathy (1969) three general theories have been proposed which describe internally controlled drying processes: the diffusion theory, the capillary flow theory and the evaporation-condensation theory. Harmathy (1969), Peck and Wasan (1974) and Rotstein et. al., (1974) cite several contributions to the development of the three theories, since the pioneer work of Lewis (1921), Buckingham (1907) and Gurr et. al., (1952) respectively.

In what follows the objective has not been to try to force the description of the phenomenon into one of the pre-established theories but to try to describe the characteristics of the porous structure and to discuss the kinetics of the water migration in order to propose a mathematical description of the process from a transport phenomena standpoint. The need to take into account the structure of the food as opposed to considering it as a homogeneous solid has been pointed out earlier (King, 1968).

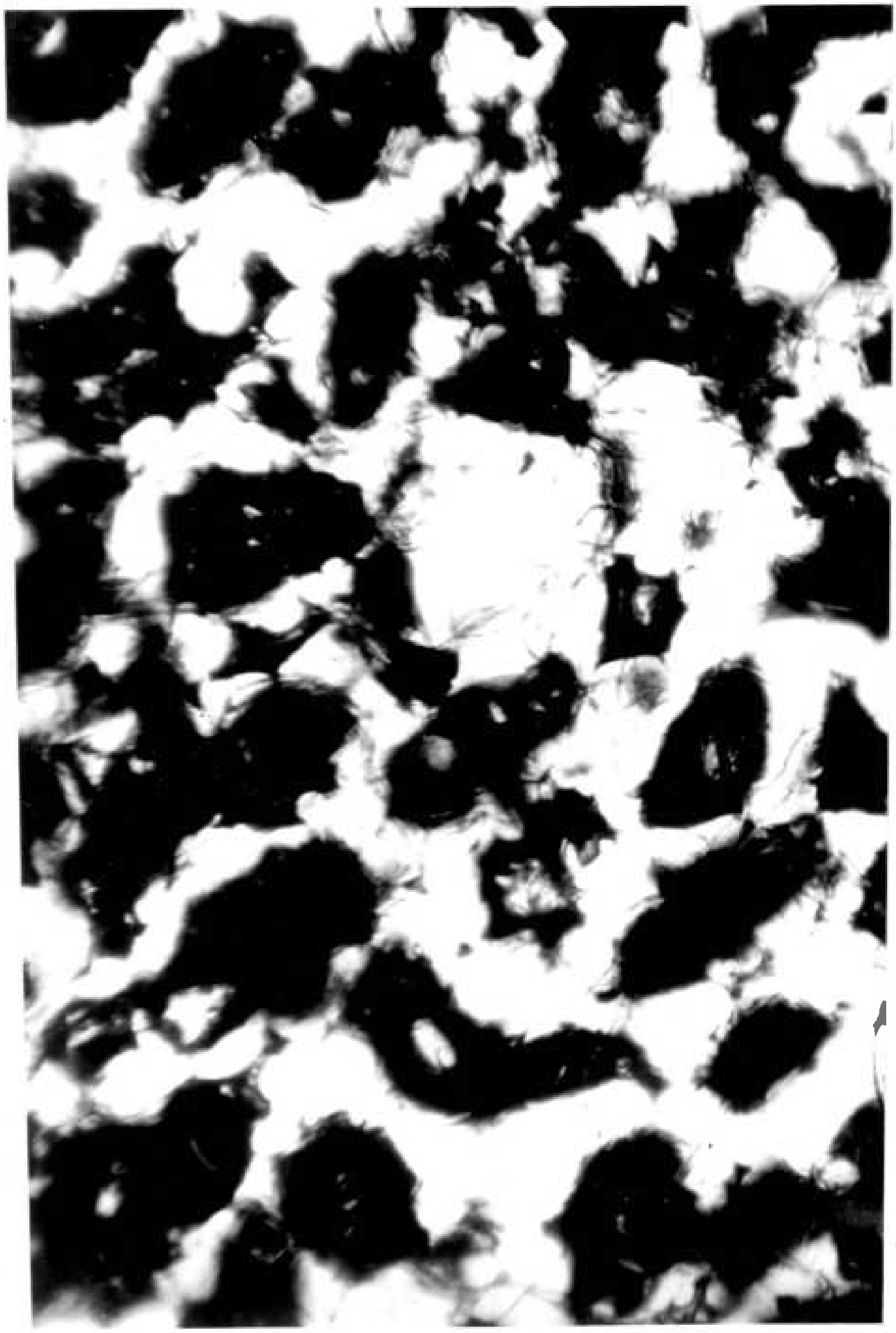
The internal structure of foodstuffs.

Foodstuffs are basically arrays of cells, in assemblages of what can be regarded as interwoven fibers. Although the cells are very similar in nature (see Chapter II), the tissues can differ widely in porosity and bulk physical properties. Thus, to test the proposed model it is necessary to concentrate on a specific foodstuff. The object of this study is to describe the process as it occurs in apples, hoping that the methodology and findings can be extended to other foodstuffs.

Figure 24 shows a microphotography of apply tissue. The most important feature has been pointed out by Reeve (1953): the porous structure is such that the intercellular spaces are large (average 541 x 275μ), interconnected and filled with air. This is to be

Figure 24

Photography of a microscopic observation of apple fruit tissue (tangential section).



expected on account of the osmometer-like behaviour of the cell. This is confirmed by Hardy (1949), Smith (1938), Skene (1966) and Slatyer (1967) as far as vegetable tissues are concerned.

The site of most of the water in the tissue is the cell (cf. page 84). Thus, the transport of water to the outside involves migration through the cell, its enveloping structure, through the porous-like structure of the tissue, and then through the outside boundary layer. As concluded earlier, the first two transfer stages are not the rate controlling steps.

The above leads to an outline of what appears to be a plausible description of the foodstuff structure, the controlling kinetic mechanism of water migration and the needed assumptions to model the process mathematically.

1) The apple tissue is regarded as a porous-like open structure. The 'solid' matrix is provided by cellular tissue, the voids are intercellular spaces.

2) The intercellular spaces are filled with air. They are large and interconnected. Initially, the temperature, humidity and pressure throughout the intercellular spaces are uniform and equal to the external conditions.

3) The intercellular air spaces define a uniform macro-porous structure.

4) Water is contained mainly in the cells. Practically all cells have part of their surface abutting onto an intercellular air space. (cf. page 84)

5) When the system is removed from equilibrium by changing the prevailing external conditions, the controlling internal water migration step is the flow of water vapour through the voids.

6) There is local equilibrium at each internal point. The local equilibrium conditions are predicted by an adequate sorption equilibrium expression.

7) The system can be defined as a quasi one phase system. Therefore it is possible to define 'effective' values of the mass diffusivity and thermal conductivity properties.

8) The process can be described as one of coupled heat and mass transfer. The water flows outwards as water vapour through a stagnant gas phase, the stagnant phase being dry air.

The mass transport equation.

The water continuity equation can be written (see Appendix A):

$$\frac{\partial \varepsilon \rho_{wv}}{\partial t} + \frac{\partial n}{\partial z} = -(1-\varepsilon)\rho_s \frac{\partial X}{\partial t} \qquad (119)$$

It should be noted that here the porosity refers to the air-filled voids while the water is contained inside the 'solid' matrix. The cells are, in effect, water reservoirs. This is a major departure from the conventional porous structures in which the water is external to the solid and the air space porosity is the difference between true porosity and the pore space occupied by water.

In equation (119) (see Appendix A),

$$\frac{\partial \varepsilon \rho_{wv}}{\partial t} = \frac{\varepsilon \rho_{wv} M_w}{RT^2} \left(T \frac{\partial y_{wv}}{\partial t} - y_{wv} \frac{\partial T}{\partial t} \right) \tag{120}$$

If the gas in the pores is assumed to be stagnant :

$$n = - \rho_g \frac{M_a M_w}{M(M - y_{wv} M_w)} \frac{\partial y_{wv}}{\partial z} \tag{121}$$

Thus, if the flow is considered to be one-dimensional:

$$\frac{\partial n}{\partial z} = - \frac{PM_w}{RT^2} \frac{D'}{(1-y_{wv})^2} \left[T(1-y_{wv}) \frac{\partial^2 y_{wv}}{\partial z^2} - T\left(\frac{\partial y_{wv}}{\partial z}\right)^2 - (1-y_{wv}) \frac{\partial y_{wv}}{\partial z} \frac{\partial T}{\partial z} \right] \tag{122}$$

The sorption equilibrium expression can be introduced

$$X = X(y_{wv},T) \tag{123}$$

Thus :

$$\frac{\partial X}{\partial t} = \left(\frac{\partial X}{\partial y_{wv}} \right)_T \frac{\partial y_{wv}}{\partial t} + \left(\frac{\partial X}{\partial T} \right)_{y_{wv}} \frac{\partial T}{\partial t} \tag{124}$$

Also:

$$\rho_{ps} = (1 - \varepsilon) \rho_s \tag{125}$$

From equations (120), (122), (124) and (125):

$$- D' \frac{1}{T(1-y_{wv})} \frac{\partial^2 y_{wv}}{\partial z^2} + D' \frac{1}{T(1-y_{wv})^2} \left(\frac{\partial y_{wv}}{\partial z}\right)^2 + D' \frac{1}{T^2(1-y_{wv})} \frac{\partial y_{wv}}{\partial z} . \frac{\partial T}{\partial z}$$

$$= \left[- \rho_{ps} \frac{R}{PM_w} \left(\frac{\partial X}{\partial y_{wv}}\right)_T - \frac{\varepsilon}{T}\right] \frac{\partial y_{wv}}{\partial t} + \left[\rho_{ps} \frac{R}{PM_w} \left(\frac{\partial X}{\partial T}\right)_{y_{wv}} + \varepsilon \frac{y_{wv}}{T^2} \frac{\partial T}{\partial t}\right] \tag{126}$$

The energy transport equation.

The general multicomponent energy transfer equation can be written as follows (Bird et. al., 1960):

$$\frac{\partial}{\partial t} \sum_i \gamma_i \hat{H}_i + \vec{\nabla} . \sum_i n_i \hat{H}_i = \vec{\nabla} . \, k \vec{\nabla} T + \frac{Dp}{Dt} - \underline{\tau} : \vec{\nabla} \hat{v} \tag{127}$$

where i indicates the components vapour, air, liquid and solid.

In the case under consideration the total pressure is constant and the $\underline{\tau}:\vec{\nabla}\vec{v}$ term, which measures the rate of irreversible conversion to internal energy, can be neglected.

The derivatives of the enthalpies of each of the constituents with time are as follows :

$$\frac{\partial \hat{H}_{wv}}{\partial t} = (\hat{c}_p)_{wv} \frac{\partial T}{\partial t} \tag{128}$$

$$\frac{\partial \hat{H}_a}{\partial t} = (\hat{c}_p)_a \frac{\partial T}{\partial t} \tag{129}$$

$$\frac{\partial \hat{H}_\ell}{\partial t} = (\hat{c}_p)_1 \frac{\partial T}{\partial t} - \left(\frac{\partial \Delta \hat{H}_{sp}}{\partial X}\right)_{P,T} \frac{\partial X}{\partial t} \qquad (130)$$

$$\frac{\partial \hat{H}_s}{\partial t} = (\hat{c}_p)s \frac{\partial T}{\partial t} \qquad (131)$$

The thermal conductivity is a function of the moisture content. Thus (see Appendix B):

$$\frac{\partial}{\partial y}\left(k \frac{\partial T}{\partial z} \right) = k \frac{\partial^2 T}{\partial z^2} + \frac{dk}{dX}\left(\frac{\partial X}{\partial y_{wv}}\right)_T \frac{\partial y_{wv}}{\partial z} \frac{\partial T}{\partial z} + \frac{dk}{dX}\left(\frac{\partial X}{\partial T}\right)_{y_{wv}} \left(\frac{\partial T}{\partial z}\right)^2$$

By evaluation of the products in the left hand side of equation (127) followed by substitution of equations (121), (124) and (128) through (132), into equation (127) the following final expression is obtained (see Appendix C);

$$\begin{aligned}
&\left\{ \frac{\varepsilon P}{R} M_w \frac{y_{wv}}{T} (\hat{c}_p)_v + \frac{\varepsilon P}{R} M_a \frac{(1-y_{wv})}{T} (\hat{c}_p)_a + X\rho_{ps}\left[-\left(\frac{\partial \Delta \hat{H}_{sp}}{\partial X}\right)_{P,T} \left(\frac{\partial X}{\partial T}\right)_{y_{wv}} + (\hat{c}_p)_i \right] + \right.\\
&\left. -\rho_{ps} \Delta \hat{H}_s \left(\frac{\partial X}{\partial T}\right)_{y_{wv}} + \rho_{ps} (\hat{c}_p)_s \right\} \frac{\partial T}{\partial t} - \left[X\rho_{ps}\left(\frac{\partial \Delta \hat{H}_{sp}}{\partial X}\right)_{P,T} \left(\frac{\partial X}{\partial y_{wv}}\right)_T + \Delta \hat{H}_{sp}\,\rho_{ps}\left(\frac{\partial X}{\partial y_{wv}}\right)_T \right] \frac{\partial y_v}{\partial t} \\
&= k \frac{\partial^2 T}{\partial z^2} + \frac{dk}{dX}\left(\frac{\partial X}{\partial T}\right)_{y_{wv}} \left(\frac{\partial T}{\partial z}\right)^2 + \left[(\hat{c}_p)_v \frac{P}{R} M_w \frac{D'}{T(1-y_{wv})} + \right.\\
&\left. + \frac{dk}{dX}\left(\frac{\partial X}{\partial y_{wv}}\right)_T \right] \frac{\partial y_{wv}}{\partial z} \cdot \frac{\partial T}{\partial z} \qquad (133)
\end{aligned}$$

Initial and boundary conditions.

The initial conditions are uniform temperature and moisture content throughout the sample, thus resulting in uniform values for y_{wv} (cf. equation (109)).

The heat and mass transfer boundary conditions are continuity in the fluxes at the interfaces. Thus :

$$T(z,0) = T_o \qquad 0 \leqslant z \leqslant L \tag{134}$$

$$X(z,0) = X_o \qquad 0 \leqslant z \leqslant L \tag{135}$$

$$y_{wv}(z,0) = (y_{wv})_o \tag{136}$$

$$q\Big|_{z=L} = -h\left[T(L,t) - T_\infty(t)\right] \tag{137}$$

$$n\Big|_{z=L} = M_w k_y \left[y_{wv}\ (L,t) - y_{wv\infty}(t)\right] \tag{138}$$

Solution of the problem

Equations (126) and (133) together with conditions (134) - (138) provide a system of two non linear partial differential equations involving two dependent variables, y_{wv} and T, which are function or position and time. From a solution of the system, temperature and water vapor concentration profiles can be obtained. By using an adequate expression for the sorption equilibrium relationship of equation (123), such as that developed previously (equation (74)), it is possible to express this variables in terms of moisture contents. The average of these moisture contents should provide a satisfactory simulation of the experimental data.

CHAPTER VI

NUMERICAL SOLUTION AND EXPERIMENTAL RESULTS

Numerical Solution.

Although equations (126) and (133) are non-linear second-order partial differential equations, it is possible to develop a relatively simple algorithm in order to solve the system.

To do so the following ideas are implemented:

1) The equations are written in terms of weight fractions and the convective term of the flux equation is not explicitly stated but is calculated separately using a guessed field which is then updated.

2) Non-linearities are accounted for by updating.

3) Integration is carried out over a control volume. This avoids the need for taking into account second order derivatives.

4) The time profile is selected so as to result in a fully implicit scheme.

5) The concentration profile follows a central differences scheme. The low flux values involved do not warrant the use of the so-called up-wind substitution schemes (Spalding, 1972).

6) The value of all coefficients is to be positive, the corresponding sign being included in the term.

The mass transfer equation is simply :

$$\frac{\partial(\varepsilon\rho_g\omega)}{\partial t} + \frac{\partial}{\partial z}(n\omega) = \frac{\partial}{\partial z}\left(\rho_g D' \frac{\partial\omega}{\partial z}\right) + \frac{\partial(-\rho_{ps}X)}{\partial t} \qquad (139)$$

by using the chain rule and rearranging equation (139) the following form is obtained :

$$Q_1 \frac{\partial\omega_v}{\partial t} + \frac{\partial}{\partial z}(n\omega) = \frac{\partial}{\partial z}\left(\rho_g D' \frac{\partial\omega}{\partial z}\right) + P_1 \frac{\partial T}{\partial t} \qquad (140)$$

where

$$Q_1 = \varepsilon\rho_g + \rho_{ps}\left(\frac{\partial X}{\partial\omega}\right)_T \qquad (141)$$

and

$$P_1 = -\rho_{ps}\left(\frac{\partial X}{\partial T}\right)_\omega \qquad (142)$$

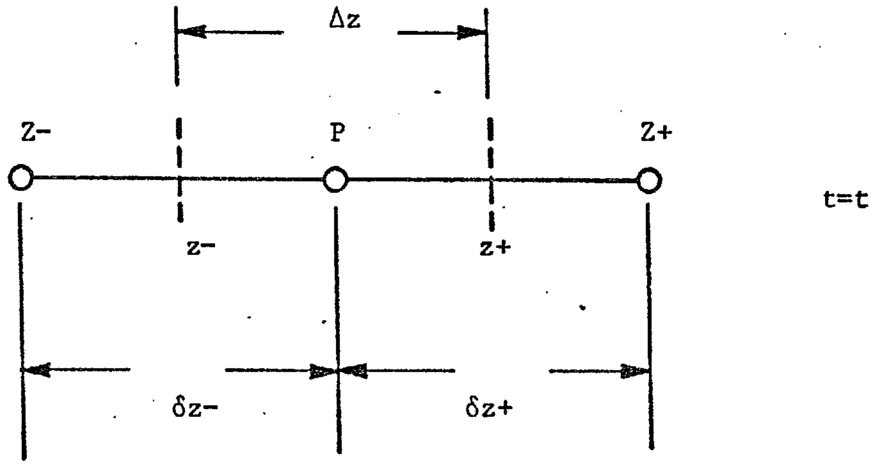
Each term can be integrated over the control volume defined by z-and z+ (figure 25), following the above outline.

$$\int_{z-}^{z+}\int_{t}^{t+\Delta t} Q_1 \frac{\partial\omega}{\partial t}\, dtdz = \Delta_z (Q^o{}_1)_P \left[(\omega)_P - (\omega)^o_P\right] \qquad (143)$$

$$\int_{z-}^{z+}\int_{t}^{t+\Delta t} \frac{\partial}{\partial z}(nW)\, dzdt = \Delta t\Big[n\omega\Big]_{z+} - \Delta t\Big[n\omega\Big]_{z-}$$

Figure 25

Control volume for the numerical solution



$$= \Delta t\,(n)_{z+}\ \frac{(\omega)_{z+} + (\omega)_P}{2} \;-\; \Delta t\,(n)_{z-}\ \frac{(\omega)_P + (\omega)_{z-}}{z} \qquad (144)$$

$$\int_{z-}^{z+}\int_{t}^{t+\Delta t} \frac{\partial}{\partial z}\left(\rho_g\ D'\ \frac{\partial \omega}{\partial z}\right) dzdt \;=\; \Delta t\ (\rho_g^o\ D')_P\ \frac{(\omega)_{z+} - (\omega)_P}{\delta z+}$$

$$-\ \Delta t\ (\rho_g^o\ D')_P\ \frac{(\omega)_P - (\omega)_{z-}}{\delta z-} \qquad (145)$$

$$\int_{z-}^{z+}\int_{t}^{t+\Delta t} P_1\ \frac{\partial T}{\partial t}\ dzdt \;=\; \Delta z\ (P_1^o)_P\ \ (T_P - T_P^o) \qquad (146)$$

By re-grouping coefficients and by singling out the variables at each point, equation (147) is obtained :

$$\left[\frac{n_{z+}}{z} - \frac{n_{z-}}{z} + \frac{\Delta z}{\Delta t}\,(Q^o{}_1)_P + \frac{\rho_g^o D'}{\delta z+} + \frac{\rho_g^o\ D'}{\delta z-}\right] \omega_P = \left(\frac{\rho_g^o D'}{\delta z-} - \frac{n_{z+}}{2}\right)\omega_{z+}$$

$$+\left(\frac{\rho_g^o D'}{\delta z-} + \frac{n_{z-}}{2}\right)\omega_{z-} + \left[\frac{\Delta z}{\Delta t}\ (P_1^o)_P\right] T_P + \left[\frac{\Delta z}{\Delta t}(Q_1^o)_P\ \omega_P^o - \frac{\Delta z}{\Delta t}\ (P_1^o)_P\ T_P^o\right]$$

$$(147)$$

In this case $\delta z+ = \delta z- = \Delta z$.

The integration is carried over a semi-infinite slab so that the leftmost point in the integration grid (i=1) corresponds to a nil vapour flux. The corresponding equation, by an analogous procedure to that used to obtain equation (147), is :

$$\left[\frac{n_{1\frac{1}{2}}}{2} + \frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(Q_1^o)_1 + \left(\frac{\rho_g^P D'}{\delta z+}\right)_{1\frac{1}{2}}\right]\omega_1 = \left[\left(\frac{\rho_g^o D'}{\delta z+}\right)_{1\frac{1}{2}} - \frac{n_{1\frac{1}{2}}}{2}\right]\omega_2 +$$

$$+\left[\frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(P_1^o)_1\right]T_1 + \left[\frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(Q_1^o)_1\,\omega_1^o - \frac{1}{2}\,\frac{\Delta z}{\Delta t}(P_1^o)_1\,T_1^o\right] \qquad (148)$$

Similarly the i=N mass boundary condition is :

$$\left[\frac{-(n)_{N-\frac{1}{2}}}{2} + \frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(Q_1^o)_N + \left(\frac{\rho_g^o D'}{\Delta z}\right)_{N-\frac{1}{2}} + K\right]\omega_N = \left[\frac{(n)_{N-\frac{1}{2}}}{z} + \left(\frac{\rho_g^o D'}{\Delta z}\right)_{N-\frac{1}{2}}\right]\omega_{N-1} +$$

$$+\left[\frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(P_1^o)_N\right]T_N + \left[\frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(Q_1^o)_N\,\omega_N^o - \frac{1}{2}\,\frac{\Delta z}{\Delta t}(P_1^o)_N\,T_N^o + K\omega_\infty\right]$$

(149)

An expression which is suitable for computation purposes is developed in Appendix D.

The energy equation can be treated in a way similar to the mass equation ;

$$\left[\varepsilon\rho_{wv}(\hat{c}_p)_{wv} + \varepsilon\rho_a(\hat{c}_p)_a + \rho_{ps}X(c_p)_1 + \rho_{ps}(\hat{c}_p)_s + \rho_{ps}(-\Delta\hat{H}_{sp})\left(\frac{\partial X}{\partial T}\right)_{\omega}\right]\frac{\partial T}{\partial t} +$$

$$+\left[(\hat{c}_p)_{wv}\, n\right]\frac{\partial T}{\partial z} + \left[\rho_{ps}\; (-\Delta\hat{H}_{sp})\;\left(\frac{\partial X}{\partial \omega}\right)_T\right]\frac{\partial \omega}{\partial t} = \frac{\partial}{\partial z}\left(k\;\frac{\partial T}{\partial z}\right)$$

$$\tag{150}$$

which can be written as

$$P_2\,\frac{\partial T}{\partial t} - Q_2\,\frac{\partial \omega}{\partial t} + (\hat{c}_p)_{wv}\, n\,\frac{\partial T}{\partial z} = \frac{\partial}{\partial z}\left(k\;\frac{\partial T}{\partial z}\right) \tag{151}$$

The negative sign of the Q_2 term is in agreement with rule number 6 above.

By integration over the control volume, again using a fully implicit time approach and a central differences scheme, equation (151) leads to equation (152)

$$\left[(\hat{c}_p)_{wv}\frac{n_{z+}}{2} - (\hat{c}_p)_{wv}\frac{n_{z-}}{2} + \frac{\Delta z}{\Delta t}(P_2^{o})_P + \left(\frac{k}{\Delta z}\right)_{z+} + \left(\frac{k}{\Delta z}\right)_{z-}\right]T_P = \left[\left(\frac{k}{\Delta z}\right)_{z+} - (\hat{c}_p)_{wv}\, n_{z+}\right]T_{z+}$$

$$+\left[\left(\frac{k}{\Delta z}\right)_{z-} + (\hat{c}_p)_{wv}\frac{n_{z-}}{2}\right]T_{z-} + \frac{\Delta z}{\Delta t}(Q_2^{o})_P\quad \omega_P + \left[-\frac{\Delta z}{\Delta t}(Q_2^{o})_P\,\omega_P^{o} +\right.$$

$$\left.+\frac{\Delta z}{\Delta t}(P_2^{o})_P\quad T_P^{o}\right] \tag{152}$$

The equations from the boundary conditions at i=1 and i=N are, respectively

$$\left[(\hat{c}_p)_{wv}\,\frac{n_{1\frac{1}{2}}}{2} + \frac{1}{2}\,\frac{\Delta z}{\Delta t}(P_2^o)_1 + \left(\frac{k}{\Delta z}\right)_{1\frac{1}{2}}\right] T_1 = \left[\left(\frac{k}{\Delta z}\right)_{1\frac{1}{2}} - (\hat{c}_p)_{wv}\,\frac{n_{1\frac{1}{2}}}{2}\right] T_2 +$$

$$+ \left[\frac{1}{2}\,\frac{\Delta z}{\Delta t}(Q_2)^o_1\right]\omega_1 + \left[\frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(P_2^o)_1\,T_1^o - \frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(Q_2^o)_1\,\omega_1^o\right] \qquad (153)$$

$$\left[(\hat{c}_p)_v\,n_n - (\hat{c}_p)_{wv}\,\frac{n_{N-\frac{1}{2}}}{2} + \frac{1}{2}\,\frac{\Delta z}{\Delta t}(P_2^o)_N + \left(\frac{k}{\Delta z}\right)_{N-\frac{1}{2}} + h\right] T_N = \left[\left(\frac{k}{\Delta z}\right)_{N-\frac{1}{2}}\right.$$

$$\left. + (\hat{c}_p)_{wv}\,\frac{n_{N-\frac{1}{2}}}{2}\right] T_{N-1} + \left[\frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(Q_2^o)_N\right]\omega_N$$

$$+ \left[\frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(P_2^o)_N\,T_N^o - \frac{1}{2}\,\frac{\Delta z}{\Delta t}\,(Q_2^o)_N\,\omega_N^o + h\,T_\infty\right] \qquad (154)$$

An expression which is suitable for computation purposes is developed in Appendix D.

Rule number one of the outlined procedure requires the separate calculation of the vapour flux. To do this equation (119) is used as the starting expression. By using the chain rule

$$\left[\varepsilon\rho_g + \rho_{ps}\left(\frac{\partial X}{\partial \omega}\right)_T\right]\frac{\partial \omega}{\partial t} + \frac{\partial n}{\partial z} = -\rho_{ps}\left(\frac{\partial X}{\partial T}\right)_\omega \frac{\partial T}{\partial t}$$

$$(155)$$

$$Q_1 \frac{\partial \omega}{\partial t} + \frac{\partial n}{\partial z} = P_1 \frac{\partial T}{\partial t} \qquad (156)$$

Integration is carried out as before and the equation for calculating the flux value to be used at the left-most control volume is :

$$n_{1\frac{1}{2}} = \left[- \frac{1}{2} \frac{\Delta z}{\Delta t} (Q_1^o)_1 \right] (\omega_1^* - \omega_1^o) + \left[\frac{1}{2} \frac{\Delta z}{\Delta t} (P_1^o)_1 \right] (T_1^* - T_1^o) \qquad (157)$$

at all other points

$$n_{z+} = n_{z-} + \left[\frac{\Delta z}{\Delta t} (P_1^o)_P \right] (T_P^* - T_P^o) - \left[\frac{\Delta z}{\Delta t} (Q_1)_P^o \right] (\omega_P^* - \omega_P^o) \qquad (158)$$

At the point N

$$n_N = K_W \; (\omega_N^o - \omega_\infty) \qquad (159)$$

The solution of the system of equations

The algorithm is implemented as follows :

Step 1) Set initial conditions.

Step 2) Find intermediate coefficients (P_1, P_2, Q_1, Q_2, etc).

Step 3) Find vapor flux and the coefficients involved in the energy and mass equations at point 1 ($z=0$).

Step 4) Repeat for all internal points.

Step 5) Repeat for point N ($z = L$).

Step 6) Solve for W and T at new time step. Mix the new values with W and T values obtained from the preceeding iteration step by means of a relaxation coefficient.

Step 7) Calculate X(I) and average X at new time step.

Step 8) Update from step 3 until convergence is obtained. The resulting W and T values are the solutions for the new time step.

Step 9) Proceed to the next time step starting from 2.

To obtain values of the intermediate coefficients as well as to calculate the new values of X (Steps 2 and 7) a subroutine based on equations (74), (75) and (77), was developed. This subroutine yields X(z) and the partial derivatives of X with respect to T and ω, when values of ω and T are given as data. The thermal conductivity was calculated using equation (105).

The solution was found to be very sensitive to slight changes in the variables, due to the fact that the equilibrium conditions are such that X changes enormously with small changes of ϕ , as indicated earlier. For that reason the solution is quite unstable and the way to implement a satisfactory and stable numerical simulation of the process is not to update the intermediate coefficients until a full cycle is over and to use a relaxation technique, mixing old and new values.

The selection of a suitable value of the relaxation coefficient is very important. Numerical experiments starting from full turgor, using the program shown in Appendix D, show that for $0.90 \leqslant \Omega \leqslant 0.975$

there is good convergence. When $\Omega = 0.85$ the fourth iteration at the first time step results in physically infeasible values of the variables, as shown in Table 18 for I=2. In turn, for $\phi > 1.0$ the iteration procedure to obtain x_w does not converge.

The convergence requirement for values of the weight fraction, ω, at each iteration was that the difference between successive values should be smaller than 10^{-6}.

The results are shown in figure 27.

TABLE 18

Values of ω and T when Ω = 0.85

I	ω	T, ^{o}C	ϕ
1	0.0583	45.1	0.95
2	0.0845	46.7	1.26
3	0.0306	55.4	0.30

Experimental

In order to test the accuracy of the numerical procedure, the results obtained were compared with experimental data which had been previously obtained by the author at Planta Piloto de Ingenieria Quimica, Universidad Nacional del Sur, Bahia Blanca, Argentina. The equipment used was a drier which allowed a continuous measure and record of the weight loss. This was accomplished by hooking the drying chamber to a torquemeter. A suitable damper avoids oscillation of the system. The air inlet and outlet pipes are assembled so as not to disrupt the equilibrium of the weighing system. Figure 26 presents a complete outline of the equipment.

Granny Smith apples were selected, washed, peeled and sliced into parallelpipeds of 2.4 x 2.4 x 1.2 cm. They were sulfited by exposure to SO_2 and dried in air at 76°C dry bulb temperature, with a relative humidity of 10% and a velocity of 10 m/s. Fourteen replications of the experiment were made, in order to insure reproducibility.

The experimental results are plotted in Figure 27 and compared with data obtained from the numerical solution.

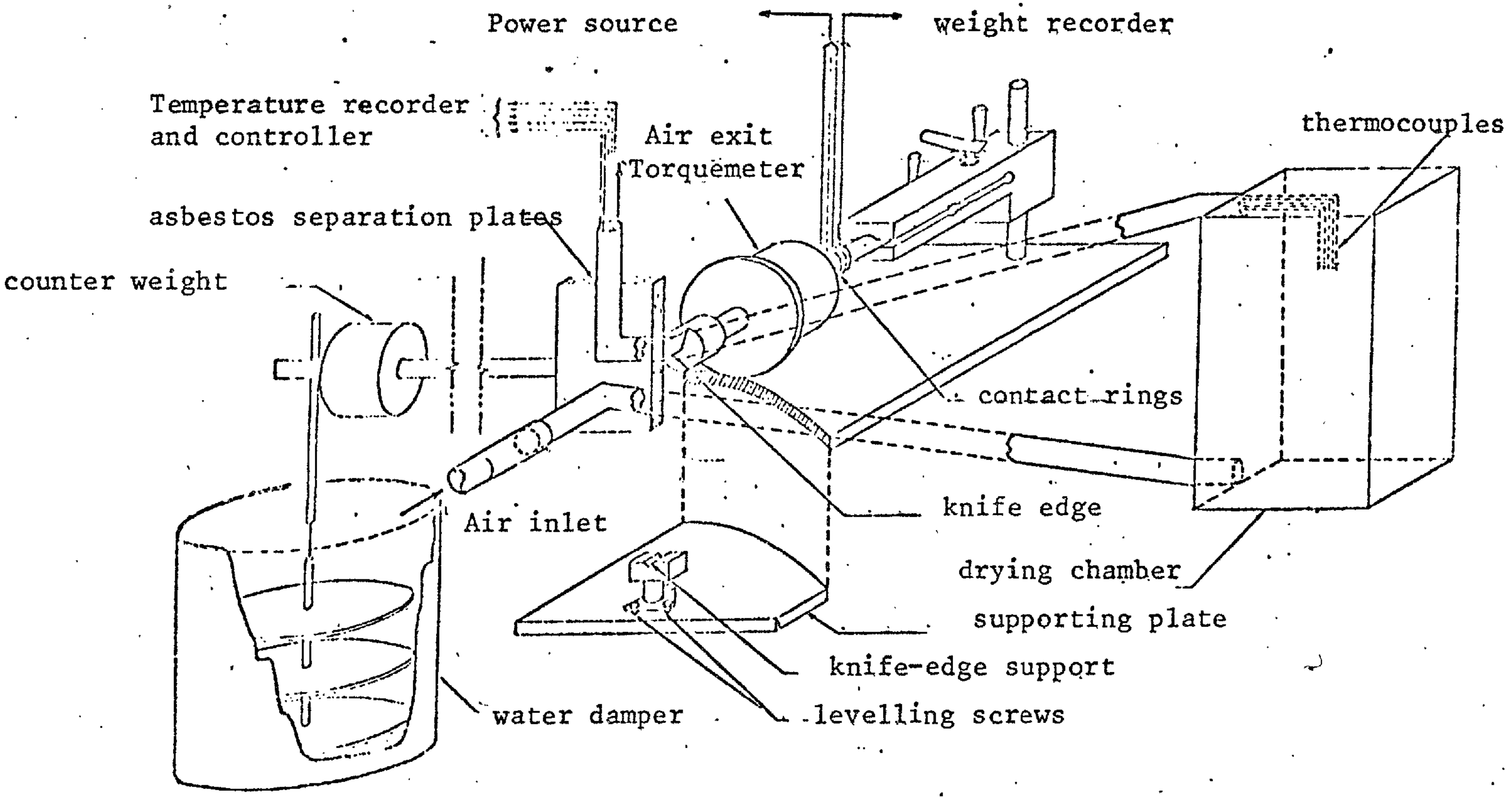
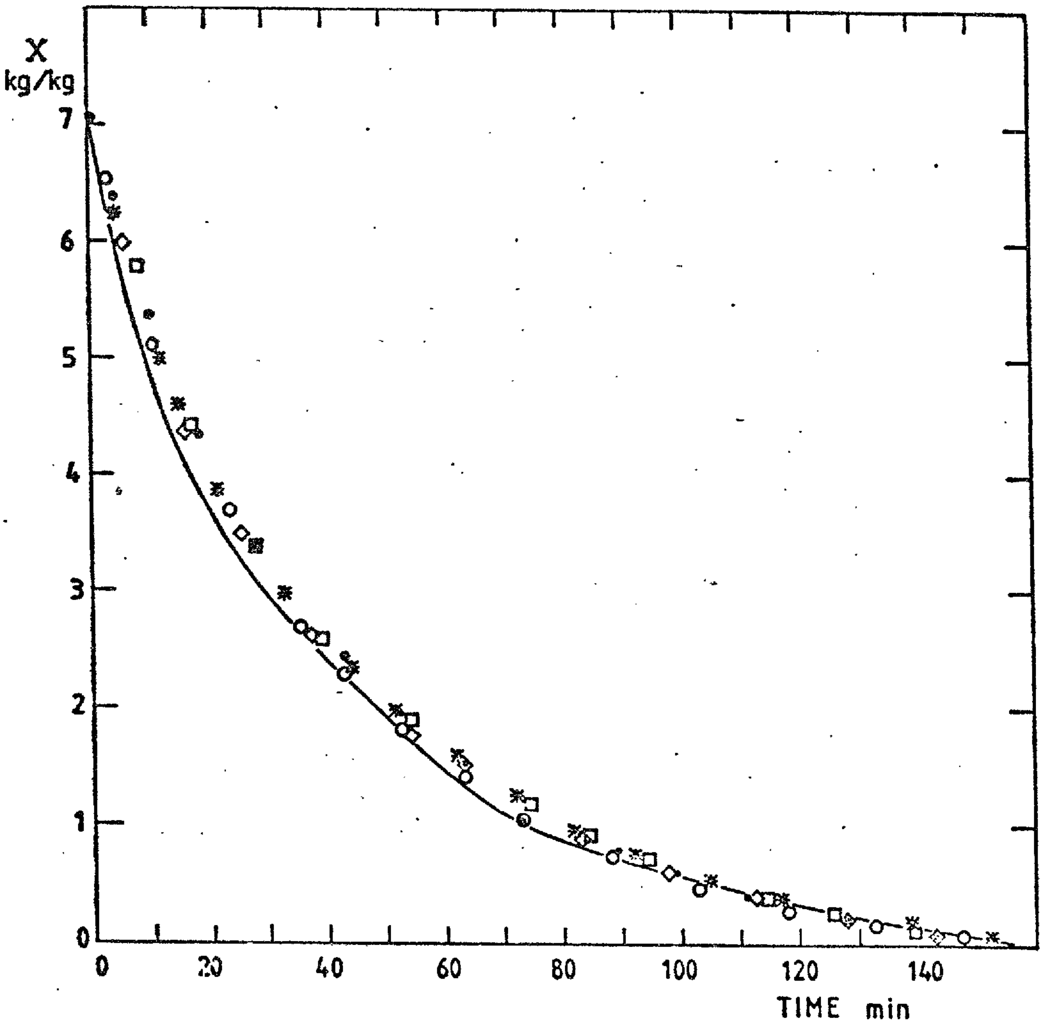


Figure 26

Experimental drying equipment.

FIGURE 27

Predicted and experimental moisture contents.



CHAPTER VII

DISCUSSION AND CONCLUSIONS

From Figure 27 it can be seen that the numerical procedure results in a good simulation of the experimental drying data. This is true even at very low moisture contents, well beyond the X = 0.32 kg/kg commercial limit. This can be taken as an indication that the assumptions made in Chapter VI, on which basis the process was modelled, may be substantially true.

On the other hand care must be exercised because the comparison has been made on the basis of average moisture contents. If experimental data on temperature and moisture profiles throughout the solid had been available they may or may not have been in agreement with the profiles predicted by the model. Experimental profiles are very difficult to obtain because of the characteristics of the material involved.

It is reasonable to conclude that the procedure described in this work simulates the actual drying performance of apples. The approach has incorporated steps that could be followed when the dehydration of other foodstuffs is studied. These are : a) devise an adequate model of the structure of the tissue; b) base the prediction of transport properties on such a model ; c) give due consideration to the role of porosity in influencing transport properties on behaviour. As pointed out in this work, data are scarce on transport properties of foodstuffs and the data that have been reported do not state the porosity of the samples. It is possible that porosity and the transport properties could provide a means of systematizing the description of the drying behaviour of foodstuffs; d) analyze the relative contribution of cellular permeability to the rate of drying; e) use an equilibrium relationship in order to couple adequately the energy and mass transport equations. An equilibrium expression for sugar based foodstuffs has been developed in this work.

APPENDICES

APPENDIX A

THE WATER CONTINUITY EQUATION

Figure 28 illustrates a cross section of cellular tissue of thickness Δz, made up of cells and intercellular air spaces. The flux of vapour is assumed to be one-dimensional.

A shell mass balance results in :

$$\Delta x\ \Delta y\ \left(n\Big|_{z} - n\Big|_{z+\Delta z}\right) = \frac{\partial M}{\partial t}\ \Delta x\ \Delta y\ \Delta z \tag{160}$$

where

$$M = \varepsilon\rho_{wv} + (1-\varepsilon)\ \rho_s\ X \tag{161}$$

In the limit as Δz approaches zero equation (160) becomes :

$$-\frac{\partial n}{\partial z} = \frac{\partial \varepsilon\rho_{wv}}{\partial t} + \frac{\partial(1-\varepsilon)\rho_s X}{\partial t} \tag{162}$$

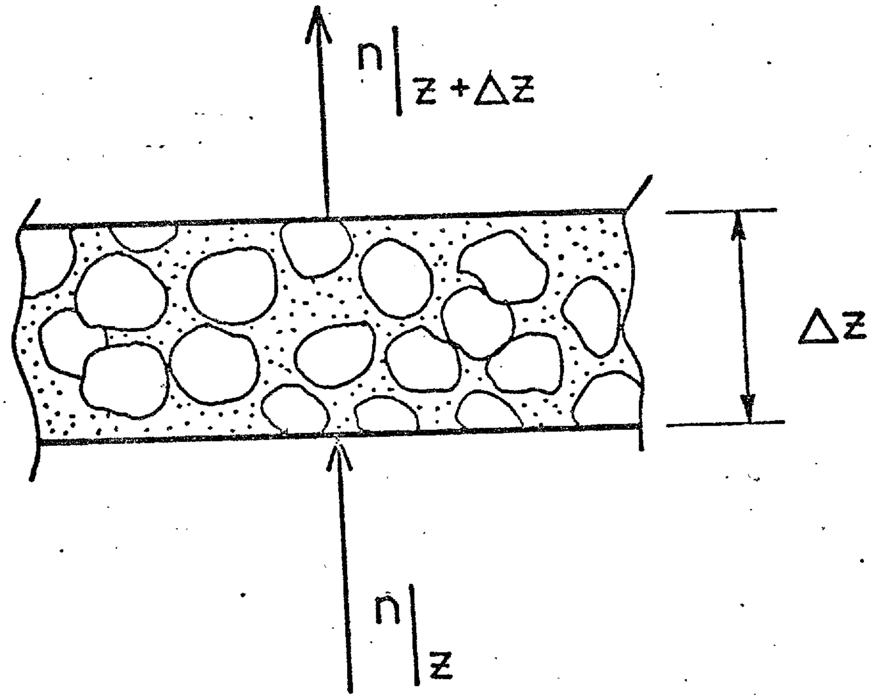
If the product $\rho_s(1-\varepsilon)$ is regarded as constant, equation (162) can be written :

$$\frac{\partial \varepsilon\rho_{wv}}{\partial t} + \frac{\partial n}{\partial z} = -(1-\varepsilon)\ \rho_s\ \frac{\partial X}{\partial t} \tag{163}$$

(equation (119) in the text).

FIGURE 28

Water continuity: a cross section of cellular tissue.



Assuming that the vapour behaves as an ideal gas, a reasonable assumption since drying is normally carried out at atmospheric or lower pressures, the water vapour density can be expressed as :

$$\rho_{wv} = y_{wv} \frac{PM_w}{RT} \qquad (164)$$

thus, at constant ε:

$$\frac{\partial \varepsilon \rho_{wv}}{\partial t} = \frac{\varepsilon \rho_{wv} M_w}{T^2} \left(T \frac{\partial y_{wv}}{\partial t} - y_{wv} \frac{\partial T}{\partial t} \right) \qquad (165)$$

Equation (165) is the same as equation (120) in the text.

APPENDIX B

THE HEAT CONDUCTION TERM IN THE ENERGY EQUATION

As indicated in Chapter IV, the thermal conductivity of a foodstuff depends strongly on its moisture content. Thus :

$$k = k(X) \tag{166}$$

The heat conduction term can be written :

$$\frac{\partial}{\partial z}\left(k\,\frac{\partial T}{\partial z}\right) = k\,\frac{\partial^2 T}{\partial z^2} + \frac{\partial T}{\partial z}\;\frac{\partial k}{\partial z} \tag{167}$$

Taking into account equation (166):

$$\begin{aligned}\frac{\partial k}{\partial z} &= \frac{\partial k}{\partial X}\;\frac{\partial X}{\partial z}\\ &= \frac{\partial k}{\partial X}\left[\left(\frac{\partial X}{\partial y_{wv}}\right)_T \frac{\partial y_{wv}}{\partial z} + \left(\frac{\partial X}{\partial T}\right)_{y_{wv}} \frac{\partial T}{\partial z}\right]\end{aligned} \tag{168}$$

As a result of equation (168), the heat conduction term can be represented by equation (169):

$$\begin{aligned}\frac{\partial}{\partial z}\left(k\,\frac{\partial T}{\partial z}\right) = k\,\frac{\partial^2 T}{\partial z^2} &+ \frac{\partial k}{\partial X}\left(\frac{\partial X}{\partial y_{wv}}\right)_T \frac{\partial y_{wv}}{\partial z}\;\frac{\partial T}{\partial z} +\\ &+ \frac{\partial k}{\partial X}\left(\frac{\partial X}{\partial T}\right)_{y_{wv}} \left(\frac{\partial T}{\partial z}\right)^2\end{aligned} \tag{169}$$

(Equation (132) in the text).

APPENDIX C

THE ENERGY TRANSFER EQUATION

From equation (127) in the text, for the case when p is constant ($\frac{Dp}{Dt} = 0$) and $\underline{\tau} : \vec{\nabla}\vec{v}$ negligible, it follows :

$$\frac{\partial}{\partial t}(\Sigma\gamma_i\hat{H}_i) + \vec{\nabla}.\Sigma\ \vec{n}_i\hat{H}_i = \vec{\nabla}.k\ \vec{\nabla}T \tag{170}$$

Where γ_i is the concentration of each constituent. In turn :

$$\frac{\partial(\Sigma\,\gamma_i\hat{H}_i)}{\partial t} = \sum\left(\gamma_i\ \frac{\partial\hat{H}_i}{\partial t} + \hat{H}_i\ \frac{\partial\gamma_i}{\partial t}\right) \tag{171}$$

Also:

$$\vec{\nabla}.\ \Sigma\ \vec{n}_i\hat{H}_i = \sum \hat{H}_i\ \vec{\nabla}.\ \vec{n}_i + \vec{n}_i.\ \vec{\nabla}\hat{H}_i \tag{172}$$

Equation (130) can be written

$$\frac{\partial\hat{H}_i}{\partial t} = (\hat{c})_{p_1}\ \frac{\partial T}{\partial t} - \left(\frac{\partial\Delta\hat{H}_{sp}}{\partial X}\right)_{P,T}\left(\frac{\partial X}{\partial y_{wv}}\right)_T \frac{\partial y_{wv}}{\partial t} - \left(\frac{\partial\Delta\hat{H}_{sp}}{\partial X}\right)_{P,T}\left(\frac{\partial X}{\partial T}\right)_{y_{wv}} \frac{\partial T}{\partial t} \tag{173}$$

On rearrangement :

$$\frac{\partial \hat{H}_l}{\partial t} = \left[(\hat{c}_p)_l - \left(\frac{\partial \Delta\hat{H}_{sp}}{\partial X}\right)_{P,T} \left(\frac{\partial X}{\partial T}\right)_{y_{wv}} \right] \frac{\partial T}{\partial t} - \left(\frac{\partial \Delta\hat{H}_{sp}}{\partial X}\right)_{P,T} \left(\frac{\partial X}{\partial y_{wv}}\right)_T \frac{\partial y_{wv}}{\partial t} \tag{174}$$

Taking into account the continuity equation (equation (119)) and equation (124):

$$\frac{\partial \gamma_v}{\partial t} = -\ (1-\varepsilon)\ \rho_s \left(\frac{\partial X}{\partial y_{wv}}\right)_T \frac{\partial y_{wv}}{\partial t} - (1-\varepsilon)\ \rho_s \left(\frac{\partial X}{\partial T}\right)_{y_{wv}} \frac{\partial T}{\partial t} - \vec{\nabla} \cdot \vec{n} \tag{175}$$

The liquid concentration is :

$$\gamma_l = X\ (1-\varepsilon)\ \rho_s = X\ \gamma_s \tag{176}$$

Thus,

$$\frac{\partial \gamma_l}{\partial t} = \gamma_s \frac{\partial X}{\partial t} = \gamma_s \left(\frac{\partial X}{\partial y_{wv}}\right)_T \frac{\partial y_{wv}}{\partial t} + \gamma_s \left(\frac{\partial X}{\partial T}\right)_{y_{wv}} \frac{\partial T}{\partial t} \tag{177}$$

Within the range of commercial drying,

$$\frac{\partial \gamma_s}{\partial t} \simeq 0 \tag{178}$$

Taking into account equations (171) and (172), equation (170) can be written:

$$\Sigma\gamma_i \frac{\partial \hat{H}_i}{\partial t} + \Sigma\hat{H}_i\left(\frac{\partial \gamma_i}{\partial t} + \vec{\nabla}.\vec{n}_i\right) + \Sigma\ \vec{n}_i.\vec{\nabla}\hat{H}_i - \vec{\nabla}.k\vec{\nabla}T = 0 \qquad (179)$$

By the use of equations (128) through (131) equations (173), (176), (175), the continuity equations and the definitions of enthalpy of each constituent, equation (179) can be expanded into the following form :

$$\gamma_{wv}(\hat{c}_p)_{wv}\frac{\partial T}{\partial t} + \gamma_a(\hat{c}_p)_a\frac{\partial T}{\partial t} + \gamma_s X\left[(\hat{c}_p)_l - \left(\frac{\partial \Delta\hat{H}_{sp}}{\partial X}\right)_{P,T}\left(\frac{\partial X}{\partial T}\right)_{y_{wv}}\right]\frac{\partial T}{\partial t} -$$

$$- \gamma_s X\left(\frac{\partial \Delta\hat{H}_{sp}}{\partial X}\right)_{P,T}\left(\frac{\partial X}{\partial y_{wv}}\right)_T\frac{\partial y_{wv}}{\partial t} + \gamma_s(\hat{c}_p)_s\frac{\partial T}{\partial t} +$$

$$+ \hat{H}_v\left[-(1-\varepsilon)\rho_s\left(\frac{\partial X}{\partial y_{wv}}\right)_T\frac{\partial y_{wv}}{\partial t} - (1-\varepsilon)\rho_s\left(\frac{\partial X}{\partial T}\right)_{y_{wv}}\frac{\partial T}{\partial t}\right] + \hat{H}_l\gamma_s\left(\frac{\partial X}{\partial y_{wv}}\right)_T\frac{\partial y_{wv}}{\partial t} +$$

$$+ \hat{H}_l\gamma_s\left(\frac{\partial X}{\partial T}\right)_{y_{wv}}\frac{\partial T}{\partial t} + \vec{n}.\ \vec{\nabla}(\hat{c}_p)_{wv}T = \vec{\nabla}.k\vec{\nabla}T \qquad (180)$$

By definition:

$$\Delta\hat{H}_{sp} = \hat{H}_{wv} - \hat{H}_l \qquad (181)$$

From equation (121) for constant vapour specific heat ;

$$\vec{n}.\vec{\nabla}(\hat{c}_p)_{wv}\,T = -(\hat{c}_p)_{wv}\,\rho_g\,\frac{M_w D'}{M(1-y_{wv})}\,\vec{\nabla}y_{wv}.\vec{\nabla}T \tag{182}$$

Equation (121), (164), (132) and (182) can be combined with equation (180), to give the following expression for an undimensional system:

$$\Big\{\frac{\varepsilon p}{R} M_w\, y_{wv}(\hat{c}_p)_{wv} + \frac{\varepsilon p}{R} M_a\,\frac{(1-y_{wv})}{T}\,(\hat{c}_p)_a + X\gamma_s\Big[(\hat{c}_p)_l - \Big(\frac{\partial \Delta\hat{H}_{sp}}{\partial X}\Big)_{P,T}\Big(\frac{\partial X}{\partial T}\Big)_{y_{wv}}\Big]$$

$$-\gamma_s\,\Delta\hat{H}_{sp}\Big(\frac{\partial X}{\partial T}\Big)_{y_{wv}} + \gamma_s(\hat{c}_p)_s\Big\}\frac{\partial T}{\partial t} - \Big[X\gamma_s\Big(\frac{\partial \Delta\hat{H}_{sp}}{\partial X}\Big)_{P,T}\Big(\frac{\partial X}{\partial y_{wv}}\Big)_T +$$

$$+\Delta\hat{H}_{sp}\,\gamma_s\Big(\frac{\partial X}{\partial y_{wv}}\Big)_T\Big]\frac{\partial y_{wv}}{\partial t} = k\frac{\partial^2 T}{\partial z^2} + \frac{\partial k}{\partial X}\Big(\frac{\partial X}{\partial T}\Big)_{y_{wv}}\Big(\frac{\partial T}{\partial z}\Big)^2 +$$

$$+\Big[(\hat{c}_p)_v\,\frac{pM_w}{R}\,\frac{D'}{T(1-y_{wv})} + \frac{\partial k}{\partial X}\Big(\frac{\partial X}{\partial y_{wv}}\Big)_T\Big]\frac{\partial y_{wv}}{\partial z}\cdot\frac{\partial T}{\partial z} \tag{183}$$

equation (183) is equation (133) in the text where γ_s in equation (183) has been replaced by the symbol ρ_{ps}.

APPENDIX D

IMPLEMENTATION OF THE NUMERICAL SOLUTION

The mass transport equation.

Equation (147) provides a recurrence formula which may be used to calculate at all points but the boundaries the relationships between weight fractions and temperatures that result from the mass transfer equation. At the boundaries these relationships are calculated using equations (148) and (149).

The analogous equation for computing purposes is obtained by splitting the total length of the semi-infinite slab from z=o to z = L into N-1 equal parts, designating the points thus created by I (from I=1 to I=N) , and defining :

$$AW(I) = \frac{n_{z+}}{2} - \frac{n_{z-}}{2} + \frac{\Delta z}{\Delta t}(Q_1^o)_p + \frac{\rho_g^o D'}{\delta z+} + \frac{\rho_g^o D'}{\delta z-} \tag{184}$$

$$W(I) = \omega_p \tag{185}$$

$$AWP(I) = \left(\frac{\rho_g^o D'}{\delta z-} - \frac{n_{z+}}{2}\right)\omega_{z+} \tag{186}$$

$$W(I+1) = \omega_{z+} \tag{187}$$

$$AWM(I) = \frac{\rho_g^o D'}{\delta z-} + \frac{n_{z-}}{2} \tag{188}$$

$$W(I-1) = \omega_{z-} \tag{189}$$

$$AWT(I) = \frac{\Delta z}{\Delta t} (P^{o}_{1})_{p} \tag{190}$$

$$T(I) = T_{p} \tag{191}$$

$$BW(I) = \frac{\Delta z}{\Delta t} (Q^{o}_{1})_{p} \quad \omega^{o}_{p} - \frac{\Delta z}{\Delta t} (P^{o}_{1})_{p} \quad T_{p}^{\,o} \tag{192}$$

By comparing with equations (148) and (149) it is clear that :

$$AWM(1) = 0 \tag{193}$$

$$AWP(N) = 0 \tag{194}$$

Thus, the equation which represents equations (147) through (149) for computational purposes is :

$$AW(I)*\omega(I) = AWP(I) *\omega(I+1)+AWM(I)*\omega(I-1)+$$

$$+ AWT(I)*T(I) + BW(I) \tag{195}$$

The energy transfer equations (152), (153) and (154) can be obtained in a similar way. The coefficients and variables are defined for the same grid as :

$$AT(I) = (\hat{c}_{p})_{wv} \frac{n_{z+}}{2} - (\hat{c}_{p})_{wv} \frac{n_{z-}}{2} + \frac{\Delta z}{\Delta t} (P^{o}_{2})_{p} + \left(\frac{k}{\Delta z} \right)_{z+} +$$

$$+ \left(\frac{k}{\Delta z} \right)_{z-} \tag{196}$$

$$T(I) = T_{p} \tag{197}$$

$$ATP(I) = \left(\frac{k}{\Delta z} \right)_{z+} - (\hat{c}_{p})_{wv} \; n_{z+} \tag{198}$$

$$\mathrm{T(I+1)} \; = \; T_{z+} \qquad (199)$$

$$\mathrm{ATM(I)} \; = \left(\frac{k}{\Delta z}\right)_{z-} + \; (\hat{c}_p)_{wv} \; \frac{n_{z-}}{2} \qquad (200)$$

$$\mathrm{T(I-1)} \; = \; T_{z-} \qquad (201)$$

$$\mathrm{ATW(I)} \; = \; \frac{\Delta z}{\Delta t} \; (Q_2^o)_p \qquad (202)$$

$$\mathrm{BT(I)} \; = \; - \; \frac{\Delta z}{\Delta t} \; (Q_2^o)_p \; \omega_p^o \; + \; \frac{\Delta z}{\Delta t} \; (P_2^o)_p \; T_P^o \qquad (203)$$

Thus the energy equation for computational purposes is :

$$\mathrm{AT(I)*T(I) = ATP(I)*T(I+1)+ATM(I)*T(I-1)} \; +$$

$$+ \; \mathrm{ATW(I)*W(I)} \; + \; \mathrm{BT(I)} \qquad (204)$$

requiring in the case of equations (153) and (154) that :

$$\mathrm{ATM(I)} \; = \; 0 \qquad (205)$$

$$\mathrm{ATP(N)} \; = \; 0 \qquad (206)$$

respectively.

The computer program listed in figure 29 was written in order to solve equations (195) and (204).

FIGURE 29

The main computer program.

```
        M3BGUA     M3BGUA                          *** IMPERIAL COLLEGE COMPUTER CENTRE ***


UCENUMBER UU        UU  MM      MM  EEEEEEEE   CCCCCC    CCCCCC    333333    222222  UMECC32
UCENUMBER UU        UU  MMM    MMM  EEEEEEEE  CCCCCCCC  CCCCCCCC  33333333  22222222 UMECC32
UCENUMBER UU        UU  MM M  M MM  EE        CC    CC  CC    CC        33        22 UMECC32
UCENUMBER UU        UU  MM  MM  MM  EE        CC        CC              33        22 UMECC32
UCENUMBER UU        UU  MM  MM  MM  EE        CC        CC             33        22  UMECC32
UCENUMBER UU        UU  MM      MM  EEEEEE    CC        CC           3333       22   UMECC32
UCENUMBER UU        UU  MM      MM  EEEEEE    CC        CC           3333      22    UMECC32
UCENUMBER UU        UU  MM      MM  EE        CC        CC             33     22     UMECC32
UCENUMBER UU        UU  MM      MM  EE        CC        CC              33   22      UMECC32
UCENUMBER UU        UU  MM      MM  EE        CC    CC  CC    CC        33  22       UMECC32
UCENUMBER UUUUUUUU UU   MM      MM  EEEEEEEE  CCCCCCCC  CCCCCCCC  33333333 22222222  UMECC32
UCENUMBER  UUUUUU       MM      MM  EEEEEEEE   CCCCCC    CCCCCC    333333  22222222  UMECC32
                    ********************************************************************
                    *                          IMPERIAL COLLEGE COMPUTER CENTRE   -   NOS 1.1
                    *        N - 012                                                   77/10/2
                    *
                    *
                    *
                    *
                    *
                    ********************************************************************




76/08/17   IMPERIAL  COLLEGE  FORTRAN  COMPILER        KRONOS  2.1.X  PSR2+    77/11/02. 1
          MNF(L=2,5)
 0000003        1.           PROGRAM ISA (INPUT,OUTPUT, TAPE6=OUTPUT)
                      C              STAGNANT PHASE MODEL
                      C              EFFECTIVE DIFFUSIVITY AND CONDUCTIVITY AS WELL AS HEAT
                      C              AND MASS TRANSFER COEFFICIENTS ARE REGARDED AS CONSTANT
                      C              INITIAL TEMPERATURE AND MOISTURE CONTENT ARE UNIFORM
                      C              BECAUSE OF SIMPSON, N MUST BE ODD IF IT STARTS FROM 1
                      C              THICK IS HALF THICKNESS
                      C        ..................................................
                      C
```

```
                C        MY OWN EQUILIBRIUM EXPRESSION
                C
                C        ...................................................
                C
                C        XNINITL= 7.     ,     HR= 10  0/0
                C
                C        ...................................................
0040408               COMMON / VAR/ W(11) , T (11), AW (50), AWP (50), AWM (50), AWT (50)
                     1, BW(50) , AT (50), ATP (50), ATM (50), ATW (50), BT (50), N,FW(50
                     2), GW(50), RW(50), C(50), PT(50), CT(50), RT(50), E(50), G(50)
0040409               DIMENSION  WO (50 ), TO (50 ) , C1 ( 50 ) , X ( 11 ) , F2 ( 50 )
                     1, VN (5  ) , DIGL (50 ), DXOT (50), DXOW (50), P1(50), C2(50)
                     2, FI(50), FOI(50)
0040403               DIMENSION SMALLL ( 50 ) , EFCOND ( 50 )
0040408               DIMENSION WOS(11), TOS(11)
0040408               DOUBLE PRECISION W, T, AW, AWP, AWM, AWT, BW, AT, ATP, ATM, ATW,BT
                     1,    WO, TO, C1, X, F2, VN, DIGL, SMALLL, DXOT, DXOW, P1, C2, FI,
                     2FOI, WINITL, FINITL, TINITL, EFCOND, DELTAZ, ROPS, DELTAH, EPS,
                     3ROGAS, CPV, CPA, CPL, CPS, TRCOEF, H, TOUTER, WOUTER, ROS, C, E, A
                     4, B, D, DF1, Y, ROG , DELTAT, EFDIF
0040408               DOUBLE PRECISION PT , CT, RT, FW, GW, RW, C, E, G

0040408               DOUBLE PRECISION OMEGA
0040409               DOUBLE PRECISION CONDK
0040418               DOUBLE PRECISION WLAST, TLAST
0040419               DOUBLE PRECISION U
0040418               DOUBLE PRECISION WOS, TOS
                C               DEFINE FUNCTIONS
0040403               DF1( D, E) = EPS * D + (1.D0- EPS) * ROS * E
0070548               Y(A)= A*2.8852D01/(A*1.0336D01 + 1.8016D01)
0071003               ROG(B, D)= (1.8016D01 * B + 2.8852D01 * (1.D0 - B)) / (8.2057D01 *
                     1( D + 2.73D02))
0071419               CONDK(U)= .2302183D-03 * U ** .6431648+2D0
0071528               READ 100, ROS, EPS, EFDIF,          DELTAH, CPV  , CPA  , CPL  , CP
                     1S  , WINITL, TINITL, WOUTER, TOUTER, TRCOEF, H, THICK, DELTAZ,
                     2DELTAT, N, JFREQ, MXTIME, ITMAX, CONSTK, VALUEN, FINITL
0072059               PRINT 101, ROS, EPS, EFDIF,          DELTAH, CPV  , CPA  , CPL  ,
                     1CPS  , WINITL, TINITL, WOUTER, TOUTER, TRCOEF, H,THICK , DELTAZ,
                     2DELTAT, N , JFREQ, MXTIME, ITMAX, CONSTK, VALUEN, FINITL
                C              INITIALIZE WEIGHT FRACTIONS AND TEMPERATURES
0072429               DO 2 I= 1, N
0072448               WO(I)= WINITL
0072458               FOI(I)= FINITL
0072503             2 TO (I) = TINITL
0072559               J = 0
0072563               TIME = 0.
0072578            99 J = J+1
0072613               TIME = TIME + DELTAT / 3.6D03
                C              NEW VALUES EQUAL OLD ONES FOR FIRST GUESS AT NEW TIME STEP
0072723               DO 3 I= 1, N
0072733               W (I) = WO (I)
0072778               FI(I)= FOI(I)
0073028             3 T (I) = TO (I)
0073113               WLAST= 0.D0
0073119               K = 1
                C              FIND CONSTANT AND VARIABLE INTERMEDIATE COEFFICIENTS
0073123               ROPS= ROS *(1.D0-EPS)
0073228               DO 9 I= 1, N
0073248               WOS(I)= WINITL
0073253               TOS(I)= TINITL
0073313             9 CALL XCALCD( W(I), T(I), X(I), DXOT(I), DXOW (I), FI (I) )
0073478               DO 8 I= 1, N
0073518               EFCOND(I)= CONDK ( X (I ))
0073548             8 SMALLL(I)= EFCOND (I) / DELTAZ
0073578            77 DO 1 I = 1, N
0073718               ROGAS=ROG(Y( W(I)), T (I))
0074023               C2(I)=ROPS* DELTAH *DXOT(I)*DELTAZ / DELTAT
0074218               F2 (I)  =(EPS * ROGAS *( W(I)  * CPV+(1.D0- W (I) ) * CPA)+ ROPS *
                     1( X (I)  * CPL + CPS  - DELTAH*DXOT(I)))* DELTAZ / DELTAT
0075218            34 P1(I)=(-ROPS)*DXOT(I)*DELTAZ / DELTAT
0075419               ROGAS=ROG(Y( W(I)), T (I))
0075549               C1 (I)  =DF1(ROGAS,DXOW(I) )*DELTAZ / DELTAT
0075718             1 DIGL (I)  = ROGAS * EFDIF / DELTAZ
```

```
                     C                 FIND VAPOR FLOW AND COEFFICIENTS AT POINT 1
0076133      49.        55 VI (1) = - Q1(1) *(W(1) - WO (1)) /2.D0+P1(1)*( T(1) - TO(1)) / 2
                          1.D0
0076433      50.           AW (1) = ( VN(1) + Q1 (1)) /2.D0+ BIGL (1)
0076519      51.           AWP (1) = BIGL (1) - VI (1)
0076553      52.           AWM ( 1 ) = 0.
0076579      53.           AWT (1)= P1(1) / 2.D0
0076633      54.           EW (1) = ( Q1 (1) * WO (1)-P1(1)* TO (1))  / 2.D0
0077019      55.           AT (1) = ( CPV * VN (1) + P2(1))  /2.D0+ SMALLL(1).
0077153      56.           ATP (1) =SMALLL(1)-CPV * VN (1) / 2.D0
0077253      57.           ATM ( 1 ) = 0.
0077303      58.           ATW (1) =Q2(1)/ 2.D0
0077333      59.           ET (1) = ( P2 (1) * TO (1)-Q2(1)* WO (1)) / 2.D0
                     C                 FIND VAPOR FLOW AND COEFFICIENTS AT ALL INTERNAL POINTS
0077519      60.           M = N - 1
0077533      61.           DO 4 I = 2, M
0077553      62.           VI (I) = VN (I - 1) +P1(I)* ( T (I) - TO (I)) - Q1 (I) * ( W (I) -
                          1WO (I))
0100139      63.           AW (I) = ( VN(I) - VN (I-1)) /2.D0+ Q1 (I) + BIGL (I) + BIGL (I-1
0100329      64.           AWP (I) = BIGL (I) - VN (I) / 2.D0
0100419      65.           AWM (I) = BIGL (I - 1) + VN ( I-1) / 2.D0
0100519      66.           AWT (I) = P1(I)
0100543      67.           EW (I) = Q1 (I) * WO (I)-P1(I) * TO (I)
0100743      68.           AT (I) = CPV * (VN (I) - VN (I-1)) /2.D0+ P2 (I)+2.D0* SMALLL(I)
0101219      69.           ATP (I) =SMALLL(I)- CPV * VN (I )     / 2.D0
0101343      70.           ATM (I) =SMALLL(I)+ CPV * VN(I - 1) / 2.D0
0101473      71.           ATW (I) = Q2(I)
0101523      72.         4 ET (I) =-Q2(I)* WO (I) + P2 (I) * TO (I)
                     C                 FIND VAPOR FLOW AND COEFFICIENTS AT OUTER END
0101733      73.           VN(N)= TRCOEF * ( W ( N ) - WOUTER)
0102039      74.           AW(N) =(- VN(N-1) + Q1 (N))/2.D0+ BIGL (N-1) + TRCOEF
0102229      75.           AWP ( N ) = 0.
0102245      76.           AWM (N) = VN (N-1) /2.D0+ BIGL (N-1)
0102349      77.           AWT (N) =P1(N)/ 2.D0
0102433      78.           EW (N) = ( Q1 (N) * WO (N)-P1(N)* TO (N)) /2.D0+ TRCOEF * WOUTER
0102718      79.           AT (N) = CPV * ( VN (N) - VN (N-1)/2.D0)+SMALLL(N)+H+ P2(N) / 2.D
0103229      80.           ATP ( N ) = 0.
0103253      81.           ATM (N) =SMALLL(N)+ CPV * VN(N-1) / 2.D0
0103419      82.           ATW (N) =Q2(N)/ 2.D0
0103443      83.           ET (N) = ( P2 (N) * TO (N)-Q2(N)* WO (N)) /2.D0+ H * TOUTER
                     C                 COMPUTE NEW WEIGHT FRACTIONS, TEMPERATURES AND AVERAGE
                     C                 MOISTURE CONTENT
0103759      84.           CALL SOLV
0104019      85.           OMEGA= .37500
0104028      86.           DO 5 I = 1, N
0104359      87.           W(I)= OMEGA * WOS(I) + ( 1.D0 - OMEGA) * W(I)
0104269      88.           T(I)= OMEGA * TOS(I) + (1.D0 - OMEGA) * T(I)
0104319      89.           WOS(I)= W(I)
0104543      90.           TOS(I)= T(I)
0104573      91.         5 CALL XCALC( W(I), T(I), X(I), DXDT(I), DXDW (I), FI (I) )
0104753      92.           SEMIL= N - 1
0104769      93.           XAVGE = SIMPSN ( N, 1., X ) / SEMIL
                     C                 WRITE RESULTS IF APPROPRIATE, TEST NUMBER OF ITERATIONS
0105033      94.           IF ( ( W (3 ) - WLAST ). LT. 1.D-06 ) GO TO 6
0105139      95.           WLAST= W(3)
0105138      96.        96 K = K + 1
0105173      97.           IF ( K - ITMAX) 55, 55, 73
0105218      98.         6 IF ((J/ JFREQ) * JFREQ . NE . J ) GO TO 73
0105253      99.           PRINT *, 'K= ', K, '     TIME= ', TIME,'      XAVGE=', XAVGE
0105428     100.           PRINT 103, W
0105503     101.           PRINT 104, T
0105509     102.           PRINT 105, X
                     C                 SEE IF TIME IS UP
0105649     103.        73 IF ( TIME - MXTIME) 87, 87, 98
0105673     104.        87 DO 7 I = 1, N
0105713     105.           WO (I) = W(I)
0105713     106.         7 TO (I) = T(I)
0105743     107.           GO TO 99
0106019     108.       100 FORMAT ( 3 ( 6X,D11.4 / ),                  6X, D 15.8 /  4( 6X, D13.
                          1/),       6X,D15.8/3( 6X,I11.4/), 6X, D 10.3 / 6X, D10.3 / 3 ( 6X,D
                          2D.3/) , ( 6X, I3 / ) ,    6X, E12.5/ 6X, F7.5/6X,D16.9/)
0106013     109.       101 FORMAT ( ' STAGNANT PHASE MODEL'/3X'ROS      = ', F8.4 / 3X, 'EPS
                          1 =   ', F8.4 / 3X, 'EFIEF    = ', F8.4 /
                          2/ 3X, 'DELTAH =   ', F 9.5 / 3X, 'CPV      = ', F10.6 / 3X, 'CPA
                          3=  ', F10.5 / 3X, 'CPL      =  ', F10.6 / 3X, 'CPS      =  ', F10.6
```

```
                             *8X, ' WINITL =    ', F8.4 / 8X, 'TINITL =   ', F6.2 / 8X, 'WOUTFP =
                             5', F8.4 / 8X, 'TOUTFP =   ', F6.2 /  8X, 'TRCOEF =   ', D11.3 / 8X,
                             6'H        =   ', D11.3 /  8X, 'THICK  =   ',F7.3 / 8X, 'DELTAZ =   ',
                             7F7.3 / 8X, 'DELTAT =   ', F7.3 / 8X, 'N         =   ', I3 / 8X, 'JFREQ
                             8 =   ', I3 / 8X, 'IXTIME =   ', I3 / 8X, 'ITMAX   =   ', I3 / 8X, 'CC
                             9NSTK =      ',D12.3/8X,'VALUEN =        ',F7.3/8X,'FINITL =   ',F8.4/)
0106019    110.    103 FORMAT(3X,'W(I)= ',    11(D11.4     ) / )
0106019    111.    104 FORMAT(3X,'T(I)= ',     11(D11.4     ) / )
0106019    112.    105 FORMAT(3X,'X(I)= ',    11(D11.4     ) / )
0106019    113.    200 FORMAT ( 3X, ' TIME, HEI', , 4X, ' K ' , 4X, ' XAVGE ' /)
0106019    114.    201 FORMAT ( 11X,F9.3,8X, I1, 5X, F8.3//)
0106019    115.    202 FORMAT ( 5X, ' I POINT', 4X, ' W(I) ', 5X. ' T(I) ',8X, ' V(I) ',
                       12X, 'X(I) ' 8X, 'DXDTD(I) ', 8X, 'DXDWD(I) '//)
0106019    116.    203 FORMAT ( 3X,'I', 5X , D10.3,6X,D10.3, 5X, D9.2, 5X, D10.3,5X, D10.3
                       1, 3X, D10.3 / 5X, 'K', 3X, D10.3, 6X, D10.3, 5X, D9.2, 5X, D10.3,
                       23X, D10.3, 3X, D10.3 / )
0106015    117.     83 STOP
                 C
0106019    117.        END
```

Subroutine SOLVE

The algorithm results in a sparse 2N x 2N matrix, as shown in Figure 30. The system lends itself to a back substitution procedure, which has been implemented as a subroutine (Subroutine SOLVE, figure 31).

Subroutine XCALCD

Every time a new set of weight fractions and temperatures is established, there is need for new values of the moisture content and its partial derivatives with respect to temperature and weight fraction to be obtained.

To do this, use is made of equation (74). This requires calculation of the water vapour activity through the following expression :

$$\phi = \frac{p\,M_a\,\omega}{p_W\left[\,M_W + \omega(M_a - M_w)\,\right]} \qquad (207)$$

From equations (68) and (74) it can be seen that it is not possible to obtain the water mole fraction explicitly. Thus, Newton's method was used to obtain its value. With this value and equation (71), the moisture content was obtained.

The water vapour pressure at each temperature is calculated by means of Goff's correlation (Goff, 1957). The derivatives are obtained numerically.

With the above elements, subroutine XCALCD was written (Figure 32). This subroutine uses values of weight fraction and temperature to

Figure 30

Sketch of the algorithm matrix when N=4.

W(1)	W(2)	W(3)	W(4)	T(1)	T(2)	T(3)	T(4)	B
1	1			1				1
1	1	1			1			1
	1	1	1			1		1
		1	1				1	1
1				1	1			1
	1			1	1	1		1
		1			1	1	1	1
			1			1	1	1

NOTES: 1 indicates non-null terms

blank indicates null terms.

Figure 31

Subroutine SOLVE.

```
000000B         SUBROUTINE SOLVE
000000B         COMMON / VAR/ W(50), T (50), AW (50), AWP (50), AWM (50), AWT (50)
               1, BW(50) , AT (50), ATP (50), ATM (50), ATW (50), BT (50), N,PW(50
               2), QW(50), RW(50), D(50), PT(50), QT(50), RT(50), E(50), G(50)
000000B         DOUBLE PRECISION W, T, AW, AWP, AWM, AWT, BW, AT, ATP, ATM, ATW,BT
000000B         DOUBLE PRECISION PT, QT, RT, PW, QW, RW, D, E, G
000000B         PW(1) = AWP(1) / AW(1)
000006B         QW(1) = BW(1) / AW(1)
000014B         RW(1) = AWT(1) / AW(1)
000023B         D(1)=AT(1)- ATW(1) * RW(1)
000033B         PT(1) = ATP(1) / D(1)
000041B         QT(1) = ( AT(1) + ATW(1) * QW(1)) / D(1)
000057B         RT(1) = ATW(1) * PW(1) / D(1)
000071B         DO 10 I= 2,N
000075B         E(I)=AW(I)- AWP(I) + PW(I - 1) - AWM(I) * RW(I - 1) * RT(I - 1 )
000122B         PW(I) = AWP(I) /E(I)
000131B         QW(I) = ( BW(I) + AWM(I) * QW(I -1)  + AWM(I) * RW(I-1) * QT (I -
               1I )) / E(I)
000166B         RW(I) = ( AWT(I) + AWM(I) * RW(I - 1 ) * PT(I - 1 ))/ E(I)
000211B         G(I)=ATP(I)* RT ( I - 1 ) + ATW (I)
000223B         D(I)=AT(I) - ATM (I) * PT ( I - 1 ) - RW (I) * G(I)
000246B         PT (I) = ATP (I) / D(I)
000255B         QT (I) = ( AT (I) + ATM (I) * QT (I-1 ) + QW (I) * G(I)) / D (I)
```

```
000306B     124.        PT (I) = PW (I) * C(I) / B(I)
000321B     125.     10 CONTINUE
000324B     126.        T (N + 1 ) = 0.
000324B     127.        W ( N + 1) = 0.
000326B     128.        DO 20 II = 1, N
000331B     129.        I = 1 + N - II
000332B     130.        T(I) = PT (I) * T ( I + 1 ) + QT ( I ) + RT (I ) * W ( I + 1 )
000355B     131.        W (I) = PW (I) * W ( I + 1 ) + QW ( I ) + RW (I) * T (I)
000377B     132.     20 CONTINUE
000402B     133.        RETURN
                   C
000404B     134.        END
```

Figure 32

Subroutine XCALCD.

```
000000B        SUBROUTINE XCALCD(WTFRAC, TEMP, X, DXDT, DXDW, FI )
         C
         C              BASED ON OUR EQUILIBRIUM RELATIONSHIP
         C
         C              NUMERICALLY CALCULATED DERIVATIVES
         C
         C              SATURATED VAPOR PRESSURE FROM GOFF' S CORRELATION
         C
         C
000000B        DOUBLE PRECISION WTFRAC, TEMP, X, DXDT, DXDW ,TRATIO, A1, A2, C,
              1D, E, F, H, A3, A4, RESULT, SATVP, WTMOLA, WTMOLW, DEN, Y, FI,
              2WDEN, XW, EPSCON, A, FXW, FXWDER, ALFA, XNEXT, COEF, WTFOLD,ADTEMP
000000B        KEY= 0
000066B     66 TRATIO=2.7316D02/( TEMP + 2.7316D02)
000077B        A1=1.079574D01*(1.D0- TRATIO)
000107B        A2=5.028D0 * DLOG10 (TRATIO)
000115B        C= 1.50475 D-4
000117B        D= - 8.2969D0
000122B        E= 4.76955D0
000124B        F= 2.2195768D0
000127B        H= 4.2873D-4
000131B        A3= C *(1.D0-1.D01**( D *(1.D0 / TRATIO -1.D0)))
000166B        A4= H * (1.D01** ( E *(1.D0-TRATIO)) - 1.D0)
000203B        RESULT= A1 + A2 + A3 + A4 - F
000223B        SATVP=1.D01** RESULT
000227B        WTMOLA= 2.8952D01
000231B        WTMOLW= 1.8016D01
000234B     88 DEN= WTFRAC *1.0936D01+WTMOLW
000244B        Y= WTMOLA * WTFRAC / DEN
000256B        FI=       Y / SATVP
         C
         C
         C              ENTERS OUR CORRELATION
         C
         C              XW IS FOUND BY ITERATION USING NEWTON'S RULE
         C
         C              ITERATION STARTS WITH FI AS INITIAL GUESS FOR XW
         C
         C
000264B        XW= FI
000266B        EPSCON= 1.D-07
000270B        K=0
000271B        ITMAX= 25
000273B        A= 1.2744659D0 - 6.354403713D02 / ( TEMP + 2.7316D02 )
000311B        DO 1 K= 1, ITMAX
```

```
000314B      161.        FXW= XW * 1.001 ** ( A * ( 1.D0 - XW ) ** 2 ) - F1
000337B      162.        IF (DABS (FXW) . LE . EPSCON ) GO TO 2
000346B      163.        FXWDER= 1.001 ** ( A * ( 1.D0 - XW ) ** 2 ) * ( 1.D0-2.D0* A * ( 1
                       1.D0 - XW ) * XW * DLOG ( 1.001 ))
000412B      164.        IK= K
000413B      165.      1 XW= XW - FXW / FXWDER
000432B      166.      2 ALFA= .76D-01
000434B      167.        IF( KEY. EQ. 1 ) GO TO 7
000437B      168.        IF( KEY. EQ. 2 ) GO TO 6
000440B      169.        X= ALFA * XW / ( 1.D0 - XW )
000456B      170.        KEY= KEY + 1
000460B      171.        COEF= .9999975D0
000463B      172.        WTFOLD= WTFRAC
000465B      173.        WTFRAC= WTFRAC * COEF
000471B      174.        GO TO 88
000472B      175.      7 XNEXT= ALFA * XW / ( 1.D0 - XW )
000510B      176.        DXDW=  ( XNEXT - X ) / ( WTFRAC - WTFOLD )
000530B      177.        KEY= KEY + 1
000532B      178.        ADTEMP= .1D-01
000535B      179.        TEMP= TEMP + ADTEMP
000541B      180.        WTFRAC= WTFOLD
000544B      181.        GO TO 66
000545B      182.      6 XNEXT= ALFA * XW / ( 1.D0 - XW )
000563B      183.        DXDT= ( XNEXT - X ) / ADTEMP
000575B      184.        TEMP= TEMP - ADTEMP
000602B      185.        RETURN
000605B      186.        END
NUMBER AND NAME CROSS REFERENCE MAP (N= N  REFERENCES IN STATEMENT)
```

obtain moisture content and water vapour activity equilibrium values as well as the derivatives referred to above.

Once the moisture contents at each point were found, the average moisture content for the time in question was obtained using Simpson's rule.

APPENDIX E

Publications

The following publications are based on material presented on this work:

1) Prediction of the Sorptional Equilibrium Relationship for the Drying of Foodstuffs. Enrique Rotstein and Alan R.H. Cornish. Proceedings of the Second Pacific Chemical Engineering Congress, Denver, Colorado, U.S.A. (1977).

2) Influence of Cellular Membrane Permeability or Drying Behaviour. Enrique Rotstein and Alan R.H. Cornish. Accepted for publication by Journal of Food Science.

PREDICTION OF THE SORPTIONAL EQUILIBRIUM RELATIONSHIP FOR THE DRYING OF FOODSTUFFS

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** Imperial College of Science and Technology, London, England

Abstract

The numerical solution of food drying problems usually involves coupling the energy and mass transfer equations through sorptional equilibrium relationships. Existing relationships are reviewed critically and a new one is proposed based on the equilibrium of the tissue, regarded as a set of cells, with its surroundings. The behavior of the new relationship over the entire moisture content is shown to be a good representation of the equilibrium properties of sugar-containing foodstuffs, and to yield well behaved analytical expressions for its derivatives with respect to temperature and water vapour activity.

NOMENCLATURE

A = constant, equation (26)
$\hat{a}_w$ = activity of water in solution
a_1, a_2 = constants, equations (11) and (10)
B, B_1, B_2, b = constants, equations (12), (6), (9) and (12)
C, C_1, c = constants, equations (6), (7) and (5)
c_s = solute concentration, Kg/m^3
D = constant, equation (7)
d = mass of dry matter, kg
H = enthalpy, J
k, k_1, k_2 = constants, equations (8) and (4)
ℓ = constant, equation (28)
M = molecular weight, kg/kmol
m_j = sugar component weight, kg
n = constant, equation (8)
n_m = number of moles of insoluble material
n_s = number of moles of solute
o = reference state
P = pressure, N/m^2
p = constant, equation (28)
q = constant, equation (6)
R = universal gas constant, J/mol ^oK
r_1 = constant, equation (10)
r^2 = square or regression coefficient
$\bar{S}_w$ = partial molar entropy of water, J/mol
T = temperature, ^oK
T_c = temperature, ^oC
T_R = temperature, ^oR
$\bar{V}_w$ = partial molar volume of water, m^3/mol
X = moisture content, kg/kg
X_I, X_{II} = moisture content in lineal and non lineal region respectively, kg/kg
X_ℓ, X_m = constants, equations (12) and (5)
x_w = water mole fraction

Greek letters

α = constant, equation (34)
β = constant, equation (35)
γ = activity coefficient
$\Delta\psi$ = $\psi - \psi_\ell$
θ = water volumetric content, m^3/m^3
κ = constant, equation (9)
μ = chemical potential, J/mol
ξ = constant, equation (9)
π = osmotic pressure, N/m
ψ = water vapor activity
χ = constant, equation (25)
ψ_m = matric potential, N/m

INTRODUCTION

The drying of foodstuffs is a problem of coupled heat and mass transfer. Mathematical modelling results in a set of coupled partial differential equations. The coupling equation, equation (1), is the equilibrium relationship which at the prevailing temperature relates the water content of the food to the moisture content of the surrounding air.

$$X = X(\psi, T) \qquad (1)$$

In addition the following derivatives of equation (1) are required

$$\left(\frac{\partial X}{\partial T}\right)_\psi = f_T(\psi, T) \qquad (2)$$

$$\left(\frac{\partial X}{\partial \psi}\right)_T = f_\psi(\psi, T) \qquad (3)$$

Applications of equations (1) to (3) extend beyond air drying to packaging, conservation, cold storage, controlled atmosphere storage, as well as to alternative dehydration processes. The differences lie in the magnitudes of the variables (X, ψ, T) as well as in the extent of changes in them.

REVIEW OF EXISTING EQUILIBRIUM RELATIONSHIPS

Equations of the form of (1), (2) and (3) have been obtained either by the use of theoretical expressions developed for the adsorption of gas molecules over non-volatile solid surfaces or by

Submitted through The Second Pacific Chemical Engineering Congress (Pachec '77)

means of empirical equations fitted to experimental data.

Equations that are applicable to foodstuffs are listed in table I (equations (4) to (12)). Their applicability has been tested against experimental data for the specific case of apples. Several authors have reported sorption equilibrium data for apples (Wolf [10], Taylor [11], Gane [12], Saravacos [13]) but only Filonenko and Chuprin [9] have reported data for desorption from fresh apples. Their data were used together with unpublished suplementary data obtained by one of the authors [E.R.] using the chamber method (Labuza [14]). When appropriate, a least squares linear regression procedure was used to obtain the parameter values reported in table I.

Table I

Earlier Equilibrium Expressions

References	Equation
Langmuir [1,2]	$X = \frac{k_1 k_2 \psi}{1 + k_2 \psi}$ (4) $k_1 = 0.076$ $k_2 = 14.293$
Brunauer et al. [3]	$\frac{\psi}{X(1-\psi)} = \frac{1}{X_m c} + \frac{c-1}{X_m c}\psi$ (5) $X_m = 0.05094$ Kg/Kg $c = 31.15873$
Rounsley [4]	$\frac{\psi(1-\psi^q)}{X(1-\psi)} = \frac{1}{B_1 C} + \frac{C-1}{B_1 C}\psi$ (6)
Harkins and Jura [5]	$\ln \psi = D - \frac{C_1}{X^2}$ (7)
Henderson [6]	$-\ln(1-\psi) = kT_R(100X)^n$ (8) $k = 1.3949 \times 10^{-4}$ $n = 0.86532$
Kuhn [7]	$X = \kappa \frac{1}{(-\ln\psi)^{\xi}} - B_2$ (9) $\xi = 0.9971$ $B_2 = 0.0003$ $\kappa = 0.0971$
Halsey [8]	$\ln \psi = -\frac{a_1}{RT}\left(\frac{X}{X_m}\right)^{-r_1}$ (10) $\frac{a_1}{RT} = 2.3858$ $r = 0.9530$
Filonenko and Chuprin [9]	$X_I = \frac{a_2 + \psi}{k}$ (11) $X_{II} = \frac{B(\psi - \psi_\ell)}{b - (\psi - \psi_\ell)} + X_\ell$ (12)

Note: parameter values are for apples at 293 °K.

It can be seen that Langmuir's equation and the B.E.T. equation provide an acceptable prediction for $\psi < 0.3$ (Figures 1 and 2). Outside of that range the actual moisture content is significantly higher than predicted. For the same reason the Rounsley equation cannot be used and a comparison with cellulose equilibrium data (Rounsley [4]) shows that only at low activities does the behavior approach that of conventional adsorption (Figure 3). A plot of the form proposed by Harkins and Jura (Figure 4) can be used only in a very restricted range of moisture content. As $\psi \to 1$, equation (4) and (12) under-

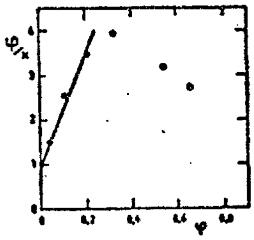
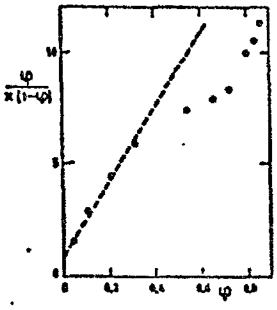


Figure 1. Langmuir equation.

Figure 2. BET equation



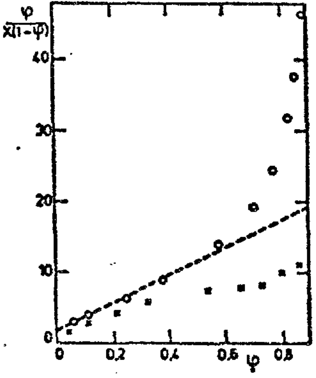
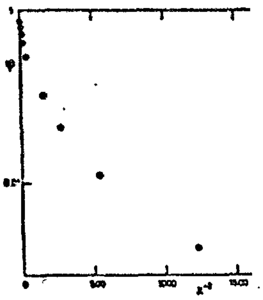


Figure 3. Rounsley equation.

- ● Apples, 293°K
- ✕ Cellulose, 293°K

Figure 4. Harkins and Jura equation.



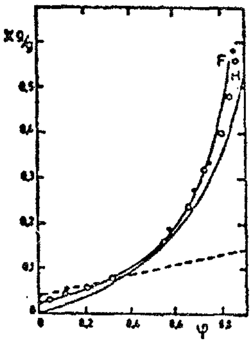


Figure 5. Filonenko and Chuprin's (F) and Henderson's (H) equations.

- ----- equation (11)
- \+ experimental data
- o Filonenko and Chuprin [9] experimental data.

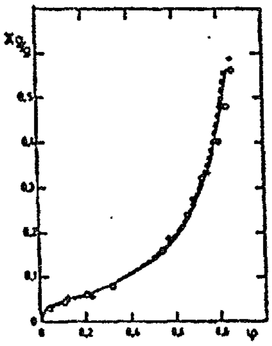


Figure 6. Kuhn's (---) and Halsey's (——) isotherms.

- \+ experimental data
- • Filonenko and Chuprin [9] experimental data.

predict the full turgor moisture content, while the B.E.T., Henderson, Kuhn and Halsey expressions predict an infinite moisture content. Aside from this unrealistic behaviour, equations (8), (9), (10) and (12) provide an acceptable fit of the experimental data for 0.03 < X < 0.50 kg/kg (Figures 5 and 6).

The derivatives $\left(\frac{\partial X}{\partial \psi}\right)_T$ and $\left(\frac{\partial X}{\partial T}\right)_\psi$

Expressions for the derivative $\left(\frac{\partial X}{\partial \psi}\right)_T$ are listed for each of the above equations in table II.

Analytical expressions for the derivative $\left(\frac{\partial X}{\partial T}\right)_\psi$ can only be obtained from Henderson's and Filonen and Chuprin's expressions. The resulting equations are also given in table II. To obtain the derivative $\left(\frac{\partial X}{\partial T}\right)_\psi$ for the other equations it would be necessary to obtain correlations of the parameters as a function of temperature. At present insufficient data are available for this purpose. Tables III and IV give numerical value of the derivatives at different water vapor activities and are compared with experimental data. With the obvious exception of Langmuir's correlation, the predictions of the derivative with respect to ψ, for activities up to $\psi = 0.6$ are acceptable. As the activity increases, equations (16), (17) and (18) increasingly overestimate the value of the derivative while equations (14) and (15) underestimate it. Moreover for saturated air, a situation equivalent to fresh fruit at full turgor, all but Filonenko an Chuprin's correlation predict an infinite value for the derivative. Equation (19) yields acceptable predictions up to $\psi = 0.7$ for the derivative with respect to temperature. At high activities it overpredicts. Equation (20) is acceptable up to $\psi < 0.5$ but beyond that value it decreases rapidly and finally changes sign.

Table II

The derivatives $\left(\frac{\partial X}{\partial \psi}\right)_T$ and $\left(\frac{\partial X}{\partial T}\right)_\psi$

Original equation number	$\left(\frac{\partial X}{\partial \psi}\right)_T$	
(4)	$k_1k_2/(1 + k_2\psi)^2$	(13)
(5)	$\frac{X_m c[1 + (c - 1)\psi^2]}{[1 + (c - 2)\psi - (c - 1)\psi^2]^2}$	(14)
(8)	$\frac{0.01[-\ln(1 - \psi)]^{\frac{1}{n} - 1}}{(kT_R)^{\frac{1}{n}}\, n(1 - \psi)}$	(15)
(9)	$\frac{\kappa\xi}{\psi(-\ln\psi)^{1 + \xi}}$	(16)
(10)	$\left(\frac{a}{RT}\right)^{1/r} \frac{X_m}{r} \frac{1}{\psi(-\ln\psi)^{1 + 1/r}}$	(17)
(12)	$\frac{bB}{(b - \Delta\psi)^2}$	(18)
	$\left(\frac{\partial X}{\partial T}\right)_\psi$	
(8)	$-\frac{X}{nT}$	(19)
(12)	$\frac{(b - \Delta\psi)(BZ_1 + Z_2\Delta\psi) - BZ_1\Delta\psi}{(b - \Delta\psi)^2} - 0.0004$ $Z_1 = 10^{-4}(1.2T_c - 0.06T_c^{\ 2} - 4k)$ $Z_2 = -2.5 \times 10^{-6}\ T_c$	(20)

3

APPLICATION OF THE CHEMICAL POTENTIAL

To describe the equilibrium content of water in vegetable tissues it is convenient to establish a model. In this case the model is a simplifie description of tissues and its unit components, the cells. (Reeve [15], Slatyer [16], Nobel [17

Tissues are regarded as assemblages of cells. Practically all cells have part of their surfac abutting on intercellular air spaces. The generalized plant cell has an outside wall consist ing of a mesh of cellulose microfibrils. Insid the outer wall there is cytoplasm, which consis mainly of proteins and water but which also con tains lipids, salts and other compounds. At th inner wall-cytoplasm interface there is a membr plasmalemma, inside of which there is a large central aqueous phase which can occupy up to 90 of the volume of a mature cell: the vacuole. I is separated from the cytoplasm by a membrane

Table III

The derivative $(\partial X/\partial\psi)_T$

ψ	Langmuir	BET	Experimental	Henderson	Kuhn	Filonenko	Halsey	$\phi = \gamma_w x_w$
0.01	0.832	0.9588	.	0.1163	0.4579	0.1264	0.4389	0.3084
0.10	0.184	0.1581	0.220	0.1845	0.1831	0.1517	0.1817	0.1889
0.20	0.073	0.1107	0.160	0.2332	0.1874	0.1889	0.1892	0.1859
0.30	0.039	0.1192	0.200	0.2867	0.2233	0.2445	0.2287	0.2102
0.40	0.024	0.1505	0.320	0.2988	0.2891	0.3266	0.3001	0.2595
0.50	0.016	0.2097	0.370	0.4452	0.4042	0.4583	0.4254	0.3468
0.60	0.012	0.3226	0.580	0.5812	0.6202	0.6891	0.6626	0.5107
0.70	0.009	0.5691	0.970	0.8085	1.0904	1.1510	1.1858	0.8654
0.80	0.007	1.2759	2.100	1.2689	2.4376	2.2988	2.7129	1.8774
1.00	0.005	∞		∞	∞	76.5306		629.2271

Table IV

The derivative $(\partial X/\partial T)_\psi$

Results for apples at 30 °C

ψ	Experimental	Correlation		
		Henderson	Filonenko & Chuprin	$\psi = \gamma_w x_w$
0.989	.	−0.02668	+0.02767	−0.00114
0.857	−0.00120	−0.00213	+0.00047	−0.00076
0.800	−0.00015	−0.00153	−0.00011	−0.00067
0.7	−0.00155	−0.00097	−0.00043	−0.00057
0.6	−0.00105	−0.00071	−0.00051	−0.00047
0.5	−0.00040	−0.00052	−0.00053	−0.00041
0.4	−0.00065	−0.00039	−0.00053	−0.00035
0.3	−0.00046	−0.00029	−0.00052	−0.00030
0.2	−0.00035	−0.00019	−0.00051	−0.00025
0.1	−0.00028	−0.00011	−0.00050	−0.00019

known as the tonoplast.

Most of the water content of the cell resides in the vacuole and frequently reaches levels of about 98% of the vacuole volume (Slatyer [16], Stocking [18]). The volumetric water content of the walls of turgid cells may be around 50% of the wall volume. The water is adsorbed on the solid surface and is retained in the interfibrillar spaces. The cytoplasm is even richer in water content. In the cytoplasm, water is bound to proteins and other hydrophilic colloids and also exists as free water. Most of the sugar in sugar-based foodstuffs, to which the following analysis is confined, are contained within the vacuole. The vacuolar sap may be regarded as a solution (Slatyer [16]).

Water equilibrium

When there is a change in water content, the solutes concentration as well as the sorptional force field resulting from the presence of the solid matrix and insoluble materials will be changed. The geometrical arrangement may also be altered.

This problem has some points of similarity with water-soil relationships. This was recognized by Slatyer [16], who suggested that the thermodynamic approach used by Babcock [19] could be applied to the above case.

If it is accepted that unique relationships can be established for the chemical potential of water as a function of volumetric water content then a general expression for a differential change in chemical potential of water is as follows:

$$d\mu_w = -\bar{S}_w dT + \bar{V}_w dP + \left(\frac{\partial \mu_w}{\partial c_s}\right)_{T,P,n_j,n_w} dc_s + \left(\frac{\partial \mu_w}{\partial \theta}\right)_{T,P,n_s} d\theta \tag{21}$$

From a different standpoint, the number of moles of solute, of insoluble materials and of water may be considered to be the relevant variables (Noy-Meir and Ginzburg [20]):

$$d\mu_w = \bar{S}_w dT + \bar{V}_w dP + \left(\frac{\partial \mu_w}{\partial n_s}\right)_{n_j,P,T} dn_s + \left(\frac{\partial \mu_w}{\partial n_m}\right)_{P,n_j,T} dn_m + \left(\frac{\partial \mu_w}{\partial n_w}\right)_{P,n_j,T} dn_w \tag{22}$$

Equation (22) can be integrated from the reference state of pure water at atmospheric pressure as expressed by the following set of initial conditions

$$P = P_o \;;\; n_s = 0 \;;\; n_m = 0$$

where the water amount can be any non-null quantity. If the temperature is taken to be constant, then in order to obtain an expression for the change in chemical potential the term $\left(\frac{\partial \mu_w}{\partial n_m}\right) dn_m$ may be integrated at P_o, $n_s = 0$, n_w, the term $\left(\frac{\partial \mu_w}{\partial n_s}\right) dn_s$ at P_o, n_m and n_w, and the $\bar{V}_w P$ term at n_s, n_m, n_w, between the reference state and the final state. Noy-Meir and Ginzburg [20] discussed alternative partitions. While the pressure and solute terms of equations (21) and (22) are readily integrable, the sorptional force field terms are not. For the purpose of the present discussion the integrated effect of these terms will be lumped into a variable ψ_m. (Slatyer [16], Nobel [17], Shepherd [21]). Then, for constant $\bar{V}_w$

$$\mu_w - \mu_w^o = \bar{V}_w(P - P_o) + RT \ln \hat{a}_w + \bar{V}_w\psi_m \qquad (23)$$

The problem under examination is that of equilibrium between tissue and humid air. Thus, the equilibrium isotherm is:

$$RT \ln\psi = \bar{V}_w(P - P_o) + RT \ln \hat{a}_w + \bar{V}_w \psi \qquad (24)$$

where the gas phase is considered to be ideal, an acceptable assumption at atmospheric pressure. Equilibrium implies that the chemical potential has the same value in each of the phases in the cell as in the surroundings. The use of equation (24) is not straightforward because of the complexity of the structure involved. The relative contributions of the terms to the value of the chemical potential value will be different for each of the phases; also the values to be used will, of necessity, be spatial averages since no techniques are available for the determination of cell properties on a microscale (Hellkvist et al. [22]).

The matric potential and the hydrostatic pressure terms

The matric potential term accounts for the capillarity, adsorption and hydration forces. The water held by matric forces roughly corresponds to bound water (Wilson and Rose [23]). Wiebe and Al-Saadi [24] measured matric water contents for tissues of several vegetable foodstuffs. From their data it can be seen that the matric water content is only of importance when the total water content is very low.

If the cell is regarded as being enclosed within ideally elastic walls, a linear relationship can be established between gauge pressure and the relative change of volume from full turgor to zero gauge pressure (Noy-Meir and Ginzburg [20]):

$$\bar{V}_w(P - P_o) = \bar{V}_w X \left(\frac{X - X^o}{X}\right) \qquad (25)$$

Sorption equilibrium prediction

A full description of the equilibrium relationships for apples should be for the full moisture content range, $0 \leqslant X \leqslant 7$ g/g, rather than for the restricted ranges covered by the existing equations. For the purposes of design or simulation of conventional drying processes, the process starts at full turgor. Fresh fruit are usually packaged and stored under conditions close to those of full turgor. Commercial hot air drying terminates at a standard moisture content X = 0.32 kg/kg while freeze drying or air drying followed by vacuum drying extends to a moisture content of almost zero.

Solubility

In the case of apples, a representative composition is shown in table V (Rotstein et al. [25], Voho and Varo [26]). The vacuolar solution is a sugar solution made primarily of glucose and fructose, with some sucrose. Studies made on honeys by Bates et al. [27] showed that sucrose could be treated as if it were fructose, from the standpoint of the solubility properties of the system. A characteristic feature of these solutions is their ability to remain in an oversaturated condition for a long period of time. Figure 7 is a plot of the solubility relationships for the system water - sucrose - invert sugar. If the glucose and fructose mixture is considered as if it were invert sugar the line WP shows the evolution of a typical apple as its moisture content changes.

Table V

Typical composition of fresh apple

(Basis: 1 kg dry matter)

Water	6.50 - 7.00 kg/kg
Glucose and fructose	0.58 kg/kg
Sucrose	0.18 kg/kg

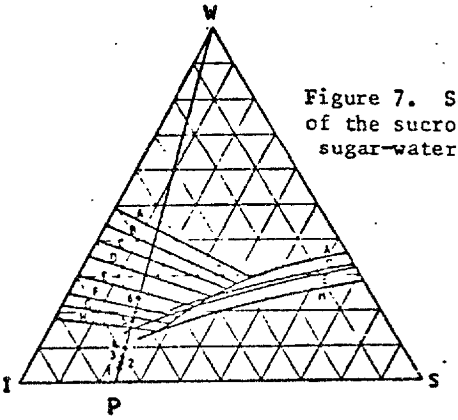


Figure 7. Solubility of the sucrose-invert sugar-water system.

1,2,3,4,5,6 are moisture contents 0.03, 0.06, 0.08, 0.16 and 0.24 Kg/Kg, respectively.
A,B,C,D,E,F,G,H = 0, 10, 15, 23.15, 30, 40, 45, 50°C, respectively.

W, I. S. = 100% water, invert sugar and sucrose vertices, respectively.

The activity coefficient of glucose solutions

Taylor and Rowlinson [28] correlated the activity coefficient of glucose as follows:

$$\gamma_w = 10^{A(1 - x_w)^2} \qquad (26)$$

Changes from one temperature to another can be made using the following equation:

$$\left(\frac{\partial \ln \gamma_w}{\partial T}\right)_{P,x} = -\frac{\overline{\Delta H_w}}{RT^2} \qquad (27)$$

If the partial molar enthalpy change of mixing of water is regarded as being practically constant within the temperature range under consideration then $\gamma_w(T)$ can be represented by equation (28)

$$\ln \gamma_w = 1 + p/T \qquad (28)$$

where 1 = 1.274 and p = -635.840 for

$r^2 = 0.992$.

Relative contributions of the chemical potential terms

Figure 8 allows a comparison to be made of the values of the water vapor and osmotic chemical potential terms at successive sets of moisture content and activity values. The calculations were made on the assumption that the solutions reached oversaturation and that the thermodynamic relationships for the solution could be extrapolated into the oversaturated region. The test of the validity of this and other assumptions will be the ability of the method to predict equilibrium relationships. x_w was calculated using equation (29).

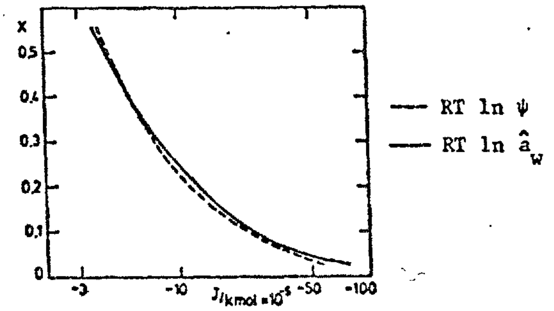


Figure 8. Total and osmotic chemical potential.

$$x_w = \frac{X}{X + \sum_j \left(\frac{m_j}{d + \Sigma m_j} \cdot \frac{M_w}{M_j}\right)} \qquad (29)$$

It can be seen that through most of the range of moisture contents under consideration, the contribution of the osmotic term is a close approximation to the total chemical potential of the system. Departures from this statement are noted mainly at extreme moisture contents both high and low. As bound, or matric, water is the last to leave the solid, it seems reasonable to conjecture that as water content is reduced it eventually becomes equal to the amount of bound water located mainly at the cell wall and cellular membrane. Throughout this process the water apportioned to the osmotic term decreases and the matric chemical potential becomes the dominant term. Obviously the point at which all of the remaining water is bound water is ill-defined.

At high moisture content, it is to be noted that the difference between water vapor chemical potential and osmotic potential is not as large as it is at low moisture contents. At full turgor, the difference for apples is about -25100 J/kmol. As an approximation it seems reasonable to consider that at full turgor the water accountability can be restricted to the vacuole. In that case the significant contributions in equation (24) are the swelling pressure and osmotic terms. The difference between the osmotic term and the water vapour chemical potential is due to the pressure term. This is consistent with the pressure term being positive.

6

Regions in the equilibrium isotherm

Three regions can be identified:

1 - The high moisture region
2 - The intermediate moisture region
3 - The bound water region.

The high moisture region

This region can be considered as extending from full turgor down to the moisture content at which the vacuolar pressure is equal to the external pressure. In terms of the foregoing analysis of the chemical potential, when attention is focused on the vacuole and matric potential is neglected, the moisture content at the lower limit of the high moisture region is located at the intersection of the curves RT ln ψ and RT ln $\hat{a}_w$ (cf. Figure 8).

A simple correlation can be presented for the pressure term by making use of equation (25) and by noting that at full turgor the fruit can be considered to be in equilibrium with saturated moist air. Then, from equations (24) and (25)

$$0 = \bar{V}_w X \left(\frac{X - X^o}{X}\right) + RT \ln (\hat{a}_w)_1 \qquad (30)$$

For the case of apples at 20°C, this results in

$$X = 1.54912 \times 10^6 \frac{J}{m^3}$$

The equilibrium relationship for the high moisture region then results:

$$RT \ln \psi = \bar{V}_w X \left(\frac{X - X^o}{X}\right) + RT \ln \hat{a}_w \qquad (31)$$

The actual significance of the pressure term is low, from the standpoint of the order of magnitude of its contribution to the moisture equilibrium content prediction. Figure 9 shows that there is little change in the predicted value if the pressure term in equation (31) is dropped. In the case under consideration this results in a maximum difference of 1% for moisture contents in the range 2 < X < 7 kg/kg dry matter and progressively even less as the moisture content decreases further.

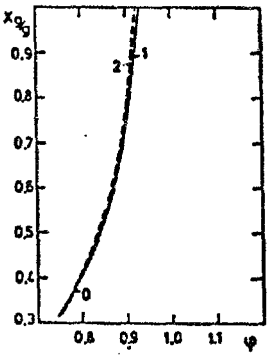


Figure 9. Hydrostatic pressure contribution.

1 - Equation (31)
2 - Equation (32)

The low moisture region

The low moisture region refers to the bound water content of the foodstuff. It has been seen that at low moisture contents the B.E.T. equation predicts accurately the equilibrium values, probably because the actual situation is close to the concepts on which the Brunauer, Emmet and Teller theory is based.

The lower bound of this region is the zero moisture content point. The upper bound is defined as the intersection of the B.E.T. line and the line drawn for the intermediate moisture region.

The intermediate moisture region

As stated earlier, this region and that of low moisture content are the regions usually described in the literature. The upper bound of this region is the point of zero gauge vacuolar pressure. It is to be noted that the literature is conflicting as to whether or not negative pressures exist inside the cell. (Slatyer [16]). The ability of a cell to retain a vacuum has been related to the cell wall capillaries, which it has been suggested (Nobel [17]) operate as hydraulic seals. If the predictions of figure 8 are correct, by the time the vacuolar gauge pressure becomes zero a substantial amount of water has left the cell. If it were to keep its volume constant, this would mean that only about 10% of this volume would be liquid. Under this circumstances it is hard to visualize the build up of a substantial vacuum.

It is possible that depending on the vegetable under consideration partial vacuum could be built up which would then collapse.

On the other hand, and from a practical standpoint it has been pointed out above that the pressure term contribution can be neglected for the purposes of equilibrium moisture content prediction.

Thus the equilibrium relationship for the intermediate region is:

$$\psi = \hat{a}_w \tag{32}$$

In practice the use of this equation can be extended to the high moisture region. Figure 10 indicates the equilibrium values predicted by the above expression for apples at 20°C.

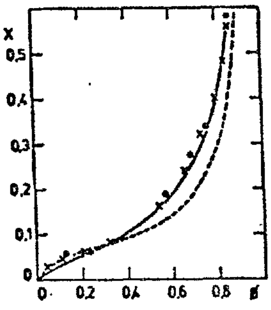


Figure 10. Predicted equilibrium data (apples 293°K).

—— equation (32)
---- BET equation
✱ experimental data
x Filonenko and Chuprin [9] experimental data.

The $(\partial X/\partial\psi)_T$ derivative

For the intermediate and high moisture content regions the derivative $(\partial X/\partial\psi)_T$ can be calculated using the following expression obtained from equations (26), (29) and (32);

$$\left(\frac{\partial X}{\partial\psi}\right)_T = \frac{\alpha}{(1-x_w)^2\ \psi\left[\frac{1}{x_w} - 2\beta A(1-x_w)\right]} \tag{33}$$

where

$$\alpha = \sum_j \frac{m_j}{(\sum_j m_j + d)} \cdot \frac{M_w}{M_j} \tag{34}$$

and

$$\beta = 2.30258\ .\ .\ .\ . \tag{35}$$

The results for apples at 20 °C using the above equations are shown in table III together with values calculated from several of the correlations described previously. It can be seen that several of the correlations yield good predictions for the intermediate moisture region. As moisture content increases, the best predictions are provided by the Filonenko and the Halsey correlations as well as by equation (33). The Filonenko and Halsey correlations tend to overestimate the effect of a change in water vapor activity whereas equation (33) tends to underestimate it.

The prediction of isotherms at different temperatures

Equations (26) and (32) enable sorptional equilibrium values to be predicted at any temperature As an example values have been predicted for apples at 40 °C (Figure 11).

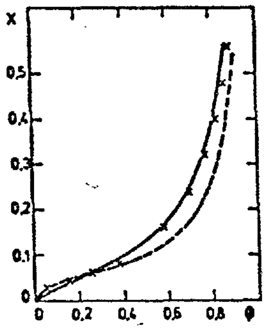


Figure 11. Predicted equilibrium data (apples 313°K)

—— equation (26) and (32)
---- BET equation
x Filonenko and Chupri [9] experimental data.

The derivative $(dX/dT)_\psi$ in the proposed correlation

Using equation (32) to describe the whole range of moisture contents, the derivative is

$$\left(\frac{\partial X}{\partial T}\right)_\psi = -\frac{\alpha bp\ (1-x_w)}{T^2\left\{2\ \ln\left(\frac{\psi}{x_w}\right) - \frac{(1-x_w)}{x_w}\right\}} \tag{36}$$

Representative values were calculated for apple at 30°C and are shown in Table IV. It can be seen that the predicted values are a reasonable representation of the measured values and that they extend into the high moisture content regi in a satisfactory manner.

Application of the proposed correlation to other foodstuffs

The proposed correlation procedure was applied to other foods and the results compared with experimental data. Typical compositional data were used to predict equilibrium data for all but the low moisture content region, where a B.E.T. equation was used, as described earlier. As some of the foodstuffs to be considered are sucrose-based instead of glucose-based, there is need for data on the water activity of sucrose solutions.

The activity coefficient of sucrose solutions

Stokes and Robinson [29] presented experimental data for the activity of sucrose solutions as well as a correlation which relates molalities to the activity coefficient of water.

The use of their correlation presents difficulties when carried beyond the scope for which it was developed ($m < 6$) and at high sugar concentrations it is not adequate. Instead, the experimental data obtained by the above authors, together with data obtained by Scatchard et al. [30], were fitted by a least square linear regression procedure in the form of equation (26). As a result, the following value was obtained

$$A = -2.789326$$

which fits the experimental data to within 0.8%. Norris [31] suggested a value of $A = -2.60$, which results in maximum errors of 3.6%.

Beetroot

Cerny [32], Dahlberg [33] and Owens et al. [34], have published data on typical compositions of beetroots from several origins. It is interesting to note that the sugar content of beetroot corresponds mainly to sucrose, instead of glucose. Equation (32) was used to predict the sorption equilibrium data in the intermediate moisture region, for beetroot at 25 °C, using a representative value of α of 0.8061.

A least square linear regression procedure yielded $X_m = 0.0518$ and $c = 16.16$ for the B.E.T. equation (equation (5)). The results are plotted in figure 12 and compared with experimental data (Iglesias et al., [35]). If can be seen that the predicted values fit the experimental results adequately.

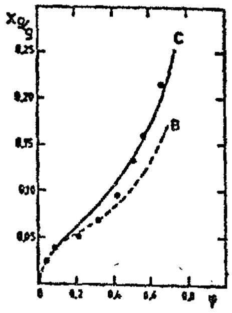


Figure 12. Beetroot, 298°K.

C, equation (32) prediction
B, BET equation
• Iglesias et al. [35] experimental data,

Prunes

The chemical composition of prunes has been thoroughly reviewed by Strachan et al. [36]. Further reports were made by Kalasek and Blaha [37] and by Chernovalova and Avetisyan [38]. It is concluded that about 70% of the sugar is sucrose. Figure 13 shows a prediction curve obtained by plotting the B.E.T. expression up to X_m and then continuing with equation (32). In this case $X_m = 0.0977$ g/g dry matter; $c = 11.7476$ as obtained by a least squares regression procedure, and $\alpha = 0.59$. It is interesting to note that the values predicted by equation (32) for $X < X_m$ are almost the same as those predicted by equation (5). The results are compared with experimental data obtained by Filonenko and Chuprin [14] and, as shown in figure 13, the theoretical prediction is satisfactory.

Apricots

The composition of apricots was reviewed thoroughly by Strachan et al. [36]. Additional data were reported by Minicone [39]. Figure 13 shows a prediction curve obtained by matching the B.E.T. line up to X_m with equation (32) from X_m upwards.

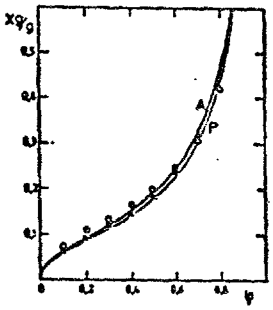


Figure 13. Apricots and plums, 293°K.
Apricots: A, equation (32)
• Filonenko and Chuprin [9] experimental data
Plums: P, equation (32)
× Filonenko and Chuprin [9] experimental data

Again the values predicted by the B.E.T. equation ($X_m = 0.1092$ g/g, $c = 0.1092$) are almost identical with those predicted by equation (32). The predicted values compare well with the experimental data obtained by Filonenko and Chuprin [9].

General comments on the proposed approach

The above discussion shows that equation (32) can be used over most of the range of moisture contents of sugar-based foodstuffs including the high moisture region, a feature not provided by any of the known correlations although high moisture content is the starting point for the study of the drying, packaging and storage problems considered earlier. Equation (32) has been found to provide simple analytical expression for $(\partial X/\partial T)_\psi$ and $(\partial X/\partial \psi)_T$ and to be well behaved at all moisture contents.

When the water content is close to the monolayer water content, the data are best represented by the B.E.T. equation. For some foodstuffs the values thus predicted agree with those predicted by equation (32), although there is no obvious thermodynamic justification for this.

The correlation is based on a simplified description of the composition of the food, so that it is sensitive to varietal or other composition differences.

The correlation may be useful in two distinct situations. First, it provides a means of predicting the equilibrium behaviour of sugar-based foodstuffs, when no data are available other than a knowledge of the average representative ratio of sugar to non-sugar dry matter together with the activity coefficient data reported above. Secondly, if experimental equilibrium data are available, they provide a simple model on which to base a correlation. In that case, α and A become the correlation parameters.

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INFLUENCE OF CELLULAR MEMBRANE PERMEABILITY ON DRYING BEHAVIOR

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INFLUENCE OF CELLULAR MEMBRANE PERMEABILITY ON DRYING BEHAVIOR

E. Rotstein & A.R.H. Cornish J. Food Science

The basic transport equations and alternative cellular membrane permeability definitions are reviewed. An analysis of data on osmotic and diffusional permeability and a discussion of boundary layer resistances allows a representative water permeability value to be chosen. The rate of drying for a cellular membrane water permeability controlled drying experiment is then predicted for two extreme cases of convective contribution to the diffusional rate. Experimental results indicate that in the case of apples the drying phenomenon is not controlled by the cellular permeability.

SUMMARY

The basic transport equations and alternative cellular membrane permeability definitions are reviewed. An analysis of data on osmotic and diffusional permeability and a discussion of boundary layer resistances allows a representative water permeability value to be chosen. The rate of drying for a cellular membrane water permeability controlled drying experiment is then predicted for two extreme cases of convective contribution to the diffusional rate. Experimental results indicate that in the case of apples the drying phenomenon is not controlled by the cellular permeability.

Introduction

The drying of foodstuffs is a complex case of coupled heat and mass transfer through tissues. The need to take into account the structure of the food, as opposed to considering it as an homogeneous solid, has been pointed out earlier (King, 1968).

In general, the main source of water in a tissue is the cell. Thus, the transport of water to the outside involves migration through the cell, its enveloping structure, through the porous-like structure of the tissue, and then through the outside boundary layer.

To be able to predict the drying behaviour it is necessary to establish the extent to which the above transport steps are controlling. There is no general answer because both the cellular structure and the characteriatics of the porous-like tissue structure are involved and the role they play in the transport process may differ widely, inasmuch as the tissue properties change from one foodstuff to another. However, it is possible that generalizations may eventually be made on the basis of grouping together various types of materials with similar structures.

Evaluation of the relative velocity of moisture migration through the cellular membrane cannot be achieved by experiment because of the difficulty involved in the isolation of cells under representative conditions. However, this velocity may be predicted from a knowledge of the membrane permeability. The predicted value can in turn be compared with experimental values of moisture fluxes in whole pieces of food.

This procedure did not prove to be straightforward because a literature survey revealed that there is a certain degree of confusion as to the value of the permeability constant. This confusion arises from the use of many different definitions of permeability, which conflict among themselves because of their mathematical expression and the driving forces considered. As a result, many different values have been published.

A critical review has allowed a conservatively representative value to be selected for use in simulated cellular permeability controlled drying process. Comparison with experimental data led to the conclusion that cellular permeability does not control the drying process of apples.

The definitions of permeability

A certain degree of confusion as to the definition of permeability results from the choice of driving force or from the use of more general coefficients which have a restricted meaning when applied to water permeability through semipermeable membranes.

Stein (1967) and Nobel (1974) define several coefficients which are used throughout the literature. They are summarized and interrelated below.

In general $$J_w = L_{ww}\Delta\mu_w + L_{ws}\Delta\mu_s \qquad (1)$$

$$J_s = L_{sw}\Delta\mu_w + L_{ss}\Delta\mu_s \qquad (2)$$

assuming the membrane is fully non-permeable to sugars, the reflection coefficient becomes unity and

$$J_w = L_{ww}\Delta\mu_w \qquad (3)$$

where L_{ww} is the phenomenological coefficient for water chemical potential driving force.

At constant T

$$\mu_w = \mu_w^o + RT\ \ln \gamma_w x_w + \bar{V}_w\ (P - P^o)$$

Thus

$$J_w = L_{ww}\left[RT\ \ln\frac{(\gamma_w x_w)^{in}}{(\gamma_w x_w)^{out}} + \bar{V}_w(P^{in} - P^{out})\right] \qquad (4)$$

This can be expressed in terms of osmotic pressure

$$RT\ \ln \hat{a}_w = RT\ \ln \gamma_w x_w = -\bar{V}_w\ \pi \qquad (5)$$

Or in terms of molar concentration

$$RT\ \ln \frac{\hat{a}_w^{in}}{\hat{a}_w^{out}} = RT\ \bar{V}_w(C_w^{in} - C_w^{out}) \qquad (6)$$

Equation (4) can written in two different ways, taking into account eqns. (5) and (6)

$$J_w = L_{ww}\left[\bar{V}_w(\pi^{out} - \pi^{in}) + \bar{V}_w(P^{in} - P^{out})\right] \qquad (7)$$

$$J_w = L_{ww}\left[RT\ \bar{V}_w(C_w^{in} - C_w^{out}) + \bar{V}_w(P^{in} - P^{out})\right] \qquad (8)$$

Note that (7) and (8) are identical if the phenomenon by which there is a water flux is osmotic and only osmotic. Otherwise they represent different problems.

An alternative definition is based on volumetric flux. The "hydraulic conductivity coefficient " or "hydraulic permeability" L_p is defined

$$J_v = L_p(\Delta P - \sum_j \sigma_j \Delta\pi_j)$$

where

$$J_v = J_w\bar{V}_w + J_s\bar{V}_s$$

For the case under consideration

$$J_v = J_w\bar{V}_w - L_p(\Delta P - \Delta\pi) \qquad (9)$$

For volumetric flux of water and "water potential" as the driving force the "water conductivity coefficient" is defined

$$J_{vw} = J_v = J_w\bar{V}_w = L_w(\psi^{in} - \psi^{out}) \qquad (10)$$

where

$$\psi = \frac{\mu}{\bar{V}_w}$$

Thus

$$J_w = L_w \frac{RT}{\bar{V}_w}\left(\Delta C + \frac{\Delta P}{RT}\right) \qquad (11)$$

$$J_w = \frac{L_w}{\bar{V}_w}(\Delta P - \Delta\pi) \qquad (12)$$

References to two types of permeability, which differ in the experimental driving force used, are frequently found in the literature. When the driving force is osmotic the permeability is called "osmotic permeability" or "hydraulic permeability".

$$J_v = -P_o(\pi^{in} - \pi^{out}) \qquad (13)$$

When the experiment is purely diffusional, typically labelled water vs. water, then the permeability is named diffusional permeability.

$$J_w = P_d(C_w^{in} - C_w^{out}) \qquad (14)$$

A more rigorous definition

The above definitions fail to account for the convective contribution to water flux, since they describe only the diffusional flux.

Lightfoot (1974) has presented an approach in which, to allow for body forces, he considered the membrane to be one of the chemical species.

From the postulate that fluxes are linearly and homogeneously related to driving forces, using a generalized mass transfer driving force $\vec{d}_i$, it follows

$$CRT\ \vec{d}_i = \sum_{j=1}^{n} L_{ij}(\vec{v}_j - \vec{v}) + L_{io}\ \vec{\nabla}T$$

$$\vec{\nabla} \ln T = \sum_{j=1}^{n} L_{oj}(\vec{v}_j - \vec{v}) + L_{oo}\ \vec{g}$$

The contribution of thermal diffusion, which is normally unimportant in biological systems, may be neglected. The phenomenological coefficient can be expressed in terms of the multicomponent mass diffusivities D_{ij}. Also, from an entropy balance it can be shown that

$$CRT\ \vec{d}_i = C_i(\vec{\nabla}\mu_i)_{P,T} + (C_i\vec{V}_i - w_i)\vec{\nabla}p$$
$$- \rho_i(\vec{g}_i - \sum_k w_k\vec{g}_k) \qquad (15)$$

Considering now the approach used by Scattergood and Lightfoot (1968) for the body forces, equation (15) becomes

$$\vec{d}_w = x_w(\vec{\nabla} \ln a_w)_{P,T} + x_w \frac{\bar{V}_w}{RT}\ \vec{\nabla}p \qquad (16)$$

Fick's equation

$$N_w = J_w + x_w(N_w + N_m) \qquad (17)$$

can be used here, redefining the diffusional term

$$\vec{J}_w = - C\,\mathcal{D}_{wm}\vec{d}_w \qquad (18)$$

Taking into account (16), (17) and (18)

$$N_w = - C\,\mathcal{D}_{wm}\left[\left(1 + \frac{\partial \ln \gamma_w}{\partial \ln x_w}\right)\frac{\partial x_w}{\partial z} + \frac{x_w\bar{V}_w}{RT}\frac{\partial p}{\partial z}\right]$$
$$+ x_w N_w \qquad (19)$$

Before proceeding further it is necessary to recall the physical description of the problem. The membrane is regarded mainly as a bimolecular lipid layer, hydrocarbon end pointing to hydrocarbon end, polar ends pointing outwards either surrounded by or indented by proteins (Stein, 1967, Nobel, 1974). It is assumed that they behave as a thin layer of oily material. Both external phases are dilute solutions, eventually one of them may be pure water.

As the membrane interphase concentrations cannot be measured, a partition coefficient is defined

$$K_{Dw} = \frac{C_w^m}{C_w} \qquad (20)$$

The total molar concentration should be essentially constant, and the same can be expected to be γ_w, throughout the membrane. Therefore, equation (19) can be simplified

$$N_w = - Ð_{wm} \left(\frac{\partial C_w^m}{\partial z} + C_w^m \frac{\bar{V}_w}{RT} \frac{\partial p}{\partial z} \right) + x_w N_w \tag{21}$$

It is interesting to note that in terms of mole fraction the assumption that these solutions are dilute is not a heavy restriction. For typical vacuolar compositions of apple tissue (Rotstein et al., 1968, Voho and Varo, 1975) table 1 shows this . The compositions are calculated assuming that the average tissue composition represents the average cellular composition. Then a material balance shows

$$x_w = \frac{X}{X + \sum_j \frac{m_j}{\Sigma m_j + d} \, ' \, \frac{M_w}{M_j}}$$

Table 1

Equation (21) can be integrated leading to

$$N_w = \frac{Ð_{wm} K_{Dw}}{z} \left(C_{we}^{in} - C_{we}^{out} + \frac{1}{RT} (P^{in} - P^{out}) \right] + (x_w)_{av} N_w \tag{22}$$

and

$$N_w = P'_w \left[C_w^{in} - C_w^{out} + \frac{1}{RT} (P^{in} - P^{out}) \right] + (x_w)_{av} N_w \tag{23}$$

Interrelationship among the permeability coefficients

Considering the above definitions, it can be seen that all but (23) neglect the convective contribution to the water flux. This is acceptable only when $(x_w)_{av}$, the membrane average water mole fraction, is zero or close enough to zero to make this term negligible. Then:

$$N_w \approx P_w \left[C_w^{in} - C_w^{out} + \frac{1}{RT} (P^{in} - P^{out}) \right] \tag{24}$$

The coefficients defined on the basis of osmotic gradients can be equated to those defined on the basis of concentrations provided there is no parallel or other mechanism superimposed on the diffusional one.

Most of the experiments with bimolecular lipid membrames (BLM) are set so as to ensure equal hydrostatic pressure at both sides of the membrane. This is not always true when cells are involved.

Taking into account these remarks, table 2 can be used to interrelate the different permeability coefficients.

Table 2

Experimental data

The literature reports experimental values for the water permeability coefficient, mostly in terms of diffusional or osmotic permeability. There is a wide range of values for these permeabilities and while a few experiments confirm the equivalence indicated in table 2, many give different values for the permeability of the same membrane when a different driving force is used. Tables 3 to 6 give observed values of water permeabilities for different membranes.

Tables 3, 4, 5, and 6

The bulk of the available data are for single cell membranes, with or without the cellular wall, and for synthetic membranes. The latter are basically bilayer lipid membranes. The data for tissue sections in terms of permeability coefficients are scarce. Because of the difficulty involved in accurately establishing the geometrical relationships, authors report permeability data in terms of half-times, i.e., a measure of the time needed to permeate one half of the total mass involved (see Kohn and Dainty, 1966; Glinka and Reinhold, 1972).

The differences among permeability values

The studies conducted on cell membrane properties appear to point to a unique basic structure. Thus, it should be expected that the water permeability of membranes from different origins would be similar in magnitude. If the theoretical description of the phenomenon underlying equation (23) or the similar equations above, is correct, there is no apparent reason why P_o and P_d should be different. Nevertheless it can be seen from table 3 that water permeability values for single cells range from 0.23 x 10^{-4} to 127 x 10^{-4} cm/s and those found by using an osmotic gradient are approximately equal to those found using a labelled water gradient in a few cases but differ significantly in other cases.

If synthetic membranes are considered it can be seen that they differ even if the scatter of data is not so wide; 2.3 x 10^{-4} to 73.0 x 10^{-4} cm/s. There is still a lack of agreement among permeabilities found using the alternative driving forces.

The data for tissues offer the same discrepancies.

It is significant from the standpoint of the later discussion that there is also an important increase in permeability when the cells are dead. Glinka and Reinhold (1972) found that the half time for tritium labelled water equilibration was three times longer for a living carrot cylinder than for a dead one, under the same experimental conditions. The tissue was killed either by exposure to chloroform vapour or by freesing and thawing.

Dick (1971) finds a correlation by plotting the osmotic water permeability of live and dissected cells as a function of the surface to volume ratio: permeability increases as the ratio increases and dissected cells show a higher permeability. Contending that diffusional resistance is important only when cells are large the author concludes that "true membrane permeabilities are of the order of 10^{-3} cm/sec". The lower values for tracer experiments were explained on the grounds of the existence of water pores or channels. These pores would allow a parallel hydraulic flow when there is an osmotic gradient.

The idea of pores has been considered by several authors (cf. Dainty, 1963, Stein, 1967) and the pore radius calculated by considering the osmotic flow a pure Pouiseille flow and the tracer flow, a Fickian one. Nevertheless there is no agreement among authors on this theory, as will be seen below.

Davson and Danieli (1952) collected early data on osmotic permeabilities. Bennet-Clark (1959) reported experimental methods and data for the same type of permeabilities. When discussing the relative permeabilities of plasmolyzed and unplasmolyzed cells, he concluded that the cell wall is relatively large-pored and permeable and the protoplast increases in permeability when plasmolyzed.

Stein (1967) regards the experimental data obtained by Paganelli and Solomon (1957) and by Sidel and Solomon (1957) as particularly reliable (cf. table 3). They show a 2.4/1.0 ratio between the osmotic and the labelled water permeability.

Tien (1974) examined the evidence in favour of the bimolecular

lipid leaflet as a suitable experimental model for the biological membrane. He also pointed out that under the electron microscope all membranes thus far examined are of the order of 100 A^o in thickness and indicated that in view of the fact that the interior of the BLM is liquid hydrocarbon-like the possibility of the existence of pores in the BLM is untenable. Andreoli and Troutman (1971) found that in BLM modified by amphotericin B, the unstirred layers account for 84% of the total resistance to the diffusion of water (they measured P_d).

Dainty has emphasized the boundary layer effect, the "unstirred layer" as it is called, as a possible explanation for the discrepancies (Dainty, 1963, Kohn and Dainty, 1966).

Kohn and Dainty (1966) and Glinka and Reinhold (1972) have tried to measure membrane permeabilities to water in sections of whole tissue. Kohn and Dainty investigated beets and artichokes. They believe that the values for P_o of the largest cells are probably accurate, particularly when obtained by the transcellular osmosis technique. These are of the order of 10^{-2} cm/s. The value of 0.26×10^{-4} cm/s for unplasmolyzed beet parenchyma tissue (Myers, 1951) is regarded as much less reliable. Using an unsteady state approach, after Phillip (1958), Kohn and Dainty (1966) claimed that if cell permeability were the sin controlling variable the half time should be independent of the sample thickness, which is contrary to their experimental evidence.

Stadelman (1963) corroborates this finding stating that the rate of exchange of labelled and unlabelled water is controlled entirely by the dimensions of the tissue and not by the diffusional permeability of the cell membranes. Glinka and Reinhold (1972) experimented with cylinders of carrot tissue subjected to labelled water exchange. They claimed that the effect of the membrane is significant enough to result in different permeability values when the membrane is treated with different chemicals. Thus, if there is a significant boundary layer effect, it is not so high as to mask the true membrane permeability change thus obtained.
Some simple considerations help to clarify the influence of the boundary layers. The classical heat/mass transfer expression for a single sphere of diameter D in a large body of fluid can be used if the cells are treated as isolated spheres. It is known that both the expressions for free convection and that for forced convection (Bird, Stewart and Lightfoot, 1960) yield for a motionless fluid.

$$k_C = 2 \frac{D_{AB}}{D} \qquad (25)$$

This is valid for equimolar counterdiffusion only, which is an acceptable description of the heavy water experiments. Osmotic experiments can be thought as diffusion of one component, the other remaining stagnant. For this case equation (26) must be used instead of (25).

$$k_C = 2 \frac{D_{AB}}{D} \frac{C}{(C_B)_{ln}} \qquad (26)$$

Typical experiments for the osmotic case, such as Zeeman (1950a) or Levitt et al (1936), have $C/(C_B)_{ln}$ values of an order of magnitude 10 .

Poznansky et al (1976) predicted internal boundary layers of about 200 μ for spherical BLM. The actual value depends on the sphere radius. If the inside of the cell is considered homogeneous and the diffusivity and total concentration is regarded as constant, the differential equation

$$\frac{d}{dr}\left(r^2 \frac{dC_w}{dr}\right) = 0$$

describes the concentration profile.

Thus

$$\frac{1}{P_t^{\,m}} = \frac{1}{P^{in}} - \frac{\delta}{D_{AB}^{in}\,(1 - \delta/R)} \qquad (27)$$

By considering the diffusivities at both sides of the membrane to be approximately equal

$$\frac{1}{P} \simeq \frac{1}{P_t^m} + \frac{R}{D_{AB}} \quad \frac{1}{1 - \delta/R}$$

This equation justifies Dick's contention that the boundary layer resistances become influential for large cells. Provided $\delta/R < 0.5$, the inner boundary layer will be more influential than the outer one.

It is concluded that the reported difference between P_d and $P_oRT/\bar{V}_w$ may be accounted for by the internal and external mass transfer coefficients. Since the transfer mechanism involved in drying is similar to that considered for P_o, the latter is the relevant value for our case.

The synthetic membranes, having a more amenable geometry and being easier to use under controlled experimental conditions, have allowed an understanding to be gained of the difference between osmotic and diffusional permeabilities and have supported the above considerations.

Everitt and Haydon (1969) noted that the build up or depletion of solute concentration (Dainty, 1963) involves a corresponding change in density and gives rise to natural convection. By using the approach suggested by Levich (1962) with suitable changes in the boundary conditions; non-nil membrane equilibrium concentration and non-zero normal velocity at the wall, the authors were able to calculate the membrane equilibrium concentration values. These values permit

a direct calculation of the true membrane permeability.

On the other hand, Everitt et al. (1969) proved that the boundary layer resistances are significant when labelled water diffusion is under consideration. The results from Everitt and Haydon (1969) and Everitt et al. (1969) indicate that there is no noticeable difference between osmotic and diffusional permeability once the boundary layer resistances are taken into account. By re-calculating their data it can be seen for their osmotic experiments the mass transfer coefficient was between 28.0×10^{-3} and 284.3×10^{-3} cm/s, while for the diffusional ones it was between 0.6 and 1.8×10^{-3} cm/s.

The selection of a representative permeability value

From the above discussion it can be seen that equations (19) to (24) seem to describe reasonably well the permeation of water through the cellular membrane.

The difference between P_o and P_d can be explained in terms of the usually unaccounted for boundary layer diffusional resistances. These are important when determining P_d and are negligible or relatively unimportant in osmotic experiments, especially at smaller cell sizes. The transfer mechanism involved in drying is closer to the one resulting in P_o, thus values of P_o can be used to estimate the rate of permeation through the cellular membrane. Since the boundary layer resistances are unimportant, bulk concentrations can be used instead of equilibrium membrane concentrations.

Dick (1966) has shown that there is a correlation between permeability coefficients and surface/volume ratio of the cells. The surface/volume ratio for apple cells, as reported by Reeve (1953) from histological studies, is within the range of 0.0190 to $0.0299 \mu^{-1}$. This corresponds, in Dick's data, to an average value

$$P_w = 4 \times 10^{-4} \text{ cm/s}$$

The value should be acceptable to depict a drying process on the grounds that, as discussed earlier, the osmotic permeabilities are very close to the true membrane permeabilities.

On the other hand, the collected data for plant cells (table 5) show a wide range of values but if the frequency of values is considered (table 7) it appears reasonable to narrow the selection to 1×10^{-4} to 10×10^{-4} cm/s. The average value within this range is

$$P_w = 4.04 \times 10^{-4} \text{ cm/s.}$$

Table 7

Most of the quoted data correspond to sugar solutions outside and/or inside the cell. There are no specific data for apple cells, but a certain similarity could be claimed for Beta vulgaris.

On the other hand, evidence like the transcellular osmosis experiments and the BLM data seem to indicate that the true membrane permeability is higher. This was indicated by Kohn and Dainty (1966). Nobel (1974) states that a good estimate for the water permeability is 10^{-2} cm/s. (1). This is very much an alive issue in the field of biophysics and the experimental techniques involved are not easy. It is to be expected that through better experiments and a more refined analysis the issue will be clarified eventually. The above values can nevertheless be used for an order of magnitude analysis and they can be regarded as conservative figures, i.e., they may be lower than the actual values thus exaggerating the influence of the cellular permeability on the drying process. The same applies if cellular death, which occurs as dehydration proceeds, is ignored.

The use of water permeability data to predict flux

The physical situation during drying is different from that for which the permeability was defined and experimentally determined, the main difference being that the intercellular space is the outside and it is filled with moist air.

Going back to equation (23) it will yield

$$N_w = P'_w \left[C_w^{vac} + \frac{1}{RT} (P^{in} - P^{out}) \right] + (x_w)_{av} N_w \quad (28)$$

provided that, for the usual drying experimental conditions

$$0 \leqslant \frac{K_{wD}^{air,m}}{K_{wD}} \leqslant 100$$

which appears to be a restriction easily met.

A further simplification can be made considering the pressure term. According to Nobel (1974) the tonoplast is slack, not taut. Thus there is no pressure drop. When stressed, two cases can be considered as representative: spherical cells and cylindrical cells. In the first case the stress would be

$$S = \frac{\Delta P \times r}{2\delta m}$$

In the second case

$$S = \frac{\Delta P \times r}{\delta m}$$

A higher limit at which most membranes rupture is (Nobel, 1971) $S = 1$ at.

Thus, the maximum contribution to the water flux due to the pressure term can be calculated by equation (29). The result is $N_{wP} = 2.7 \times 10^{-12}$ moles/cm^2 s based on spherical cells with a representative membrane thickness of 100 A^{o} and a cellular radius of 125μ, the average value for apple tissue cells (Reeve, 1953).

$$N_{wP} = \frac{P_w}{RT}\,\frac{2S\delta^m}{r} \qquad (29)$$

The pressure term is thus negligible and equation (30) can be regarded as suitable for the calculation of N_w

$$N_w = P'_w \,\frac{C_w^{vac}}{1-(x_w)_{av}} \qquad (30)$$

To be able to predict the water permeation flux, $(x_w)_{av}$ needs to be known. This is not easily available (Tien, 1974, Slatyer, 1967, Stein, 1967), but two cases can be considered. One assumes that the phase composition at the membrane is equal to that in the vacuole. The other corresponds to the concept of the membrane being a pure lipid and because of the very low solubility of water in such a system the average water mole fraction can be regarded as being practically zero.

Thus, the two cases to be studied are:

a) $(x_w)_{av} = x_w^{vac}$

b) Assuming very slight water solubility in the membrane, as would be the case if it were a pure lipid, $(x_w)_{av} = 0$.

Experimental drying water fluxes

Granny Smith apples were selected, washed, peeled and cut into parallelepipeds of 2.4 cm x 2.4 cm x 1.2 cm. They were sulfited by exposure to SO_2 and air dried on a weighing tray. The air was filtered and heated through a heat exchanger. To secure the desired

air moisture, steam was injected. The steam injection was countercurrent to insure good mixing. The air velocity was measured by a hot wire anemometer. Dry and wet bulb temperatures were continuously recorded and controlled. Air velocity was 10.0 ± 0.1 m/s, dry bulb temperature 76.0 ± 5^{o}C, and relative humidity of air, 10%. The weight of the drying sample was recorded as a function of time.

A geometrical model for the intercellular spaces

Reeve (1953) reported the total cell wall area per unit volume of apple flesh parenchyma, for several varieties. To calculate the experimental rates of drying in terms comparable with the permeation fluxes it is necessary to know the effective amount of cellular area i.e., the fraction of total cellular wall area abutting onto the intercellular spaces. Reeve (1953), Lee et al. (1967), published histological studies that give some insight into the geometry of the system. On this basis a simple geometrical model is proposed.

The cells do not behave as perfect spheres with only point contact among them. It is suggested that they appear as cubically truncated spheres, i.e., they occupy the common volume of a cube and a sphere intersecting in such a way that they have a common center, the cube diameter being 2 λ r. The portions of sphere outside the cube are removed (Figure 1).

Figure 1

The values of λ must be

$$\frac{1}{\sqrt{3}} < \lambda < 1 \qquad (31)$$

between the two limiting situations of the cube inscribed within the sphere and the sphere inscribed within the cube.

The value of λ can be calculated from porosity data using equation (32)

$$\lambda = \left(\frac{4\pi}{4(1-\varepsilon)+\pi}\right)^{\frac{1}{2}} \cos\left\{\frac{1}{3}\cos^{-1}\left(\frac{-\left(\frac{1-\varepsilon}{\pi}+1\right)^{\frac{1}{2}}}{1.5}\right)+\frac{2\pi f}{3}\right\} \qquad (32)$$

where f = 0, 1, 2.

Porosity

Smock and Neubert (1950) estimated that 25% of the volume of the apple parenchymatic tissue is occupied by intercellular spaces.

Czerski (1964) used a gasometric method to measure porosity of leaves of several species, obtaining a range of values between 7.4% and 57.7%. Hardy (1949) found that the porosity of fresh samples of Cox Orange Pippin was 33.3%. More comprehensive determinations of porosity were made by Smith (1938) and by Reeve (1953). Both covered seven different apple varieties.

On the basis of the above, a value of ε = 0.225 appears to be representative. A value of this order of magnitude has been confirmed by Skene (1966).

Effective cell wall area

The total area of a sphere is related to the area of the truncated sphere abutting onto the intercellular spaces by

$$\eta = -2 + 3\lambda \qquad (33)$$

For ε = 0.225

equation (32) yields three roots of λ of which two can be disregarded on account of equation (31). This results in

$$\lambda = 0.8473$$
$$\eta = 0.5419$$

Reeve(1953) reported the area of apple cells regarded as spheres in point contact. This area when used in conjunction with the value of n calculated above results in an effective cell wall area of 1000 cm^2 in a sample of tissue of the dimensions used in the experiments described above.

Comparison of experimental and permeation fluxes

Figure 2 indicates the experimental water fluxes and permeation water fluxes calculated on the basis of hypotheses (a) and (b) above.

Figure 2

It can be seen that the predicted permeation fluxes are between one and three orders of magnitude higher than the actual fluxes. Thus there is a strong indication that the drying process is controlled by resistances external to the cell.

For hypothesis (a) to represent the experimental data at high moisture contents it would be necessary to accept that either the permeability is one order of magnitude lower than that deduced earlier or that the effective cell wall area is 1/20th of that calculated above or that there is a suitable compromise between these extremes. At low moisture contents as well as in the case of hypothesis (b) it would be necessary to accept even larger departures from the selected values.

For conventional air drying processes, a volume shrinkage is to be expected. For the case under consideration and using the above geometrical model this effect becomes significant below a water content of .1 kg/kg (Chirife, 1969). Although this results in a slight increase in the experimental values, the predicted fluxes based upon the two hypothesis are still

widely separated at low moisture contents. Thus it is reasonable to postulate that shrinkage does not change the relative importance of the transport process involved. This is particularly so at low moisture content, when a deterioration of the cellular structure and an increase in its permeability is to be expected.

Since the cellular permeability is not the controlling factor then either the resistance to the flux of water vapor through the tissue or the resistance presented by the boundary layer external to the piece of food, or both, are controlling resistances. Thus, the cellular permeability may be neglected in a design model which is valid in the case of apples or of tissues with analogous structures.

Summary and Conclusions

An examination of the conflicting definitions of permeability has led to the presentation of a more rigorous and comprehensive definition (equation (19)). Using this definition as a basis it was possible to interrelate the various definitions of permeability and to present experssions for this interconversion (table 2).

By this means it was possible to put all the collected experimental data onto a common basis. This in turn showed considerable discrepancies between the values reported by different authors. A discussion of the problem, taking into account the often neglected boundary layer resistances, enables the conclusion to be drawn that the reported differences could be explained in terms of internal and external mass transfer coefficients. It was concluded that the values reported as osmotic permeability are adequate for use in drying of vegetable foodstuffs.

When a value of water permeability had been selected, the basic equation (equation (19)) was examined term by term in order to assign values to the different variables and thus to obtain a final expression for the prediction of water permeation fluxes (equation (30)).

A comparison of the predicted fluxes with actual drying fluxes obtained experimentally, indicated that the predicted permeation fluxes are significantly faster than the actual fluxes shown. Only at the highest moisture contents could a particular comgination of the values involved result in the predicted permeation flux being of

of comparable magnitude to the experimental flux.

The permeation fluxes that can be calculated on this basis show that the cellular membrane permeability is not the controlling step in the drying of apples and of similarly-structured foodstuffs. Thus, the design or simulation of the drying process can safely be based on a model which accounts for the resistances to vapor transport through the porous tissue structure and the external boundary layer.

Notation

a = activity

d = generalized driving force, cm^{-1}

g = acceleration, cm/s^2

k = mass transfer coefficient

n = moles

p = pressure, at

q = heat flux, cal/cm^{2}s

r = radius, cm

t = time, s

v = velocity, cm/s

w = weight fraction, g/g

x = mole fraction

z = co-ordinate axis

A = area, cm^2

C = concentration, mol /cm^3

D = diffusion coefficient, cm^2/s

$Đ$ = multicomponent mass diffusivity, cm^2/s

J = diffusional flux, mol /cm^{2}s or cm^3/cm^{2}s

K = coefficient

L = phenomenological coefficient

N = mass flux with respect to a fixed point, mol /cm^2 s

P = pressure

P = permeability, cm/s or cm/s at

P' = permeability, when convective flux is taken into account, cm/s

R = gas constant, cm at/mol ^{o}K

S = stress, at

T = temperature, K

V = volume, cm^3

$\bar{V}$ = partial molar volume, cm^3/ mol

X = moisture content, g water/g dry matter

δ = internal boundary layer thickness

ε = porosity

η = ratio area collapsed sphere/area full sphere

γ = activity coefficient

λ = ratio cube side/sphere diameter

ψ = water potential, at

μ = chemical potential, cm^3 at/mol

π = osmotic pressure, at

ρ = density, g/cm^3

σ = reflection coefficient

Subscripts

c = defined on the basis of concentration

d = diffusional

ex = external

i = a general component

j = general solute

ln = logarithmic mean

m = membrane

o = osmotic

out = outside

p = hydraulic permeability

s = solute

t = true

v = volumetric

w = water

wp = water, due to a pressure effect

x = defined on the basis of mole fraction

Superscripts

in = inside

m = membrane

out = outside

vac = vacuole

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Table 1

Typical vacuolar water mole fraction
as a function of moisture content

X g H_2O/g dry material	x_W
7	0.9905
1	0.9368
0.48	0.8768
0.32*	0.8259
0.16	0.7034

* commercial dehydration limit.

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Table 2

Water Permeability Coefficient

Equation	Symbol	Driving Force	Units	$P_w =$
(24)	P_w	C and P	cm/s	P_w
(23)	P'_w	C and P	cm/s	$P'_w/(1 - x_w)$
(22)	$\mathcal{D}_{wm}$	C and P	cm^2/s	$\mathcal{D}_{wm} K_{Dw}/\Delta z(1 - x_w)$
(10)	L_v	ψ	cm/s at	$L_v RT/\bar{V}_w$
(9)	L_p	P and π	cm/s at	$L_p RT/\bar{V}_w$
(3)	L_{ww}	μ	mol^2/at s cm^5	$L_{ww} RT\bar{V}_w$
(13)	P_o	π	cm/s at	$P_o RT/\bar{V}_w$
(14)	P_d	C	cm/s	P_d

Table 3

Water Permeabilities of Animal Cells

Cell			$P_oRT/\bar{V}_w$ 10^4 cm/s	P_d 10^4 cm/s	References
Arbacia punctulata	Sea Urchin (Atlantic coast)	unfertilised	2.2	--	Lillie (1916,1917) Lucke et al (1931)
		fertilised	4.5 - 6.7	--	Lillie (1916,1917) McCutcheon & Lucke (1932)
Paracentrolus lividus	Sea Urchin (Mediterranean)	unfertilised	2.2	--	Maxia (1934)
		fertilised	4.5	--	Maxia (1934)
Stronglyocentrotus, Dendraster, Patiria Pisaster (unfertilised)	Sea Urchin, Sand Dollar, Starfish (Pacific coast) (temp. 17-22°C)		2.2 - 8.9	--	Leitch (1931)
Zoothanium sp.	Fresh water peritrich ciliate		2.7 - 5.6	--	Kitching (1938)
Gregarina			4.5	--	Adcock (1940)
Chaetopterus Pergamentaceus	Marine annelid (Atlantic coast)		8.9 -11.2	--	Lucke et al (1939)
Cumingia tellenoides	Marine mollusc (Atlantic coast)		8.9 -11.2	--	Lucke et al (1939)
Mouse, rat, chick	fibroblasts		8.9 -22.3	--	Brues & Masters (1936)
Rabbit	leucocytes		6.7	--	Shapiro & Parpart (1937)
Human	leucocytes		29.0	--	Shapiro & Parpart (1937)
Ox	erythrocytes		55.8	--	Jacobs (1932)
Human	erythrocytes		67.0	--	Jacobs (1932)
	Amoeba		0.37	0.23	Prescott & Zeuthen (1953)
	Frog, ovarian egg		89.1	1.28	ibid
	Frog, body cavity egg		1.30	0.75	ibid
	Xenopus, body cavity egg		1.59	0.90	ibid
	Zebra fish, ovarian egg		29.30	0.68	ibid
	Zebra fish, shed egg		0.45	0.36	ibid
	Human (adult) erythrocyte		127.0	53.00	Sidel & Solomon (1957) Paganelli & Solomon (1957)
	Human (adult) erythrocyte		116.0	41.0	Sjolin (1954) Barton & Brown (1964)
	Human (fetal) erythrocyte		61.0	23.00	ibid

Table 5

Water Permeability of Vegetable Cells

Cell	$P_oRT/\bar{V}_w$ 10^4 cm/s	P_d 10^4 cm/s	References
Chlorophyceae:			
Cladophora glomerata (pH = 7)	12.3	-	Seeman (1950a)
Rhizonium hieroglyphicum	6.4	-	Lenk (1956)
Oedogonium echinospermum	4.3	-	Lenk (1956)
Spyrogira affinis	3.1	-	Lenk (1956)
Spyrogira communis	3.8	-	Lenk (1956)
Spyrogira condensata	6.7	-	Lenk (1956)
Spyrogira gracilis	7.5	-	Lenk (1956)
Spyrogira porticalis	2.5	-	Lenk (1956)
Spyrogira pseudovarians	2.0	-	Lenk (1956)
Spyrogira singularis	11.2	-	Lenk (1956)
Spyrogira stictica	2.7	-	Lenk (1956)
Spyrogira varians	3.2	-	Lenk (1956)
Spyrogira sp.	4.6	-	Lenk (1956)
Spyrogira sp.	3.2	-	Huber & Höfler (1930)
Spyrogira sp.	2.2	-	Bochsler (1948)
Spyrogira H. (pH = 7)	15.3	-	Seeman (1950a)
Zygnema velox	16.8	-	Huber & Höfler (1930)
Zygnema sp.	5.3	-	Bochsler (1948)
Zygnema sp.	17.7	-	Hofmeister (1935)

cellular membrane 52

Table 4

Water Permeabilities of Cells in Tissues (Vegetable & Animal)

Tissue	$P_oRT/\bar{V}_w$ 10^4 cm/s	P_d 10^4 cm/s	References
Toad, bladder:			
no vasopressin	4.1	0.95	Hays & Leaf (1962)
with vasopressin	188.0	1.6	ibid
Rat:			
luminal surface of intestinal mucosal cells	83	-	Lindemann & Solomon (1962)
kidney, proximal tubule	2400.0	-	Ullrich et al. (1964)
kidney, distal tubule	1100.0	-	Ullrich et al. (1964)
Beet root:			
unplasmolyzed	0.3	-	Myers (1951)

cellular membrane 51

Characeae:			
Mougeotia scalaris	0.9	-	Lenk (1956)
Nitella flexilis (Transcellular osmosis)	154.0-416.0	-	Kamiya & Tazawa (1956)
Nitella mucronata, live cell	-	13.7	Collander (1954)
dead cell	-	17.0	Collander (1954)
isolated protoplast	-	50.0	Collander (1954)
Chara australis (Transcellular osmosis)	123.0	-	Dainty & Hope (1959)
Tolypellopsis stelligera, live cell	-	5.6	Wartiovaara (1944)
dead cell	-	16.8	Wartiovaara (1944)
membrane	-	8.9	Wartiovaara (1944)
intact cell	24.0	-	Palva (1939)
Phaeophyceae:			
Fucus vesiculosus (egg cell of sea water alga)	3.6	-	Resuhr (1935)
Filicinae:			
Salvinia natans (glycerine)	1.8	-	Seeman (1950b)
Salvinia natans	3.6	-	Seeman (1953)
Salvinia auriculata (leaf cell of fresh-water fern)	12.3	-	Huber & Höfler (1930)
Dicotyledonae:			
Caltha palustrio	4.0	-	Hofmeister (1935)
Anemone hepatica	0.7	-	Hofmeister (1935)
Ramunculus repens	3.5	-	Heinrich (1962)
Beta vulgaris	4.8	-	Myers (1951)
Stachys annua	3.6	-	Huber & Höfler (1930)
Stachys recta	5.4	-	Heinrich (1962)
Lamium maculatum	5.1	-	Heinrich (1962)
Solanum tuberosum	14.4	-	Heinrich (1962)
Physalis alkekengi	2.3	-	Heinrich (1962)

cellular membrane 53

Monocotyledonae:			
Valisneria spiralis (pH = 7)	2.6	-	Seeman (1950a)
Allium cepa (cell of onion)	7.8	-	Levitt et al.(1936)
Majanthemum bifolium	1.2	-	Seeman (1950b)
Majanthemum bifolium	1.7	-	Höfler (1934)
Majanthemum bifolium	2.2	-	Höfler (1930)
Majanthemum bifolium	2.0	-	Heinrich (1962)

cellular membrane 54

Table 6

Water Permeabilities of Synthetic Membranes

	$P_o RT/\overline{V}_w$ 10^4 cm/s	P_d 10^4 cm/s	References	
Bimolecular Lipid Membrane	8.3 -14.4	2.3	Hanai et al. (1965)	
Dialysis Tubing	230	-	Durbin (1960)	
Cellophane	870	-	ibid	
Wet gel	3400	-	ibid	
Dialysis tubing	380	10.9	Ginzburg & Katchalsky (1963)	
Wet gel	1200	19.2	ibid	
Brain lipids in chloroform:methanol	24.0	-	Mueller et al. (1964)	
Lecithin (egg) in chloroform:methanol	17-120	4.4	Huang & Thompson (1966)	
Lecithin (egg) + Cholesterol in decane, NaCl	18	-	Hanai et al. (1966)	
sucrose	18	-	ibid	
urea	21	-	ibid	
Brain lipids + cholesterol	7- 21	-	Finkelstein & Cass (1967)	T = 36°C
Lecithin (egg); THO	-	4-5	Vreeman (1966)	T = 20°C
Oxidized cholesterol in octane	8.5±0.5	-	Tieng & Ting (1968)	T = 22.5°C
Cholesterol and HTDAB	8.2±0.5	-	ibid	T = 22.5°C
Cholesterol and DAD	8.8±0.5	-	ibid	T = 22.5°C
Oxidized cholesterol + 2.5×10^{-5}M valinomycin	9.5	-	ibid	
Chloroplast extract	51.0	-	Ting et al. (1968)	
Lecithin + cholesterol	31.7	-	Prince & Thompson (1969)	T = 25°C
Lecithin (egg) + 1.7×10^{-9}M vasopressin	39.3	-	Graziani & Livne (1971)	T = 28°C
Monogalactosyl diglyceride	73.1	-	Graziani & Livne (1973)	T = 37°C
Lecithin (egg), phosphatidyl choline and cholesterol in n-decane	20.0*	19.7*	Everitt & Haydon (1969) Everitt et al. (1969)	

(* boundaries resistances discounted)

Table 7

Frequency of measured values of permeability for plant cells

(all values x 10^4 cm/s)

< 1	1 to 10	11 to 20	21 to 30	31 to 40	41 to 50	> 51
4	62	12	1	0	1	3

Figure 2

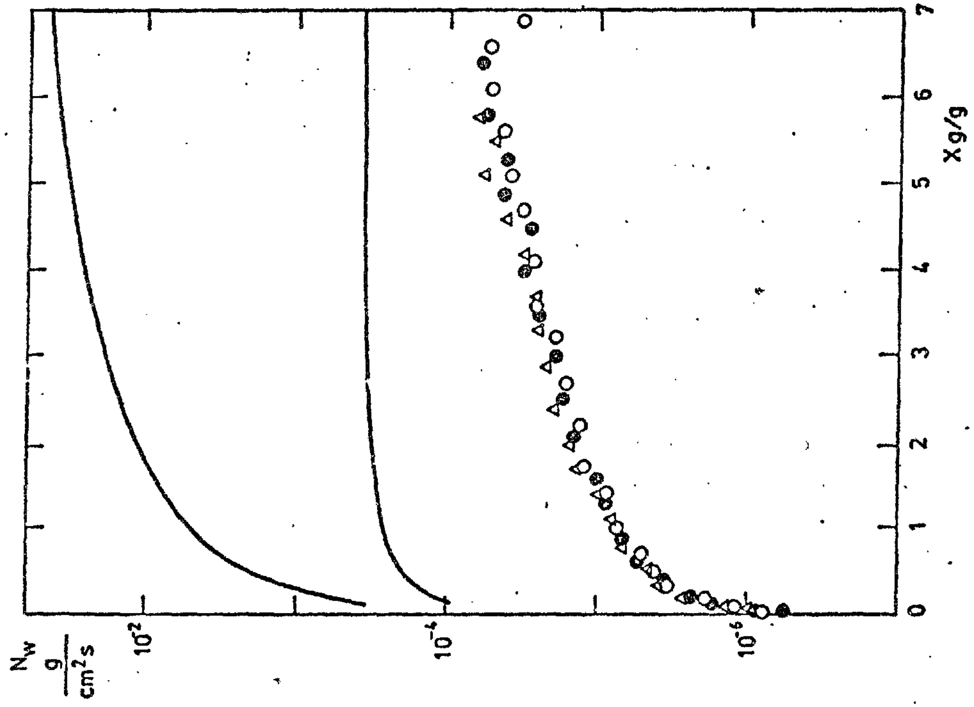
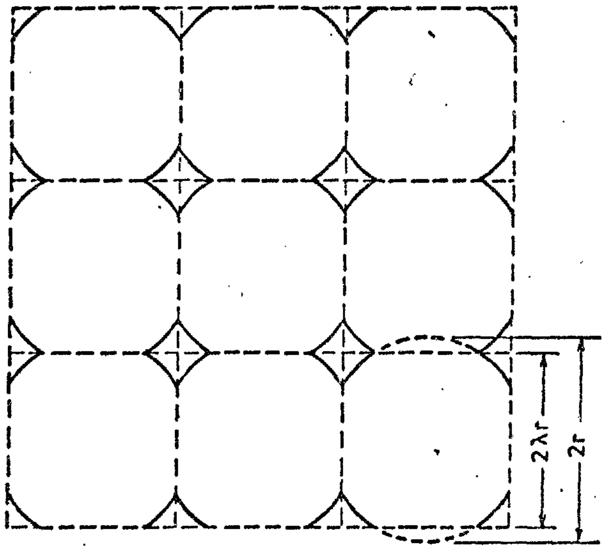


Figure 1



Legends for figures

Figure 1

THE MODELLED POROUS STRUCTURE

Figure 2

APPLE DRYING FLUXES

From top to bottom: Hypothesis (b), Hypothesis (a), experimental results (3 runs).

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