TITLE AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE MIGRATION OF MOISTURE IN COCOA BEANS

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ABSTRACT

This work is essentially an investigation of non-convective moisture movement as the result of a temperature gradient in hygroscopic porous materials, in particular, cocoa beans. The aim of the research has been to determine experimentally the bulk moisture diffusion coefficient for cocoa, and, by quantifying it, to investigate the contribution of such diffusion to wetting and mould damage that has occurred on the surface of cargoes during shipment from West Africa to Northern Europe.

Theory for the analysis of experimental results and for the application of the coefficient to real situations has been developed by the modification of the Fick diffusion equations to allow their scope to include diffusion as the result of a thermal gradient through hygroscopic porous materials. The general theory has been simplified in ways applicable both to particular experiments and to real situations, enabling the approximate solution of the resulting equations by finite difference methods.

During initial experiments, the problem of a variability in moisture content greater than that for other grains was encountered. After investigation, this was attributed to the wide disparity between the moisture contents of the husk and kernel of the cocoa bean, and the variation in husk to kernel weight ratio from bean to bean.

Experiments were performed to measure both the intra-particle and the bulk diffusion coefficients. The intra-particle rate was found to be of a low enough value that the bulk diffusion rate was determined by that through the inter-particle airspaces, and this was confirmed by direct experiment.

Applying this result to a practical situation during a cocoa voyage, the moisture migrating as a result of the thermal gradient in a ventilated hold was compared with that reaching the surface as the result of convection in an unventilated hold. The hypothesis that ventilation of a hold containing bagged cocoa might stimulate the production of a quantity of condensation greater than that occurring in an unventilated hold was shown to be mistaken.

CONTENTS

LIST OF SYMBOLS

C	Concentration
C_b	Bulk concentration
C_i	Interstitial concentration
C_m	Molar concentration
C_p	Specific heat at constant pressure
D, D_{cc}	Coefficient of moisture diffusion with respect to a concentration gradient
D', D_{cp}	Coefficient of moisture diffusion with respect to a vapour pressure gradient
D_H	Coefficient of thermal diffusion
D_{pp}	"Coefficient" of vapour pressure increase as a result of moisture diffusion with respect to a vapour pressure gradient
J	rate of vapour transfer per unit area
J_m	molar rate of diffusion per unit area
k	thermal conductivity
$\bar{M}$	$= \dfrac{\bar{m} - m_e}{m_o - m_e}$
$\bar{m}$	final average percentage moisture content
m_o	uniform initial percentage moisture content
m_e	surface percentage moisture content
p	pressure
p_{RH}	vapour presure at relative humidity of RH
p_{sat}	saturated vapour pressure
Q_A	rate of heat flux per unit area
Q_{Asens}	rate of sensible heat flux per unit area
Q_{Alat}	rate of latent heat flux per unit area
Q_{Atot}	rate of total heat flux per unit area
R	universal gas constant

r_o	radius of sphere
T	absolute gas temperature
t	time
u	temperature difference
V	volume
w	dry weight moisture content
α	$= \varepsilon\gamma$
α_H	$= \sqrt{\frac{k}{\rho C_p}}$
γ	(inverse) tortuosity
ε	porosity
θ	temperature
λ	specific latent heat of vaporisation of water
μ	viscosity
ρ	density

1 INTRODUCTION

Two very different problems have been approached under the general heading of "the diffusion of water vapour through porous media". One concerns the diffusion of moisture through media where the particles are impermeable and liquid moisture is present in the spaces between them, the remaining air spaces being saturated with water vapour. The other concerns diffusion through hygroscopic materials, where moisture is present in the particles or grains, exerting less than its normal vapour pressure, and the inter-particle air spaces are not saturated with water vapour. In this latter case, there is the subsidiary problem of intra-particle diffusion to be considered, which is especially relevant to the commercial drying of grain.

The first type of diffusion occurs in soils and sands, and the apparent anomaly usually considered is the diffusion rate being much greater than that predicted by a simple analysis in terms of the diffusion rate of water vapour in free air reduced by porosity and tortuosity factors. This was explained by Woodside and Kuzmak (1958) in the following terms:

"the flow mechanism consists of multiple vapor diffusion and liquid flow steps in series, the resistance to flow in the liquid phase being negligible, so that the flow rate is determined by the vapor pressure gradients in the pore spaces.... these gradients are of the order of six times the over-all gradient previously used to calculate the flow rate."

The higher than assumed temperature gradients observed in the cusps where the particles meet, which result in these locally high vapour pressure gradients, contribute to a heightened diffusion rate only when a film of moisture exists on the surface of the particles, in which resistance to flow is negligible, thus providing a reservoir of moisture in the region of high gradients. When it is rather the diffusion of moisture through the air spaces or out of the particles of a hygroscopic material which could supply the extra localised flow, the process is too slow to affect the overall diffusion rate.

This mechanism is not, then, effective in the case of diffusion through hygroscopic materials. In this context, hygroscopic materials are those described above, in the first paragraph of this section, or in BS 4672 (1971), and are principally biological materials such as wood, food grains and seeds. Observed rates of diffusion in this type of material, where it has been distinguished from moisture movement by convective air currents, have not been higher than that of water vapour in free air (Pixton and Griffiths, 1971, wheat; Milton et al., 1969 and the Appendix of this thesis, maize). It may then be deduced that the intra-particle diffusion rate of these grains at least must be less than that of water vapour in free air. Indeed, Becker and Sallans (1955) found by experiment that this was so. Equally, it is apparent (Thorpe, 1981) that the time for grain to equilibrate with the diffusing water vapour may be neglected when considering the macroscopic inter-particle diffusion rate, which would seem to suggest a rather higher value for the intra-particle diffusion rate. An analysis of the apparent incompatibility of these two requirements on the intra-particle diffusion rate was considered necessary to an understanding of the process of inter-particle diffusion in such hygroscopic materials.

It had been suggested, however, by R.F.Milton (1968) that a much more rapid diffusion rate in cocoa might be responsible for damage to cargoes carried from West Africa. In these cases, hold ventilation would normally be carried out after the large drop in ambient temperature occuring off Dakar to avoid "ship sweat". This type of condensation occurs on the ship's metalwork, principally on the undersurface of the weatherdeck, when a hygroscopic cargo is carried through a region where the ambient temperature is below the dewpoint temperature of the atmosphere created in the hold airspace by the cargo. If sufficient condensation forms, it drips down onto the cargo surface, causing wetting and mould growth. It was suggested by Milton that hold ventilation in the case of cocoa, whilst preventing "shipsweat", might, by cooling the outer surface of the cargo, give rise to condensation directly on the cargo surface not only by convective currents to the upper surface but also horizontally by diffusion to the surfaces at the sides. Since such horizontal transfer does not appear in practice to be significant in grain cargoes, it could only be so in cocoa if the diffusion rate were substantially higher. It was thought that this might indeed be the case because the breakdown of the cell structure during fermentation would facilitate the movement of moisture through the bean, and this was believed to be an important factor in determining the migration rate through the bulk.

It was, then, partly because of this reported anomalously high moisture migration rate in cocoa that it was considered a suitable material for studying the mechanism of water vapour diffusion through hygroscopic materials.

2. THEORETICAL BACKGROUND

2.1 FUNDAMENTAL EQUATIONS

Fick's Laws of Vapour Diffusion were derived in 1855 by analogy from Fourier's heat conduction equations of 1822. For one-dimensional heat flow in a uniform medium:

$$Q_A = -k \frac{\partial\theta}{\partial x} \qquad \text{........(2.1.1)}$$

$$\frac{\partial\theta}{\partial t} = \frac{k}{\rho C_p} \frac{\partial^2\theta}{\partial x^2} \qquad \text{........(2.1.2)}$$

where Q_A is the rate of heat flux per unit area,
k is the thermal conductivity,
θ is the temperature at time t, at distance x, along the direction of heat conduction,
ρ is the density,
and C_p is the specific heat at constant pressure (the group $\frac{k}{\rho C_p}$ is known as the thermal diffusivity, D_H),

Whereas heat and temperature are distinct, giving rise to distinct equations for heat flux and temperature change, the vapour diffusion equations are conflated, in that the presence of the diffusing vapour is a direct measure of its concentration. Thus, the vapour diffusion analogies of ρ and C_p are given the value unity, yielding, as Fick's equations:

1st Law

$$J=-D\frac{\partial C}{\partial x} \qquad \text{......(2.1.3)}$$

2nd Law

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} \qquad \text{.......(2.1.4)}$$

where J is the rate of vapour transfer per unit area,
C(x,t) is the concentration at time t, at distance x along the direction of diffusion,
and D is the coefficient of diffusion.

(For the situations under consideration, the integral of J over time at x = 0 provides the quantity of diffusing substance arriving at the surface, whilst that of $\frac{\partial C}{\partial t}$ at various values of x provides the quantity of accumulation or depletion of diffusing substance in the material.)

Since most commonly encountered materials are uniform with respect to heat conduction, the Fourier equations provide a complete account of thermal conduction for those materials. Unfortunately, however, since, in the general case, materials cannot be treated as uniform with respect to diffusion, the basic Fick equations do not completely describe vapour diffusion. For diffusion in a gaseous medium, because concentration C is defined in terms of mass per unit volume, both equations only hold for isothermal conditions. Because of the peculiar nature of hygroscopic materials, neither equation holds as it stands for water vapour diffusion, even under isothermal conditions.

Hygroscopic materials are distinguished by the non-linearity of the moisture concentration/partial vapour pressure relationship under isothermal conditions, and the dependence of this relationship, given constant mass per mass concentration and isobaric conditions, on temperature. Whereas, for ideal gases, by the Gas Laws and Dalton's Law, under isobaric and isothermal conditions, the partial pressure/ concentration curve for any particular component gas in a mixture is linear, under the same conditions, for water vapour in a hygroscopic medium, the curve is sigmoid in shape. Further, whereas, for ideal gases, under isobaric and constant mass per mass concentration, the partial pressure is constant with varying temperature, in a hygroscopic medium, the partial pressure of water vapour varies with temperature in a complex way. In effect, the concentration of moisture in the medium determines a constant proportion of the saturated vapour pressure, this latter varying in a complex way with temperature.

Thus, if diffusion through such materials is to be considered as in some way analogous to diffusion in a purely gaseous medium, a distinction must be made between concentration in the inter and, by assumption, intra-particle airspaces, and that in the medium as a whole. With this distinction, the above equations, valid only under isothermal conditions, become:

$$J = -D \frac{\partial C_i}{\partial x} \qquad \text{.......(2.1.5)}$$

$$\frac{\partial C_b}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} \qquad \text{.......(2.1.6)}$$

where C_i is the interstitial concentration
and C_b is the concentration in the medium as a whole,

and a set of further equations is necessary relating these concentrations for each temperature, θ:

$$C_i = f_\theta(C_b)$$

In order to extend the equations (2.1.3) and (2.1.4) to cover non-isothermal conditions for gaseous diffusion in a gaseous medium, a form of Fick's first equation is:

$$J_m = -D \frac{\partial C_m}{\partial x} \qquad \text{.......(2.1.7)}$$

where J_m is the molar rate of diffusion per unit area,
D the coefficient of diffusion and
C_m the molar concentration.

For an ideal gas

$$pV = nRT$$

where n is the number of moles of diffusing substance in the volume V.

and T is the absolute gas temperature (K)

$$p = \frac{n}{V} RT = C_m RT$$

Substituting in equation (2.1.7):

$$J = \frac{-D}{RT} \frac{\partial p}{\partial x}$$

From this may be derived an analogue of Fick's second equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[\frac{D}{RT} \frac{\partial p}{\partial x} \right] \qquad ....(2.1.8)$$

Thorpe (1981) quotes Kusuda (in Wexler, 1965) as recommending as an expression for the diffusion coefficient of water vapour through air:

$$D = 9.1 \times 10^{-9} \frac{T^{2.5}}{(T+245.18)} .$$

Thus, the dependence of D on temperature is of the form:

$$k \frac{T^{2.5}}{(T+245.18)} ,$$

and of $\dfrac{D}{RT}$:

$$k \frac{T^{1.5}}{(T+245.18)} .$$

For the temperature range of interest, 0 to 40°C, the deviation from the value at 20°C is reduced from ± 13.5% for D to ± 6.5% for D/RT. In practical cases the latter deviation is usually ignored (for example, Thorpe, 1981 and 1982) and equation (2.1.8) is simplified to:

$$\frac{\partial C}{\partial t} = \frac{D}{RT} \frac{\partial^2 p}{\partial x^2} \qquad \text{.......(2.1.9)}$$

The validity of this simplification is examined in section 8.

Using the equations (2.1.7) and (2.1.9) as an analogy, whilst refraining from identifying D′ with $\dfrac{D}{RT}$ at this time, the above equations (2.1.5) and (2.1.8) may be generalised for hygroscopic media as:

$$J = -D' \frac{\partial p}{\partial x} \qquad \text{.......(2.1.10)}$$

$$\frac{\partial C}{\partial t} = D' \frac{\partial^2 p}{\partial x^2} \qquad \text{.......(2.1.11)}$$

where $p(x,t)$ is the interstitial vapour pressure at time t, at distance x along the direction of diffusion,

D' the coefficient of diffusion relative to vapour pressure gradient,

and C is now C_b.

2.2 EQUATIONS ASSUMING NEGLIGIBLE CHANGE IN CONCENTRATION

In the real world case of moisture migration during the type of voyage described in the introduction, the vapour pressure gradient is the result of a temperature gradient and the effects of the concentration gradient are usually negligible. In this case, then, the diffusion equations may be rewritten:

$$J = -D' \frac{\partial p}{\partial \theta} \frac{\partial \theta}{\partial x} \qquad \text{.......(2.2.1)}$$

$$\frac{\partial C}{\partial t} = D' \left[\frac{\partial p}{\partial \theta} \cdot \frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 p}{\partial \theta^2} \cdot \left(\frac{\partial \theta}{\partial x} \right)^2 \right] \qquad \text{..(2.2.2)}$$

where $\theta(x,t)$ is the temperature at time t, at distance x in the direction of diffusion (θ rather than T because the temperature scale is arbitrary, rather than absolute gas temperature),

and $p(\theta)$ is the vapour pressure corresponding to the temperature θ, at the assumed constant relative humidity.

When a stow is cooled at its surface, it behaves as a semi-infinite slab, the size of the stow, the time of the voyage and the magnitude of the thermal diffusion coefficient combining to ensure that the majority of the cargo is still at the loading temperature at the end of the voyage. In such a case, the thermal gradient at right angles to the surface is at any particular time steepest at the surface. The vapour pressure/temperature gradient, however, is most gradual at low temperatures, or, when the surface is being cooled, at the surface. It was supposed that these two opposite curvatures would combine to yield a nearly linear vapour pressure/distance into stow curve, which, by equation (2.1.11), would imply negligible accumulation in the stow. That is, with θ at a minimum at $x = 0$, $|\partial p/\partial\theta|_{x=0}$ is at a minimum, while $|\partial\theta/\partial x|_{x=0}$ is at a maximum, and vice versa at a distance into the stow. Thus, the composite, $\partial p/\partial\theta \times \partial\theta/\partial x$, would be more constant with varying x than either of its components, as long as the ratio of $|\partial p/\partial\theta|_{x=0}$ to $|\partial p/\partial\theta|_{x=d}$ was of a similar magnitude to that of $|\partial\theta/\partial x|_{x=d}$ to $|\partial\theta/\partial x|_{x=0}$ at various distances, d, into the stow.

In order to fix the meaning of "more constant" and "similar magnitude", the above argument may be formalised:

from the physical factors discussed above, we have over the region of the temperature gradient:

with f as $\partial p/\partial\theta$ and

g as $\partial\theta/\partial x$

$$\forall x_i \forall x_j \; (x_i < x_j \rightarrow (|f|_{x_i} < |f|_{x_j} \wedge |g|_{x_j} < |g|_{x_i}))$$

so

$|f|_{x_j}$ can be represented by $b_{ij}|f|_{x_i}$

and $|g|_{x_j}$ by $\dfrac{1}{a_{ij}} |g|_{x_i}$

with a_{ij} and b_{ij} positive reals > 1,

thus,

$$|\partial p/\partial x|_{x_j} = \frac{b_{ij}}{a_{ij}} |\partial p/\partial x|_{x_i}$$

Then, over the region of temperature gradient, $\partial p/\partial x$ is more constant than either of its components iff

$$\forall x_i \forall x_j \; (x_i < x_j \rightarrow (a_{ij} < b_{ij}^2 \wedge b_{ij} < a_{ij}^2))$$

This criterion is applied to data from a simulation of the conditions of a typical voyage in section 6, where it may be seen that a linear temperature gradient would provide less variation in $\partial p/\partial x$ than the unsteady state temperature gradient for the types of material and time period of the average voyage. Other justifications for this simplified treatment of the diffusion equations, depending on these particular conditions of the average voyage, are also discussed in section 6.

The further analysis of equations (2.2.1) and (2.2.2) may be divided into two sections, the relation of vapour pressure to temperature and the temperature profiles developed as a result of cooling at the surface.

2.2.1 The relation of vapour pressure to temperature

The relation of vapour pressure to temperature is provided by the empirically derived Magnus formula:

$$\log_{10} p_{sat} = \frac{B\,\theta}{C + \theta} + D$$

where p_{sat} is the saturated vapour pressure,
and B, C, D are empirically determined constants:
$B = 7.5 \qquad C = 237.3 \qquad D = 0.78571$
with p_{sat} in millibars, and θ in $^{\circ}$C.

(It may be remembered that hygroscopic materials create an interstitial water vapour pressure which is a proportion, fixed by moisture content, of the saturated vapour pressure at the temperature of the material.)

Since $\ln p = 2.3026 \log_{10} p$

$$p_{sat} = \exp\left[2.3026\left[\frac{B\,\theta}{C + \theta} + D\right]\right]$$

or

$$p_{sat} = \exp\left[\frac{B\,\theta}{C + \theta} + D\right]$$

where $\mathbf{B} = 2.3026\ B = 17.269$

$\mathbf{D} = 2.3026\ D = 1.80916$

$\mathbf{C} = C \qquad = 237.3$

By the definition of relative humidity

$$p_{RH} = \frac{RH}{100}\, p_{sat}$$

where p_{RH} is the vapour pressure at relative humidity RH,

and RH is the percentage relative humidity.

Expressions for $\frac{\partial p}{\partial \theta}$ and $\frac{\partial^2 p}{\partial \theta^2}$ may be obtained from the above:

$$\frac{\partial p}{\partial \theta} = \frac{RH}{100} \cdot \frac{\mathbf{CB}}{(\mathbf{C}+\theta)^2} \cdot \exp\left[\frac{\mathbf{B}\theta}{\mathbf{C}+\theta} + \mathbf{D}\right]$$

$$\frac{\partial^2 p}{\partial \theta^2} = \frac{RH}{100} \cdot \frac{\mathbf{C}^2\mathbf{B}^2 - 2\mathbf{CB}(\mathbf{C}+\theta)}{(\mathbf{C}+\theta)^4} \cdot \exp\left[\frac{\mathbf{B}\theta}{\mathbf{C}+\theta} + \mathbf{D}\right]$$

2.2.2 The relation of temperature to distance into the stow

As mentioned above, because of the combined effects of the size of stow, the time of voyage and the magnitude of the thermal diffusion coefficient for the types of hygroscopic materials carried, for the purposes of modelling the temperatures in a stow, it may be characterised as a semi-infinite slab.

A general equation for thermal conduction into a semi-infinite slab is:

$$u(x,t) = \frac{2}{\sqrt{\pi}} \int_{X}^{\infty} e^{-\beta^2} F\left(t - \frac{x^2}{4\alpha_H^2\beta^2} \right) d\beta$$

$$= \frac{2}{\sqrt{\pi}} \int_{X}^{\infty} e^{-\beta^2} F\left[t \left[1 - \frac{X^2}{\beta^2} \right]\right] d\beta$$

where u(x,t) is the difference in temperature from the initial after time t at depth x

F(t) is the difference in temperature from the initial applied at the surface at time t

$$X = \frac{x}{2\alpha_H\sqrt{t}}$$

and $\alpha_H = \sqrt{\frac{k}{\rho C_p}}$

with k the thermal conductivity

ρ the density

and C_p the specific heat at constant pressure

A special case of this occurs when F(t) is constant, that is, when a constant temperature is suddenly applied, the step function temperature. The above equation then reduces to:

$$u(x,t) = \frac{2\,F}{\sqrt{\pi}} \int_{X}^{\infty} e^{-\beta^2}\, d\beta$$

The above equations are formulated in terms of temperature difference, rather than temperature itself. If θ_i is the initial uniform temperature of the "slab", then $u(x,t)$ is $\theta(x,t) - \theta_i$ and $F(t)$ is $\theta_{\mathrm{applied}}(t) - \theta_i$. It is apparent by inspection that $\frac{\partial \theta}{\partial x} = \frac{\partial u}{\partial x}$, as θ_i is a constant.

Leibniz' Rule for the differentiation of integrals provides the schema:

$$\frac{d}{dx} \int_{u(x)}^{v(x)} f(x,t)\, dt$$

$$= \int_{u}^{v} \frac{df}{dx}\, dt + f(x,v)\, \frac{dv}{dx} - f(x,u)\, \frac{du}{dx}$$

and, applying it to the above general equation, yields:

$$\frac{\partial u}{\partial x} = \frac{2}{\sqrt{\pi}} \left[\int_{X}^{\infty} \frac{\partial}{\partial x} \left[e^{-\beta^2} . F\left[t \left[1 - \frac{X^2}{\beta^2} \right] \right] \right] d\beta \right.$$

$$\left. - e^{-X^2} . F\left[t \left[1 - \frac{X^2}{X^2} \right] \right] \frac{\partial X}{\partial x} \right]$$

since $e^{-\beta^2} \longrightarrow 0$ as $\beta \longrightarrow \infty$ and F(t) is finite.

The second term on the right hand side reduces to:

$$- \frac{1}{2\alpha_H \sqrt{t}} e^{-X^2} F(0)$$

and the first term to:

$$\int_{X}^{\infty} e^{-\beta^2} . \frac{dF}{ds} \frac{\partial s}{\partial X} \frac{\partial X}{\partial x} d\beta$$

where:

$$s = t\left(1 - \frac{X^2}{\beta^2}\right) \qquad \frac{\partial s}{\partial X} = -\frac{2Xt}{\beta^2}$$

$$X = \frac{x}{2\alpha_H\sqrt{t}} \qquad \frac{\partial X}{\partial x} = \frac{1}{2\alpha_H\sqrt{t}}$$

Substituting:

$$-\frac{x}{2\alpha_H^2}\int_X^{\infty} \frac{e^{-\beta^2}}{\beta^2} F'\left[t\left(1 - \frac{X^2}{\beta^2}\right)\right] d\beta$$

Putting these two expressions together and multiplying by $\frac{2}{\sqrt{\pi}}$:

$$\frac{\partial u}{\partial x} = -\frac{e^{-X^2}}{\alpha_H\sqrt{\pi}\sqrt{t}} \,.\, F(0)$$

$$-\frac{x}{\alpha_H^2\sqrt{\pi}} \,.\, \int_X^{\infty} \frac{e^{-\beta^2}}{\beta^2} F'\left[t\left(1 - \frac{X^2}{\beta^2}\right)\right] d\beta$$

This expression for $\frac{\partial u}{\partial x}$ may be substituted for $\frac{\partial \theta}{\partial x}$ in equation (2.2.1). For very small x, however, where the value of $\partial\theta/\partial x$ is needed for the calculation of total flow to the surface, the evaluation of the integral becomes computationally problematic, since, as β nears 0, $e^{-\beta^2}/\beta^2$ becomes very large, and the integral is multiplied by the very small value of x.

Solutions of the original heat diffusion equation are available using the Laplace Transform, but, being specific to the particular boundary conditions in effect, are not directly applicable to the case involving an arbitrary applied temperature function, F(t).

For the case where the applied temperature (i.e. F) is a constant, and $F' = 0$, the step function temperature case, the expression reduces to:

$$\frac{\partial u}{\partial x} = - \frac{e^{-X^2}}{\alpha_H \sqrt{\pi} \sqrt{t}} \cdot F$$

For the calculation of accumulation of moisture in the stow, using the integration over time of the right hand side of equation (2.2.2), a numerical method of calculating $\frac{\partial^2\theta}{\partial x^2}$ is used.

The considerably simpler theory used in the first series of experiments, described in section 5, arose from the constant and linear temperature gradient imposed by the lagged thick walled aluminium tube used.

Hence, in this case:

$$\theta = k.x$$

$$\frac{d\theta}{dx} = k$$

and $$\frac{d^2\theta}{dx^2} = 0$$

which considerably simplifies the analysis of equations (2.2.1) and (2.2.2), i.e.

$$J = -D' \frac{\partial p}{\partial \theta} k \qquad \text{............(2.2.2.1)}$$

$$\frac{\partial C}{\partial t} = D' \frac{\partial^2 p}{\partial \theta^2} k^2 \qquad \text{............(2.2.2.2)}$$

2.3 EQUATIONS FOR ISOTHERMAL DIFFUSION

The equations for diffusion under these conditions in a hygroscopic medium have been set out above (equations (2.1.5) and (2.1.6)), but are not complete in the sense that an equation giving the relationship of C_i to C_b for the particular medium is also required. This would take the form of an experimentally determined C_b/ERH relationship, the relation between p_{sat} and temperature used in the previous section, and the relation between temperature, vapour pressure and moisture concentration in free air. If this is not done, as has usually been the case, and the basic equations (2.1.3) and (2.1.4) are used, with C being taken to be C_b, then the diffusion coefficient D obtained is specific not only to one temperature but also to one concentration, and thus is of little other than phenomenological use, unless further interpreted. Since the further interpretation would involve the interstitial vapour pressure, which would then determine the interstitial concentration, there is a simplification in omitting this last step, and using a diffusion coefficient dependent on vapour pressure gradient.

In order to allow direct comparison with the results of Becker and Sallans (1955) for wheat, calculation of an intra-particle diffusion coefficient for cocoa used their method for calculating D. The values for both cocoa and wheat were then converted to D′ for further comparison.

The solution of equation (2.1.4) for isothermal diffusion out of a sphere is derived in Crank (1975), p.89 ff, the form which yields Becker and Sallans (1955) equation being equation 6.22 in Crank (1975), p.91:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-Dn^2\pi^2 t/a^2\right)$$

where a is Becker and Sallans r_o, radius of sphere,
M_t is the total amount of diffusing substance that has entered or left the sphere after time t,

M_∞ is the total amount of diffusing substance that has entered or left the sphere after an infinite time.

M_t is, thus, Becker and Sallans $(m_o - \bar{m}) \times w/100$ and
M_∞ is $(m_o - m_e) \times w/100$,

where $\bar{m}$ is the average moisture content (%) after time, t,
m_o is the uniform initial moisture content (%),
m_e is the surface moisture content (%) (i.e. $\bar{m}$ as t tends to ∞), and
w is the dry weight of a sphere.

Rearranging Crank's equation, one obtains:

$$1 - \left[\frac{m_o - \bar{m}}{m_o - m_e}\right] = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-Dn^2\pi^2t/a^2\right)$$

where the left hand side may be rearranged to give:

$$\frac{\bar{m} - m_e}{m_o - m_e}$$

The latter form is used in section 7 to determine an intra-particle diffusion coefficient for cocoa which is directly comparable with that for wheat found by Becker and Sallans (1955).

2.4 EQUATIONS ALLOWING FOR CHANGE IN CONCENTRATION AND A THERMAL GRADIENT

In this case, there are no generally simplifying analytic approaches to the basic equations (2.1.10) and (2.1.11), and the numerical method of solution to be used must be considered, in order to decide how to transform the equation into a soluble form.

Of the various finite difference methods available for the approximate solution of stiff parabolic partial differential equations, the most widely used are the FTCS (forward time, centre space) explicit method, which may be simplified in the linear case to Schmidt's method, and the Crank Nicolson implicit method.

2.4.1 FTCS explicit method

This method approximates equations of the form:

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

by substituting the usual numerical approximation of the second differential for the term on the right hand side of the above equation, that is:

$$\frac{\partial^2 C}{\partial x^2} \simeq \frac{C(x - \delta x) - 2C(x) + C(x + \delta x)}{(\delta x)^2}$$

whence:

$$\frac{\delta C}{\delta t} = D \cdot \frac{C(x - \delta x) - 2C(x) + C(x + \delta x)}{(\delta x)^2}$$

or:

$$\delta C = \frac{D\ \delta t}{(\delta x)^2} (C(x - \delta x) - 2C(x) + C(x + \delta x))$$

By choice of δt and δx, we may put:

$$r = \frac{D\delta t}{(\delta x)^2} = \frac{1}{2} \qquad ....(2.4.1.1)$$

when:

$$\delta C = \frac{C(x - \delta x) + C(x + \delta x)}{2} - C(x)$$

Since $C(x) + \delta C$ is $C(x)_{t+\delta t}$, we have:

$$C(x)_{t+\delta t} = \frac{C(x - \delta x) + C(x + \delta x)}{2}$$

which is the simplified formula used in Schmidt's method.

This method is stable, in this linear case, for values of r in equation (2.4.1.1) less than or equal to 1/2.

Reformulated to:

$$\delta C = \frac{D'\ \delta t}{(\delta x)^2} (p(x-\delta x) - 2p(x) + p(x+\delta x))$$

this method was used to provide approximate solutions to equation (2.1.8); the problem of stability of this more complex form is discused in section 8.

2.4.2 Crank Nicolson method

(Crank and Nicolson, 1947)

This method provides numerical approximations of equations of the same form as the above:

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

In this method, the equation is considered equivalent to:

$$\left[\frac{\partial C}{\partial t}\right]_{(x,(t+\delta t/2))} = D \left[\frac{\left[\frac{\partial^2 C}{\partial x^2}\right]_{(x,t)} + \left[\frac{\partial^2 C}{\partial x^2}\right]_{(x,(t+\delta t))}}{2}\right]$$

The left hand side may be numerically evaluated as:

$$\frac{C(x,(t+\delta t)) - C(x,t)}{\delta t}$$

and the right hand side as:

$$\frac{D}{2}\left[\frac{C((x+\delta x),t) - 2C(x,t) + C((x-\delta x),t)}{(\delta x)^2}\right.$$

$$\left.+\ \frac{C((x+\delta x),(t+\delta t)) - 2C((x+\delta x),t) + C((x+\delta x),(t-\delta t))}{(\delta x)^2}\right]$$

where C(x,t) is the concentration at point x at time t.

Putting $r = \frac{D\delta t}{(\delta x)^2}$, the equation may be rewritten:

$$\begin{aligned} &- rC((x-\delta x),(t+\delta t)) + (2+2r)C(x,(t+\delta t)) \\ &\qquad - rC((x+\delta x),(t+\delta t)) \\ &= rC((x-\delta x),t) + (2-2r)C(x,t) + rC((x+\delta x),t) \end{aligned}$$

or, by choice of δt and δx, putting $r = 1$:

$$\begin{aligned} &- C((x-\delta x),(t+\delta t)) + 4C(x,(t+\delta t)) - C((x+\delta x),(t+\delta t)) \\ &\qquad = C((x-\delta x),t) + C((x+\delta x),t) \end{aligned}$$

This method is unconditionally stable in the linear case.

Thus, the Crank Nicolson method, when applied to the simple diffusion equation, gives rise to a set of simultaneous linear equations, which may be solved using matrix methods. There are, however, limitations on this method, in that, unless the equation to be approximated can be manipulated into a form similar to this simple equation, it is necessary to solve a set of non-linear equations at each time step.

It is to be seen, then, whether the general diffusion equation for hygroscopic materials can be manipulated into such a form.

To emphasise that this is algebraic manipulation, without assumption as to the constancy of the D's, a different nomenclature is used. Whereas, for hygroscopic materials, to obtain a true D one must calculate the vapour pressure gradient in the air spaces, which gives legitimacy to D' as a physical value, here the concern is rather to obtain a numerical solution by algebraic manipulation.

For gaseous diffusion in a gaseous medium:

$$\frac{\partial c}{\partial t} = D_{cc}\frac{\partial^2 c}{\partial x^2} \qquad \text{..........(2.4.2.1)}$$

$$\frac{\partial c}{\partial t} = D_{cp}\frac{\partial^2 p}{\partial x^2} \qquad \text{..........(2.4.2.2)}$$

$$\frac{\partial p}{\partial t} = D_{pp}\frac{\partial^2 p}{\partial x^2} \qquad \text{..........(2.4.2.3)}$$

with all D's constant for constant temperature.

For gaseous diffusion in a hygroscopic porous medium:

Equation (2.4.2.2) holds with constant D_{cp}, by derivation from the original Fick equation, modified for hygroscopic materials, the vapour pressure being a measure of the interstitial moisture concentration; equation (2.4.2.1), unless rewritten in the form of equation (2.1.6), when it is equivalent to (2.4.2.2), and equation (2.4.2.3) do not hold with constant D's, because the ERH/MC relationship is not linear.

Because of the requirement for similar quantities on each side of the equation, to solve (2.4.2.2) numerically by the Crank Nicolson method, it should be reformulated in the form of (2.4.2.1) or (2.4.2.3), with D a function of some or all of x, p, C;

i.e. for (2.4.2.1)

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} D_{cp} f(x,p,c) \frac{\partial C}{\partial x} .$$

To demonstrate the problems involved in these courses, an attempt is made to analyse equation (2.4.2.2) into a form similar to that of (2.4.2.1).

At any point x:

$$p = ERH(C_x).MF(\theta_x)$$

where ERH(C) is the equilibrium relative humidity corresponding to the concentration C

MF(θ) is the saturated vapour pressure corresponding to the temperature θ

C_x is the concentration at the point x

and θ_x is the temperature at the point x

From Fick's second law, we have then:

$$\frac{\partial C}{\partial t} = D_{cp} \frac{\partial^2 p}{\partial x^2}$$

$$\begin{aligned} &= D_{cp} \Bigg\{ ERH(C_x) . \frac{\partial^2}{\partial x^2} MF(\theta_x) \\ &\quad + 2 \frac{\partial}{\partial x} ERH(C_x) . \frac{\partial}{\partial x} MF(\theta_x) \\ &\quad + \left[\frac{\partial^2}{\partial x^2} ERH(C_x) \right] . MF(\theta_x) \Bigg] \end{aligned}$$

From the theoretical work set out in section 2.2.1, we have already expressions for:

$$MF(\theta_x) \qquad \frac{\partial}{\partial x} MF(\theta_x) \qquad \frac{\partial^2}{\partial x^2} MF(\theta_x)$$

as simple functions of x, and they may be renamed as:

$$f(x) \qquad g(x) \qquad h(x)$$

respectively.

Similarly, expressions may be obtained by curve fitting to tabulated values for:

$$\mathrm{ERH}(C) \qquad \frac{\partial}{\partial C}\mathrm{ERH}(C) \qquad \frac{\partial^2}{\partial C^2}\mathrm{ERH}(C)$$

as functions of C, and may be renamed as:

$$u(C) \qquad v(C) \qquad w(C)$$

respectively.

Then:

$$\frac{\partial}{\partial x}\mathrm{ERH}(C_x) = \frac{\partial}{\partial C}\mathrm{ERH}(C) \cdot \frac{\partial C}{\partial x}$$

$$= v(C) \cdot \frac{\partial C}{\partial x}$$

and:

$$\frac{\partial^2}{\partial x^2}\mathrm{ERH}(C_x) = \frac{\partial}{\partial C}\mathrm{ERH}(C) \cdot \frac{\partial^2 C}{\partial x^2} + \left[\frac{\partial C}{\partial x}\right]^2 \cdot \frac{\partial^2}{\partial C^2}\mathrm{ERH}(C)$$

$$= v(C) \cdot \frac{\partial^2 C}{\partial x^2} + w(C) \cdot \left[\frac{\partial C}{\partial x}\right]^2$$

From the above, then:

$$\frac{\partial C}{\partial t} = D_{cp} \left[h(x).u(C) + 2\, g(x).v(C).\frac{\partial C}{\partial x} + f(x) \left\{ v(C).\frac{\partial^2 C}{\partial x^2} + w(C).\left(\frac{\partial C}{\partial x}\right)^2 \right\} \right]$$

Thus, although a decomposition into an equation involving effectively only C (and it is C_b on both sides) has been obtained, the equation is too complex to be reduced to a set of linear equations by the Crank Nicolson method.

Limitation to the case of a thermal gradient constant with respect to time allows another approach, and this is acceptable for the purpose of analysing the results of the closed tube experiment, described in section 8. Since the choice of a numerical method must depend on a detailed assessment of the particular conditions of the experiment it is intended to model, a fuller discussion is included in that section.

The aim is to manipulate equation (2.4.2.2):

$$\frac{\partial C}{\partial t} = D_{cp} \frac{\partial^2 p}{\partial x^2}$$

into the form of equation (2.4.2.3):

$$\frac{\partial p}{\partial t} = D_{pp} \frac{\partial^2 p}{\partial x^2}$$

Since

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial p} \cdot \frac{\partial p}{\partial t}$$

(as C(p,x) only depends on t via p's dependence on t, as long as the temperature gradient is constant through time (otherwise, C(p,x), which is really C(p,θ(x)), should be C(p,θ(x,t)))

then

$$\frac{\partial p}{\partial t} = \left[\frac{D_{cp}}{{}^{\partial C}/_{\partial p}} \right] \frac{\partial^2 p}{\partial x^2}$$

(This is also more suitable, as the end conditions for the closed tube, $\frac{\partial p}{\partial x} = 0$, at x = 0 and x = 1, are not easily expressed in terms of C (except in isothermal cases, when $\frac{\partial C}{\partial x} = 0$).)

Unfortunately, the $\left[\frac{D_{cp}}{{}^{\partial C}/_{\partial p}} \right]$ term is a variable diffusion coefficient, dependent on the variable to be solved, p, leading again to a set of non-linear simultaneous equations, if the Crank Nicolson method is used.

A three time level implicit finite difference method was found that could be used to approximate equations of the form:

$$\frac{\partial C}{\partial p}\frac{\partial p}{\partial t} = D_{cp}\frac{\partial^2 p}{\partial x^2}$$

or

$$\frac{\partial C}{\partial p}\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[D_{cp}(x)\frac{\partial p}{\partial x}\right]$$

using only linear matrix methods, and this is described in section 8.

3. APPLICATION OF THEORY TO EXPERIMENTAL WORK

Two types of experiment were carried out using the theoretical analysis of section 2.2. In the first series, a steady state near linear temperature gradient was ensured by using a lagged thick-walled aluminium tube to contain the cocoa beans, whilst moisture flow was unsteady state, but developing from a constant relative humidity at the high temperature end.

In the second series, both the temperature gradient and the moisture flow were unsteady state. The case of varying or constant low applied temperatures has important directly practical applications to the situation when a vessel loads a warm cargo and carries it to a colder port. In order to ensure an axial flow of heat in the tube, that is, to allow the use of an analysis in terms of a semi-infinite slab, and so mimic the conditions in the hold of a ship, the experiments used a larger diameter PVC tube of low thermal conductivity, efficiently lagged.

The case of isothermal conditions with diffusion dependent on a concentration gradient alone, the theory of which was discussed in section 2.3, although used by many workers in this field (for example, Pixton and Griffiths, 1971) was not considered as directly relevant to conditions during the carriage of a cargo. Since most cargoes are loaded at a fairly consistent moisture content, and most voyages are of two weeks to a month in length, the readjustment of moisture contents in the interior of the stow as the result of isothermal diffusion is generally of little import. The rapidly changing ambient temperatures during many voyages, on the other hand, give rise to significant temperature gradients near the surface of a stow, raising the question of whether moisture diffusion as a result of these gradients is of a non-negligible quantity.

The measurement, however, of the diffusion coefficient into the individual bean, rather than through the bulk, is most simply carried out under isothermal conditions. The assessment of this intra-particle diffusion coefficient was found to be very relevant to an understanding of the interrelationship between the rate of diffusion through the air spaces, that through the beans themselves, and the resultant bulk diffusion rate. An experiment, similar in principle to that of Becker and Sallans (1955), but, of course, using cocoa rather than wheat, was therefore carried out.

The theory of section 2.4, the general case, was used for the analysis of the results of an experiment, using the same lagged aluminium tube as used in the first series of experiments, but with both ends sealed. The temperature gradient was thus steady state and near linear, whilst the moisture flow resulted in a non-negligible redistribution of concentration.

A similar experiment on wheat was carried out by Griffiths (1964), analysed by Thorpe (1982), but, whereas in that experiment a temperature gradient was set up between two plates, eventually reaching a steady state constant linear gradient by thermal conduction through the wheat, in the "closed tube" experiment, this was ensured from very shortly after the start of the experiment by the highly conductive aluminium tube, lagged to minimise heat loss to the ambient air. Also, the greater length of material through which diffusion took place, permitted by the use of the tube to control the thermal gradient, allowed the measurement of weight loss and gain of a number of samples spread along the tube, thus compensating to some extent for the inherent inconsistency of moisture content in the cocoa bean.

4. MOISTURE CONTENT VARIABILITY IN THE COCOA BEAN

4.1 VARIABILITY OF MOISTURE CONTENT DURING INITIAL EXPERIMENTAL WORK

Early experiments highlighted a problem of repeatability, which was considered likely to be the result of an insufficiently consistent method of moisture content determination. The redistribution of moisture in the beans at the end of the repeated experiments showed no discernible pattern, and it appeared that the method of determining moisture content used might have had no greater consistency than the increase or decrease in moisture content experienced as a result of the conditions of the experiment.

4.2 ASSESSMENT OF VARIOUS METHODS OF MOISTURE CONTENT DETERMINATION

A series of experiments was undertaken to compare alternative methods. The effects of three parameters considered likely to affect accuracy were investigated:

a. using ground or whole samples,

b. drying at atmospheric pressure or in a vacuum oven,

c. drying at or below the standard temperature of 105°C.

(As, at atmospheric pressure and at 105°C, the drying time was considered as long as practical, experiments using temperatures lower than 105°C were limited to those carried out in a vacuum oven.)

The standard method used previously was the drying, at atmospheric pressure, in an oven equipped with fan assisted circulation, at a temperature of 105°C, of samples ground to a coarse meal in a domestic electric coffee grinder. Moisture content was then calculated on a wet basis (i.e. weight loss due to drying as a percentage of the pre-dried weight).

The first tests concerned the use of whole bean samples rather than ground, in order to avoid variation due to the following:

a. grinding did not produce a homogeneous meal, and it was difficult to ensure that each sample contained the whole spectrum of particle sizes in the correct proportions,

b. it was difficult to remove all the fines (which are slightly oily) from the grinder,

c. it was considered possible that the heat produced during grinding might cause varying amounts of moisture loss especially amongst the fines,

d. it was considered possible that, during drying, the draught in the oven might blow some of the fines out of the sample dishes.

The possibility of using a lower temperature and a shorter drying time by employing a vacuum oven was also investigated. Tests were carried out at 70 and 85°C, but drying times were not comparable with the standard method at temperatures below 95°C.

As the experiments were carried out over a period of time, three sample groups were used. Each was conditioned in a closed bag for four weeks, yielding groups each equilibrated within itself, though not to any fixed relative humidity, nor to another group.

4.2.1 Results at atmospheric pressure, 105°C (oven with fan assisted circulation)

Sample group A

hrs drying	apparent m/c (%)			
	whole beans		ground beans	
	no.1		no.2	
17	7.81		7.69	
24	7.84		7.79	
42	7.88		7.89	
66	8.10		8.07	
72	8.10		8.07	
	no.3		no.4	
39	7.72		7.78	
63	8.03		8.14	
70	8.03		8.14	
	whole beans		ground beans	
	no.5	no.6	no.7	no.8
40	7.91	7.59	8.05	7.43

66	8.18	7.87	8.36	7.70
72	8.18	7.88	8.36	7.70

(samples 6 and 8 were taken from a different bottle, which seems not to have been effectively sealed)

4.2.2 Results at atmospheric presure, 105°C
(oven without fan)

Sample group C

hrs drying	apparent m/c (%)			
	whole beans		ground beans	
	no.1	no.2	no.3	no.4
4.5	4.58	4.98	5.33	5.71
24.5	6.00	6.12	6.08	6.43
28	6.03	6.14	6.12	6.46
71	6.14	6.29	6.17	6.54
77.5	6.15	6.31	6.20	6.55

4.2.3 Results of drying in a vacuum oven, 85°C

Sample group B

hrs drying	apparent m/c (%)			
	whole beans			
	no.1	no.2	no.3	no.4
4.5	6.07	5.96		
47	7.59	7.57	7.73	7.76
52.5	7.64	7.62	7.75	7.82
143	7.98	7.94	8.03	8.09

147.5	7.86	7.94	8.07	8.10

4.2.4 Results of drying in a vacuum oven, 95°C

Sample group C

hrs drying	apparent m/c (%)			
		whole beans		
	no.1	no.2	no.3	no.4
19	5.61	5.53	5.67	5.70
24.5	5.71	5.62	5.72	5.81
43.5	5.80	5.82	5.90	5.94
48.5	5.86	5.86	5.93	5.99
92.5	6.00	6.05	6.05	6.19
96.5	6.00	6.06	6.05	6.19
		ground beans		
	no.5		no.7	no.8
4.5	5.18		5.59	5.59
24.5	5.84		6.10	6.21
28	5.85		6.13	6.23
71	6.19		6.38	6.52
78.5	6.20		6.39	6.52

(sample 6 was discarded after accidental spillage)

The method used by Henderson (1984) as being close to the International Standard method (ISO 2291-1972E)

"which involved grinding between 10 and 15 beans with a pestle and mortar, then drying duplicate 5 g samples for 16 hr at 103°C" produced results with rather greater sample to sample variation than the above.

Since none of the above methods had displayed any great improvement in consistency, a compromise method was adopted for all the following experiments except where otherwise stated. The beans were ground in a domestic coffee grinder, producing a finer meal than could be obtained using a pestle and mortar, divided into lots of some 10g, and then dried in an oven with fan assisted circulation for 25 hours at 105°C.

4.3 ASSESSMENT OF MOISTURE CONTENT VARIABILITY

Henderson (1984) describes her results:

"The moisture content equilibrium relative humidity relationships for cocoa beans grown in nine different countries were similar to each other, and the maximum safe storage moisture content in equilibrium with 70% relative humidity was between 6.0 and 7.9% at 25°C. There was a large variation between the moisture content of individual beans within each sample, the maximum standard deviation observed in a sample of thirty beans being 0.97, after the moisture content had been increased by adding water."

and, further,

"It is usual with cereal grains (Pixton and Warburton, 1971; Pixton and Henderson, 1981) for the difference between duplicate m.c. results to be 0.2% m.c. or less, and the difference between the extremes of the four results to be 0.5% m.c. or less. The method used to determine the m.c. of cocoa beans stipulates a difference not exceeding 0.3% m.c. between replicates, or the results should be disregarded. Results of this and later investigations, however, frequently showed differences in excess of this amount especially at high moisture contents and it was, therefore, decided to accept all results."

It should be noted that cereal grains have an equilibrium moisture content about twice that of cocoa, and the usual 0.2% variability in cereal moisture contents found by researchers cited above would correspond to a variability in cocoa moisture content of 0.1%. It appears, though, that even for cereal grains variability due to differences in methods of measurement, whether such differences are intentional or otherwise, is more of a problem than generally recognised (see Henderson, 1986, and Henderson and Wilkin, 1985 and 1987).

Whilst it is undoubtedly true that, with respect to this relationship:

"the biggest differences are those between oily and non-oily seeds; the former reach lower moisture contents at equivalent r.h. values to an extent dependent on the oil content. Recalculation of the moisture content on a fat-free dry matter basis usually adjusts the values to a similar order to those for non-oily seeds." (Nellist and Hughes, 1973, p.617), the problem of variability in this relationship for cocoa beans seems to be based on differences between individual beans, and standard methods of fat content analysis require samples of some 200g.

Since the Henderson paper was unable to account for the much greater variability in this property in cocoa beans, an investigation was undertaken. It seemed likely that the fibrous husk of the bean would be low in fat, and, thus, have a higher equilibrium moisture content, whereas the kernel rich in fat would be much lower. A variability in the size of bean, the thickness of husk, or the degree of mould formation on it might then explain difficulties in obtaining repeatable results.

A sample of beans was taken from those that had been prepared for a further run of the large tube experiment, and some beans dissected into husk and kernel portions. Moisture contents were measured as detailed below:

whole beans	8.01%		
	7.62%	average	7.82%

dissected samples

a. mixture	kernel	19.9849g	@	6.57%
	husk	2.5196g	@	16.70%

by weight, husk is 11.196% of whole bean,
giving combination m/c of 7.70%

b. light coloured, unmoulded beans

kernel	14.9225g	@	6.66%
husk	1.6964g	@	16.63%

by weight, husk is 10.208% of whole bean,
giving combination m/c of 7.68%

c. dark coloured, moulded beans

kernel	22.0184g	@	6.68%
husk	3.7097g	@	16.42%

by weight, husk is 14.419% of whole bean,
giving combination m/c of 8.08%

It seems that a difference in husk to kernel weight ratio may well be responsible for the variability found, which is, thus, independent of the method of moisture content determination used and inherent in cocoa.

5. STEADY STATE TEMPERATURE, CONSTANT APPLIED HUMIDITY EXPERIMENT

A preliminary experiment, the first of the series described in this section, was carried out before registration for a research degree.

5.1 APPLICABLE THEORY

As described in section 2.2, the combination of a constant linear temperature gradient with the neglect of the effect of any change in concentration on the vapour pressure gradient, yields a very simple theory:

$$\theta = k\,x$$

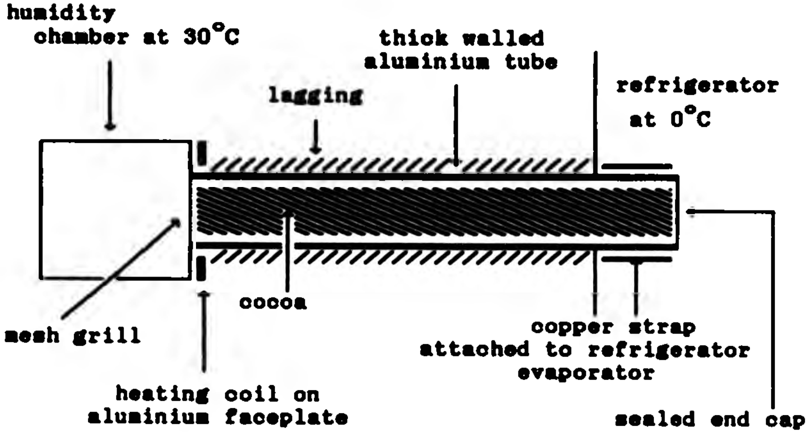
$$J = -D' \frac{dp}{d\theta} k$$

$$\frac{dC}{dt} = D' \frac{d^2p}{d\theta^2} k^2$$

The Magnus formula, which relates p_{sat} to θ (p in the above being a constant proportion of p_{sat}), is differentiable, as was done in section 2.2.

5.2 EXPERIMENTAL ARRANGEMENT

A 42 inch long thick walled aluminium tube, of 3 inch internal diameter, was filled with cocoa beans, closed at one end, and fitted with a grill at the other. The closed end was coupled with a copper thermal bridge to a refrigerator evaporator, and the other end placed in a heated chamber kept at a constant relative humidity. The hot end was held at a temperature of 30°C and the intended constant humidity was 70%; it became clear subsequently, however, that the hygrometer used was consistently under-reading, and that the relative humidity reached was probably more than 90%. The cold end was kept at a temperature of 0°C, and the experiment was ended after 30 days when the apparatus failed.



5.3 RESULTS OF FIRST RUN

Apart from mould and surface moisture preventing any meaningful result from the hot end and adjacent sample point, the results from the the other three sample points and from the cold end were surprisingly consistent with each other. After applying a simple correction for the increase in moisture content, the values of the coefficient of moisture diffusion relative to vapour pressure gradient were calculated as:

a. Sample Point	3	0.00503 lbs/ft^2.day per mb/ft
b.	2	0.00529
c.	1	0.00401
d. Cold End		0.00528

The average of values a, b and d is 0.00520, and this was used in subsequent theoretical calculations, converted to metric units, i.e.

3.225×10^{-4} kg/m.mb.hr
(or 8.96×10^{-8} kg/m.mb.sec).

5.4 FAILURE OF ATTEMPTED REPEATS

Unfortunately, attempts to repeat this experiment were unsuccessful on five occasions. Various values of relative humidity were tried at the hot end of the tube, including that of 90%, but the increases of moisture content along the tube were of random quantity, quite different from those predicted on the basis of the above value for the diffusion coefficient.

At this point, the series of experiments described in section 4 was undertaken to devise a method of moisture content determination which would be more consistent and accurate than that used previously. No great improvement was found, however, using the various methods tried, the bean to bean variation, as discussed in section 4, proving the limiting factor.

Re-examining the assumptions made before the first experiment was devised in order to account for its subsequent unrepeatability, the most significant was that the saturated vapour pressure/temperature relationship was sufficiently linear over the range of temperatures used that accumulation in the tube would not occur, but that moisture would condense into a measuring cylinder tapped into the cold end of the tube, in the refrigerator. This linearity assumption is often made in the literature, for example, Eckert and Faghri, 1980, and Faghri and Eckert, 1980. When no moisture appeared during the experiment and the moisture content of samples was measured after the experiment, more exact analysis showed that, on the basis of neglecting the effect of moisture content change, accumulation would occur most at the hot end, and least at the cold end, conditions under which that neglect of the effect of changes in concentration was, perhaps, questionable.

Further, since the intended controlling relative humidity in the hot end chamber was the same as the initial equilibrium relative humidity of the beans, accumulation, under these intended conditions, would not occur at the hot end, and the final moisture content profile would depend very much on the concentrations reached. As it was, the hot end chamber relative humidity was above 90%, whilst the beans' equilibrium was 69%, and considerable moulding and wetting of the first fifteen inches of beans in the tube occurred.

Because of the bean to bean variability in moisture content peculiar to cocoa, discussed in section 4, this approach was unlikely to be successful, as, if the increments in concentration were to be kept small enough effectively not to disturb the vapour pressure gradient, they would not be consistently measurable. Thus, only if the experiment was so arranged that the majority of the diffusing vapour did not accumulate in the cocoa, but reached the cold end to condense, were consistent results likely. Further, the length of time that the experiment was run, on the first occasion and those subsequent, was decided on the basis of a proposed very high diffusion coefficient, some fifteen times higher than that found in later experiments. Although the cause of the result of the the first experiment is uncertain, given a diffusion coefficient of the magnitude of that found subsequently, the predicted increases in moisture content would not be consistently measurable, accounting for the subsequent unrepeatability.

6. UNSTEADY STATE TEMPERATURE, LARGE TUBE EXPERIMENT

6.1 THEORETICAL CONSIDERATIONS

The first series of experiments arranged a linear temperature gradient, which, combined with the non-linear vapour pressure/temperature relation, resulted in the accumulation of most of the diffusing vapour in the cocoa.

In the second series of experiments, the large tube experiments, however, which more nearly mimicked conditions in a vessel during a voyage, the temperature profile was that determined by unsteady state heat conduction through the cocoa. At any time, then, this profile was curved, with the steepest gradient at the applied cold temperature end. The combination of this with the vapour pressure/temperature curve, being most gradual at the lower temperature, was intended to result in a very nearly linear vapour pressure/distance into the stow curve at any particular time, with a much greater proportion of the diffusing moisture reaching the cocoa surface there to condense. For this reason, the assumption of negligible change in concentration would also be more realistic for this type of experiment, with a more easily measurable quantity, that of condensate in an absorbent end pad.

This was found not to be the case for the times and temperature differences studied here. Examination of intermediate results of the computer programs revealed that, under these conditions, a linear temperature gradient would have yielded a more constant value of

$\partial p/\partial x$ than that actually achieved. Further discussion of this issue is postponed until section 6.6.

From this mistaken assumption and the high value of D′ derived from the result of the first experiment (Section 5), it appeared that, on a voyage, there would be little accumulation of moisture in the stow, but that significant quantities would be available to condense beneath an impervious barrier on the periphery of the stow.

The theory behind the analysis of the case where negligible accumulation occurs is described in section 2.2, where the simplification possible for the case of a constant applied temperature, rather than a varying one, is also discussed. Briefly, the expressions containing $p(\theta)$ and its differentials are calculated using the Magnus formula (since the change in concentration is assumed negligible, p is a fixed proportion of p_{sat}), and $\theta(x)$ and its first differential use the standard thermal conduction formulae, the second differential is calculated using numerical methods.

The simplification possible with a step function applied temperature yields:

$$\frac{\partial \theta}{\partial x} = \frac{\partial u}{\partial x} = - \frac{F}{\alpha_H \sqrt{\pi} \sqrt{t}} \; e^{-X^2}$$

$$\frac{\partial^2 \theta}{\partial x^2} = \frac{\partial^2 u}{\partial x^2} = \frac{2FX}{\alpha_H \sqrt{\pi} \sqrt{t}} \, e^{-X^2}$$

6.2 EFFECTIVE THERMAL CONDUCTIVITY WITH LATENT HEAT FLOW

Using this unsteady state temperature approach involves the apportioning of a value to the thermal diffusivity of cocoa, or more particularly to its thermal conductivity. If a large quantity of moisture is being moved in the vapour phase, the transport of latent heat becomes significant in the calculation of total heat transfer. The majority of the moisture in the bean is in liquid form; for it to diffuse, heat of vaporisation is required, and, when it condenses, whether in the material before it reaches the surface or at the surface, this latent heat is released. The subsidiary question is, then, whether such an increased apparent thermal conductivity can be approximated by adding a constant to the real k.

By equation (2.1.1), sensible heat flux per unit area,

$$Q_{Asens} = - k \frac{\partial \theta}{\partial x}$$

by equation (2.1.10), latent heat flux per unit area,

$$Q_{Alat} = - \lambda D' \frac{\partial p}{\partial x}$$

where λ is the specific latent heat of vaporization of water.

Then, total heat flux per unit area,

$$Q_{Atot} = - \left\{ k \frac{\partial \theta}{\partial x} + \lambda D' \frac{\partial p}{\partial x} \right\}$$

or, assuming negligible change in C,

$$= - \left\{ k + \lambda D' \frac{dp}{d\theta} \right\} \frac{\partial \theta}{\partial x}$$

giving, by equation (2.1.2),

$$\frac{\partial \theta}{\partial t} = \frac{1}{\rho C_p} \left\{ k + \lambda D' \frac{dp}{d\theta} \right\} \frac{\partial^2 \theta}{\partial x^2}$$

Thus, the problem is reduced to that of whether, over the temperature range of interest, $\frac{dp}{d\theta}$ may be regarded as constant, though the condition of negligible change in concentration should be emphasised.

Faghri and Eckert (1980) deal with a case where transfer of sensible heat is considered negligible compared with that caused by moisture migration, which apparently is justified under certain conditions in moisture diffusion through sands and soils. In fact, the moisture migration rate of cocoa seems to be much smaller than that calculated from the first experiment, and in this case is certainly small enough to allow the neglect of moisture movement in assigning a value to the effective thermal conductivity of cocoa.

Although the assumptions of the following section are no longer accepted, that the moisture vapour diffusion coefficient for cocoa is as high as that found in the first experiment, and that the real thermal conductivity had to be replaced by a higher apparent one, because of the predicted large amount of moisture movement, the section is included because it was the disparity between the computed values and those found by experiment that suggested the current opinion of the results of that first experiment.

6.3 COMPUTER PROGRAMS AND RESULTS OF CALCULATIONS

Computer programs based on the theory of section 2.2, assuming a change in concentration negligible as far as the vapour pressure gradient was concerned, were written to allow the calculation of flow to the surface and accumulation or depletion in a stow:

a). Data entry.

b). Calculation of temperature at various values of x and t.

c). Using the results of b)., calculation of the accumulation or depletion of moisture at the points x after time t_{max}.

d). Calculation of temperature gradient at the surface (i.e. $x \simeq 0$) for various values of t.

e). Using the results of d)., calculation of the accumulated flow to the surface after time t_{max}.

Versions of d). and e)., modified to use the simplification when F(t) is a constant or step function applied temperature, were also written.

Values for the constants employed in practical cases were:

k = 1.558 kJ/hr m^2 per °C/m
(= 3 BTU/hr ft^2 per °F/in)
ρ = 580 kg/m^3
(= 36.2 lb/ft^3)
c = 1.663 kJ/kg °C
(= 0.4 BTU/lb °F)
$\alpha_H = 4.02 \times 10^{-2}$ m/$\sqrt{\text{hr}}$
$D' = 3.225 \times 10^{-4}$ kg/m mb hr

The value of D′ was obtained from the experiment described in section 5, that of α_H from the values of k, ρ and c set out above. The value of k was chosen to allow for a certain amount of moisture migration. These figures are currently thought to be in error; specifically, k is now thought to be three times less than this, and D′ some fifteen times less, but, since it was the discrepancy between the computed results and those from the experiment that prompted a re-evaluation of these values, they are left to stand in this discussion.

These programs were applied to the actual voyage data of a vessel carrying cocoa, and an experiment devised to test the above values.

6.3.1 Step function calculations

Original moisture content (cocoa):	7.5%
Initial bulk temperature:	28°C
Applied temperature:	18.5°C

Calculations were performed for 11 and 13 days, and, in the case of flow to the surface, for 11, 12 and 13 days.

In the latter case the results were:

After 11 days,	flow to surface:	1.104 kg/m^2
12 days,		1.153 kg/m^2
13 days,		1.200 kg/m^2

In addition, accumulation/depletion was calculated at various depths into the stow:

Depth (m)	after 11 days	after 13 days
0.005	+0.078%	+0.085%
0.010	+0.077%	+0.082%
0.015	+0.074%	+0.080%
0.020	+0.072%	+0.077%
0.025	+0.069%	+0.074%
0.050	+0.058%	+0.061%
0.075	+0.042%	+0.046%

0.100	+0.027%	+0.031%
0.125	+0.012%	+0.016%
0.15	-0.003%	0.0%
0.20	-0.033%	-0.031%
0.25	-0.060%	-0.059%
0.50	-0.136%	-0.140%
0.75	-0.128%	-0.136%
1.00	-0.094%	-0.106%
1.25	-0.063%	-0.074%
1.5	-0.036%	-0.049%
2.0	-0.012%	-0.017%
2.5	-0.003%	-0.005%
3.0	0.0%	-0.001%

By integrating these values over length, the total depletion, less the accumulation near the surface, in each case was calculated:

After 11 days,	depletion:	0.776 kg/m^2
13 days,		0.897 kg/m^2

6.3.2 Varying applied temperature

Original moisture content (cocoa):	7.5%
Initial bulk temperature:	26°C

Applied temperatures (derived from readings provided by the Meteorological Office, Bracknell):

day 1:	25.0°C
2:	24.5°C
3:	23.5°C

4: 26.5°C
5: 27.5°C
6: 25.5°C
7: 23.0°C
8: 26.5°C
9: 23.0°C
10: 22.0°C
11: 18.0°C
12: 17.0°C
13: 16.0°C
14: 17.0°C
15: 16.0°C
16: 16.0°C
17: 18.0°C
18: 19.0°C
19: 20.5°C
20: 20.4°C
21: 16.0°C

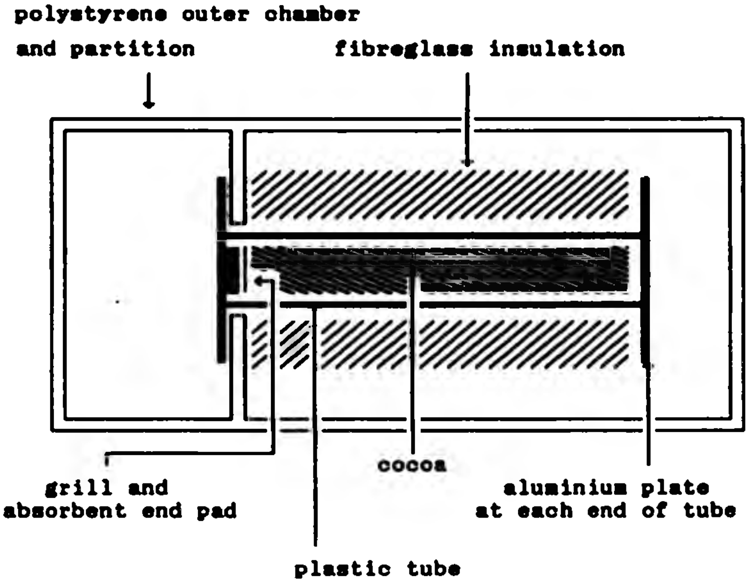
Total flow to surface was calculated as:

$$0.971 \text{ kg/m}^2$$

An experiment was set up to simulate the effect on the cocoa stow of temperatures experienced during the voyage.

6.4 EXPERIMENTAL APPARATUS

A rigid plastic tube of 200mm diameter and 1.55m length was placed in an insulated enclosure. Alloy plates 600mm square were attached to each end, and the tube was wrapped with a total thickness of 200mm of mineral wool insulation. An insulated partition was arranged near one end of the enclosure, dividing the latter into two chambers, so that one of the alloy plates protruded into the smaller chamber. Temperature probes were placed in the centre of the tube at intervals along its length and at each end. Heaters with accurate proportional temperature controllers were placed in both chambers.



6.5 EXPERIMENTAL RESULTS

6.5.1 Varying applied temperature experiment

For the first run of this experiment, a blotting paper and cotton wool pad was placed against the alloy plate situated in the smaller chamber, and was separated from the cocoa with which the tube was filled by a metal grill. The temperature inside the enclosure was raised to 26°C, and that of the cocoa was allowed to equilibrate with this.

The temperature in the small chamber was then varied on a daily basis to follow the temperatures provided by the Meteorological Office, that in the large chamber being maintained at 26°C. At the end of 21 days the experiment was stopped, and samples were taken of the cocoa at various points along the length of the tube. The pad was weighed to determine the quantity of moisture absorbed, and moisture contents of the various samples of cocoa were measured.

Original moisture content (cocoa):		9.09%
Moisture content at depth	0.25m:	8.80%
	0.50m:	9.00%
	1.00m:	9.20%
Moisture absorbed by pad:		$241.5 g/m^2$

6.5.2 First step function applied temperature experiment

For the second run of this experiment, a layer of hessian, cut from the bag in which the cocoa was shipped, replaced the pad used in the previous experiment, and the metal grill was removed. This was done in order to determine whether non-convective moisture migration could account for moisture actually found on the surface of bags after voyages of this type.

As some difficulty had been encountered in ensuring the accuracy of the daily change of temperature, after the cocoa had been heated to 28°C, a steady temperature of 18.5°C was applied in the small chamber, that in the larger chamber being maintained at 28°C. This corresponds to the step function or suddenly applied constant temperature model discussed above.

As the ambient temperature had increased somewhat by the time this second experiment was carried out, a refrigerator with fan was connected to the small chamber, controlled by an accurate thermostat, to ensure that the temperature of 18.5°C was maintained.

After 14 days the experiment was stopped, and samples were taken as before. The hessian was found not to be visibly wet or moist to the touch; later moisture content measurement found the absorption to have been very slight, though cocoa close to this end had absorbed more moisture than expected.

Original moisture content (cocoa):	6.84%
Moisture content at depth 0.015m:	7.71%
0.025m:	7.24%

0.075m: 6.97%
0.15m: 6.86%
0.3m: 6.83%
Moisture absorbed by hessian: 12.34g/m^2
Total moisture accumulated: 31.80g/m^2

(This latter figure includes excess accumulation in the first 0.15m of cocoa in the tube.)

6.5.3 Analysis of results

From a comparison of the temperatures which were obtained from the monitoring carried out during the two experiments with those calculated as described above, it was apparent that the value of α_H used in the calculations differed from that found experimentally.

Experiment 1

after 20 days

depth (m)	experimental	theoretical
0.25	22.8°C	20.5°C
0.5	24.5°C	21.6°C
1.0	25.6°C	23.5°C

Experiment 2

after 14 days

0.25	24.2°C	18.97°C
0.5	25.5°C	21.36°C
1.0	26.0°C	23.61°C

New values of α_H were chosen by trial and error substitution in the computer programs:

Experiment 1 $\alpha_H = 0.014$

yielding	temperatures
0.25	22.40°C
0.5	24.80°C
1.0	25.97°C

Experiment 2 $\alpha_H = 0.009$

yielding	temperatures
0.25	23.87°C
0.5	25.76°C
1.0	26.00°C

From these results and the measured accumulation, new values of D′ were calculated, giving a value of 2.35 × 10^{-5} kg/m mb hr for the first experiment, and 2.5 × 10^{-6} kg/m mb hr for the second, compared with 3.225 × 10^{-4} kg/m mb hr assumed in the computed results. In the case of the second run, the excessive accumulation of moisture found near the surface was added to that deposited in the hessian; this value for D′, however, is much lower than expected, suggesting some error in the measurement.

The computer programs with these new values give, for the first experiment:

Flow to the surface: 246g/m^2

Moisture content at depth 0.25m: 8.89%
0.5m: 9.05%
1.0m: 9.09%

and, for the second:

Flow to the surface: 38g/m^2

(In this case moisture contents at the various depths are not illuminating, as the change is small and it is assumed that a large amount of transfer back from the hessian to the adjacent cocoa occurred.)

6.5.4 Further step function applied temperature experiments

Two further runs of this experiment were carried out, using a step function applied temperature and a blotting paper and cotton wool pad at the cooled end. Both runs yielded a similar quantity of moisture in the end pad, 101.9 g/m^2 and 99.38 g/m^2, but the change in moisture content of the cocoa in the tube showed little discernible pattern, except very near to the cooled surface, and were probably exhibiting the sample to sample variation described in section 4. As already set out, this is not really unexpected; even on a high diffusion coefficient, the computed values of change in moisture content in the tube are within uncertainty limits for moisture content measurement.

Analysing these new results, it was apparent that the value for α_H, or more particularly for k, based on the final temperature profile, would be similar to that found after the very first run, but that, based on daily temperature readings, the measured temperatures along the tube did not match computed values. On other information, it seemed that k for cocoa should be about 1 BTU/hr ft^2 per °F/in or 519 J/hr m^2 per °C/m and certainly not less, giving a value for α_H of 2.32×10^{-2} m/$\sqrt{\text{hr}}$, 0.577 of the value first used in computation, and 1.66 times that apparently found in the first run of the experiment.

Comparing temperature values computed using this new k with the experimental data, a good match was displayed for the first five days in the third run and ten days in the fourth, with divergency after these points. It is evident that with this lower than expected k value the thermal insulation around the tube was not good enough (and probably not properly applied in the third run) to ensure purely axial heat flow. The high temperature in the larger chamber was distorting the temperature by leakage through the mineral wool insulation. Allowing for this, by, in the latter case, using an overall time of ten days, and, in the former, a five day period of unsteady state heat conduction, followed by a ten day period of a constant temperature gradient (this latter using the theory of the first experiment), these results were consistent with a k of 519 J/hr m^2 per °C/m and a D' of 14.25×10^{-6} kg/m mb hr.

The value of D' was chosen as a result of study of the papers of Pixton and Griffiths (1971), Thorpe (1981 and

1982) and Becker and Sallans (1955) for wheat, and an analysis, discussed in section 7, of the likelihood that the diffusion coefficient of bulk cocoa would be of a similar magnitude.

6.6 DISCUSSION

To some extent this result is unsatisfactory, in that the computed results are not very sensitive to k and D' values and the experimental data could probably be manipulated into fitting other values; it is important rather in showing that the experimental data are consistent with these new values of k and D'.

The assumption of negligible change of concentration in the stow was vindicated, not on the mistaken grounds that the value of $\partial p/\partial x$ was nearly constant over the range of x-values of interest, but rather that the value of D' was small enough that moisture movement did not disturb the original concentration to any significant extent. The maximum change measured, except in the first 0.025m of the second experiment, would have caused a 1 to 1.5% change in relative humidity, and a maximum error of 2% in vapour pressure (see the equilibrium curves included in section 8).

While such changes in moisture content were not reliably measurable, the absolute weight change in an end pad due to moisture absorption could be ascertained, even though the quantity of migrating moisture was small.

To consider the original hypothesis regarding constancy of $\partial p/\partial x$ as a result of the combination of $\partial p/\partial \theta$ and $\partial \theta/\partial x$, the most favourable data occours at the end of 13 days, with relative humidity of 75.2%:

	depth (m)			
	0.2	0.6	1.0	
$\partial p/\partial \theta$	1.067	1.200	1.316	(mb/°C)
$\partial \theta/\partial x$	5.844	4.986	3.630	(°C/m)

Briefly restating the criterion of section 2.2,

with f as $\partial p/\partial \theta$ and
g as $\partial \theta/\partial x$

$$\forall x_i \forall x_j (x_i < x_j \rightarrow (|f|_{x_j}/|f|_{x_i} < (|g|_{x_i}/|g|_{x_j})^2$$

$$\wedge\ |g|_{x_i}/|g|_{x_j} < (|f|_{x_j}/|f|_{x_i})^2))$$

there are three combinations of x_i and x_j with $x_i < x_j$:

$x_i = 0.2$ $\qquad |f|_{x_i} = 1.067$ $\qquad |g|_{x_i} = 5.844$

$x_j = 0.6$ $\qquad |f|_{x_j} = 1.200$ $\qquad |g|_{x_j} = 4.986$

where $\qquad |f|_{x_j}/|f|_{x_i} = 1.125$ $\qquad |g|_{x_i}/|g|_{x_j} = 1.172$

and the criterion is satisfied.

$x_i = 0.6$ $\qquad |f|_{x_i} = 1.200$ $\qquad |g|_{x_i} = 4.986$

$x_j = 1.0$ $|f|_{x_j} = 1.316$ $|g|_{x_j} = 3.630$

where $|f|_{x_j}/|f|_{x_i} = 1.097$ $|g|_{x_i}/|g|_{x_j} = 1.374$

and the criterion is not satified, since $1.374 > (1.097)^2$.

$x_i = 0.2$ $|f|_{x_i} = 1.067$ $|g|_{x_i} = 5.844$

$x_j = 1.0$ $|f|_{x_j} = 1.316$ $|g|_{x_j} = 3.630$

where $|f|_{x_j}/|f|_{x_i} = 1.233$ $|g|_{x_i}/|g|_{x_j} = 1.610$

and the criterion is not satisfied, since $1.610 > (1.233)^2$.

Thus, even with the most favourable data, the combination $\partial p/\partial x$ cannot be claimed as more constant than either of its components, under the conditions of a voyage of the type under discussion. Since it is the temperature gradient, $\partial \theta/\partial x$, which shows the greater variability, the pressure gradient, $\partial p/\partial x$, would show less variation with x if a linear temperature gradient were imposed.

During the second of the later runs, hygrometer probes were introduced into the tube, at three points along its length and at the cooled end, in the pad. Unfortunately, these were found to be sensitive to some substance in the cocoa bean, and, even when a crude filter was fitted by the manufacturers, a steady diminution in sensitivity occurred during the experiment. From calibration before and after the run, those probes situated in the tube experienced little or no change in relative humidity, as expected. That situated near the cooled cocoa surface, in the end pad, displayed no change in sensitivity, but the value of relative humidity was above 80% (rather than the Equilibrium Relative Humidity of the beans on loading the tube of 65%) from 24 hours after the application of the cooling temperature to that end of the tube. This would cause "back pressure", and lessen the amount of moisture reaching the end pad. An allowance for this was made when calculating consistency with the assumed value of D'.

7. THE INTRA-PARTICLE DIFFUSION COEFFICIENT

7.1 THE SIGNIFICANCE OF INTRA-PARTICLE DIFFUSION

The significance of the intra-particle diffusion coefficient to the present programme of research is solely to assess the contribution of diffusion through the beans to the bulk rate. Thorpe had stated (1981, 1982) that, for wheat, the intra-particle rate measured by Becker and Sallans (1955) was too slow to affect the bulk diffusion rate, which could, thus, be calculated purely in terms of diffusion through the inter-particle air spaces. As set out later in this section, the effective diffusion coefficients for wheat were found to be:

Intraparticle	6.78×10^{-13}s
Bulk	3.946×10^{-11}s

a ratio of some 1:58. The above experimentally determined bulk coefficient was shown by Thorpe to be explicable solely in terms of the coefficient of diffusion of water vapour through air, reduced by factors correcting for the porosity and tortuosity of the bulk. If, then, the intraparticle diffusion coefficient for cocoa is of the same order as that for wheat, the bulk coefficient may be predicted to be similar to that of wheat, a prediction that may be tested by further experimentation.

The use of a temperature gradient to induce diffusion would not be possible in measuring the diffusion rate into individual beans, as a temperature gradient would have to be sustained from the outside to the centre of a number of individual beans over a period of time. It is not difficult, however, to keep beans formerly equilibrated to one humidity level in an atmosphere at a constant second humidity, and measure the moisture adsorption or desorption.

7.2 COMPARISON OF PREVIOUS RESULTS

At this point it may be useful to unify the various units used previously for a diffusion coefficient by conversion into standard SI units:

D or D_{cc} $m^{2}s^{-1}$

reduced from kg $m^{-2}s^{-1}$ per kg m^{-3} per m

D' or D_{cp} s

reduced from kg $m^{-2}s^{-1}$ per Pa m^{-1}

Thus, the assessment of the first experiment:

0.00520 lb $ft^{-2}day^{-1}$ per mb ft^{-1}

or 3.225×10^{-4} kg $m^{-2}hr^{-1}$ per mb m^{-1}

becomes:

0.896×10^{-9} s

the first assessments of the early large tube experiments:

2.35×10^{-5} and 2.50×10^{-6} kg $m^{-2}hr^{-1}$ per mb m^{-1}

become:

6.53×10^{-11} and 0.694×10^{-11} s respectively

and the quoted figure for maize:

0.000353 lb $ft^{-2}day^{-1}$ per mb ft^{-1}

becomes:

6.08×10^{-11} s

As set out above in section 2.3, except in the case of intra-particle diffusion, diffusion coefficients of type D or D_{cc} for water vapour in free air are not directly comparable with those for hygroscopic materials, unless, in the latter case, they relate interstitial water vapour concentration to overall change in concentration. The usual methods have been to try to relate overall concentration to overall concentration, as is used successfully for water vapour in free air, ignoring the special properties of hygroscopic materials. Thus, to list some measured values for D_{cc}:

a. water vapour in free air (Coulson and Richardson, 1977, p.274)

25.6×10^{-6} m^2s^{-1} at 25°C

b. wheat in bulk (Pixton and Griffiths, 1971)

2.4 to 2.6×10^{-10} m^2s^{-1} at 5°C

7.1 to $8.9 \times 10^{-10}\ m^2 s^{-1}$ at 22.5°C

c. intra-particle wheat (Becker and Sallans, 1955)

$0.089 \times 10^{-10}\ m^2 s^{-1}$ at 20.8°C
$0.097 \times 10^{-10}\ m^2 s^{-1}$ at 24.7°C
$0.118 \times 10^{-10}\ m^2 s^{-1}$ at 27.0°C

Since the conversion of these wheat values to a real D in terms of water vapour concentration in the interstitial air spaces involves the calculation of interstitial water vapour pressure, it is more reasonable, even for working in cases of diffusion due to a concentration gradient alone, to convert to a D' or D_{cp} for comparison.

Using $\frac{D}{RT}$ to convert value a. (water vapour in free air, at 25°C):

with $R = 461.52\ J\ kg^{-1} K^{-1}$
and $T = 298\ K$

$$D_{cp} = 18.61 \times 10^{-11}\ s$$

To convert values b. and c.,

$$J = -D \frac{\partial C}{\partial x} = -D \frac{\partial C}{\partial p} \frac{\partial p}{\partial x}$$

or

$$D' = D \frac{\partial C}{\partial p} = D \rho \frac{\partial w}{\partial p}$$

where ρ is the density (kg m^{-3})

w is the fractional dry weight moisture content (kgkg^{-1})

and $C = \rho w$, with ρ assumed constant for the materials under discussion.

ρ = 690 kg m^{-3} for bulk wheat and 1150 kg m^{-3} for the individual grains.

For wheat, at the moisture contents of the relevant experiments:

$$\frac{\partial w}{\partial p} = 4.5 \times 10^{-5} \text{ Pa}^{-1} \text{ at } 22.5^\circ\text{C, and}$$

$$5.9 \times 10^{-5} \text{ Pa}^{-1} \text{ at } 25^\circ\text{C}$$

(derived from a formula quoted in Thorpe (1982))

From these, then, the different values of ρ, and taking an average value of D_{cc}:

b. Pixton and Griffiths (1971)

D_{cc} of 8×10^{-10} $m^2 s^{-1}$ is equivalent to

D_{cp} of 2.5×10^{-11} s

and

c. Becker and Sallans (1955)
D_{cc} of 0.1×10^{-10} m^2s^{-1} is equivalent to
D_{cp} of 6.8×10^{-13} s

Thorpe (1981) actually found a better fit for Pixton and Griffiths data to be 3.948×10^{-11} s, being D_{cp} for water vapour in free air reduced by a factor, α, of 0.212, made up of ε, the porosity of the bulk grain, being 0.4, and γ, the tortuosity of the air paths through the grain bulk, of 0.53, where $\alpha = \varepsilon\ \gamma$. The bulk rate may be seen, then, as the water vapour in free air rate, reduced by this restrictive factor, whatever its precise value.

7.3 THE RATIO OF INTRA-PARTICLE AND BULK DIFFUSION RATES WITH REFERENCE TO EQUILIBRATION

Comparing the rates for wheat, intra-particle and bulk, either for D_{cc} or for D_{cp}, the differences being solely due to the differing densities, the ratios are approximately 1:50 for D_{cp} and 1:80 for D_{cc}. The intra-particle rate is slow enough not to affect the bulk rate, in terms of diffusion through the interstitial air spaces, but rapid enough to ensure negligible delay in equilibration of the grain moisture content with the interstitial concentration. If the diffusion into a single grain, modelled as a sphere, is considered, one can approximate a sphere of the bulk grain with a comparable diffusion time to equilibrium.

As the reduced units of the coefficient suggest (m^2s^{-1}), it is not the linear but rather the square of the linear dimension which is the measure of the proportionality. Thus, using the extended units for D_{cc} (kg $m^{-2}s^{-1}$ per kg m^{-3} per m), although the surface area of the sphere, and, thus, the quantity diffusing for the same concentration gradient, is proportional to r^2, the concentration gradient is inversely proportional to r^4. Ignoring, then, the problem of D_{cc} for hygroscopic materials, and the difference in density of bulk wheat and individual grains,

$$\frac{(D_{cc})_{bulk}}{R^2} = \frac{(D_{cc})_{grain}}{r^2}$$

or

$$\frac{(D_{cc})_{bulk}}{(D_{cc})_{grain}} = \left(\frac{R}{r}\right)^2$$

where

r is the individual grain radius, modelled as a sphere

R is the radius of bulk with an equivalent diffusion time.

The diffusion coefficient ratio, on the above figures of Pixton and Griffiths, and Becker and Sallans, is about 80, at about 25°C, from which

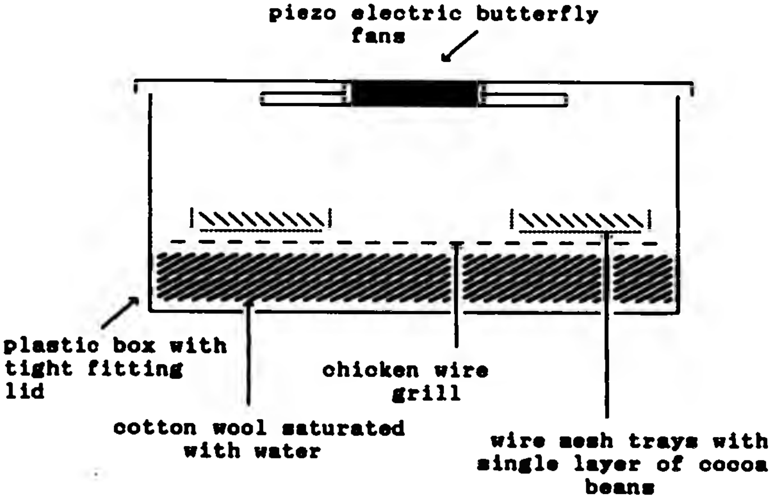
$$\frac{R}{r} = \sqrt{80} = 8.9$$

Thus, if r is 2mm, R is 17.8mm. For a sphere of bulk of radius much less than about 18mm, the rate of diffusion into the individual grains will determine the rate of change of grain moisture content, whereas for a bulk sphere of radius much above this, the bulk diffusion coefficient will determine the rate of change.

In the case of cocoa, if the intra-particle diffusion rate is of a similar magnitude to that for wheat with an allowance for the greater particle size, then the above argument regarding the bulk coefficient holds, that for distances similar to those of the experiments, and those occurring in actual cases, the overall bulk diffusion rate will be that of water vapour through the inter particle air spaces. Since the reduction in area and tortuosity would be similar for the similar shaped cocoa bean, this bulk coefficient should also have a similar value to that for wheat. It is important, then, to measure the intra-particle rate for cocoa to see if this analysis is applicable.

7.4 EXPERIMENTAL ARRANGEMENT

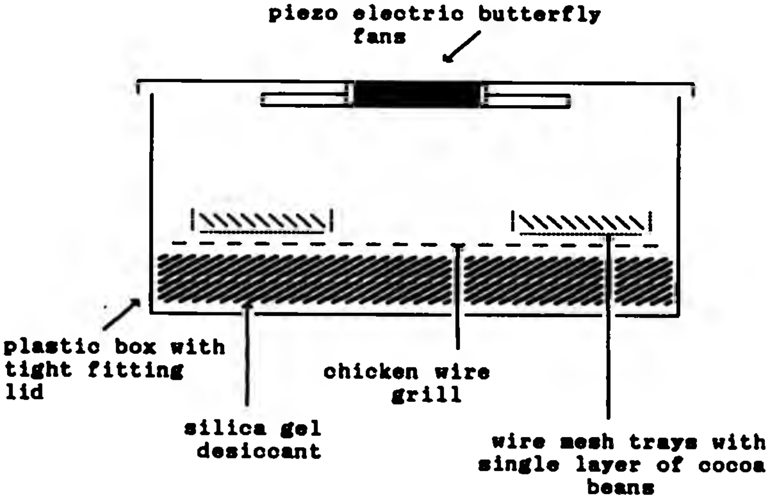
Accordingly, an experiment was devised to measure the intra-particle diffusion coefficient for cocoa. A plastic box with a tight fitting lid was used; wet cotton wool was placed in the bottom covered, with separation, by a coarse chicken wire grill. Two trays of 6.5mm square mesh wire were made, each capable of holding about twenty beans in a single layer, each bean separate from each other. Two piezo electric "butterfly" fans were attached to the inside of the lid to ensure constant humidity within the chamber. A hair hygrometer was used to check the relative humidity reached, which was 95% for the whole experiment.



Two small plastic containers with tight fitting lids were used for weighing the samples. The beans had equilibrated to 60% relative humidity before the start of the experiment, and, as it was carried out in a constant ambient temperature of 21°C, the samples being weighed at this temperature, it was possible to remove the samples from the humidity chamber into the small plastic pots, weigh them and return them within five minutes, with little effect on the overall time.

Unfortunately, this experiment yielded inconclusive results, thought to be due to condensation on the inside surfaces of the humidity chamber at the very high humidities reached.

Using the same apparatus, with silica gel substituted for the wetted wadding, similar experiments measuring drying, rather than absorbing, rate were carried out.



7.5 ANALYSIS OF RESULTS

To allow direct comparison with Becker and Sallans (1955) results for wheat, the same method of calculation was used, the form of the equation for diffusion out of a sphere derived in section 2.3:

$$\bar{M} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp -n^2\pi^2 D_c t/r_o^2 \qquad (7.5.1)$$

where:

$$\bar{M} = \frac{\bar{m} - m_s}{m_o - m_s}$$

$\bar{m}$ is the final average moisture content (%),
m_o is the uniform initial moisture content (%),
m_s is the surface moisture content (%),
D_c is the diffusion coefficient, D_{cc} ($cm^2 sec^{-1}$),
r_o is the kernel radius (cm), and
t is the drying time (sec),
with all moisture contents being on a dry weight basis.

The surface moisture content, m_s, is the bean moisture content which is in equilibrium with the relative humidity of the drying atmosphere, or $\bar{m}$ as t approaches ∞. This was measured by keeping bean samples in the drying chamber for three months, with frequent renewal of silica gel and measurement of weight loss. At the end of this period, further change in weight was negligible. The moisture content of the samples was then measured by drying the whole beans for seven days in an oven at 105°C.

Having determined the value of m_s, the experiment itself was run four times in all, with two samples in each case, twice for twenty and twice for forty minutes. The weight loss and the final average moisture content, $\bar{m}$, were measured, the latter by oven drying the complete sample as whole beans for 96 hours, and, from this, the initial moisture content, m_o, was calculated. The initial moisture contents of the actual samples used were employed in the calculations, rather than a general moisture content of the beans from which the samples were extracted, because of the sample to sample variation discussed in section 4.

Results:

1st 20 minute run

		sample wts (g)	
		1	2
a)	original wt	22.6628	24.1417
b)	wt after 20min	22.5778	24.0538
c)	wt after oven drying	20.9614	22.3502

	moisture contents (%)	
	1	2
m_o (= 100 × (a-c)/c)	8.1168	8.0156
$\bar{m}$ (= 100 × (b-c)/c)	7.7113	7.6223
$\bar{M}$	0.91961	0.92064

(Although the calculated results are presented here in a truncated form, intermediate results were entered in fuller precision when calculating $\bar{M}$, in order to avoid cumulative rounding errors. $\bar{M}$ itself, as an intermediate result, is also shown to greater precision than warranted. An error analysis later in this section shows the effective limits imposed by weighing imprecision and the inconsistency of cocoa bean moisture content described in section 4.)

2nd 20 minute run

	moisture content (%)	
	1	2
m_o	9.2466	9.1324

$\bar{m}$	8.6885	8.5709
$\bar{M}$	0.90827	0.90754

(Whereas all other experiments were carried out at 21°C, this was carried out at the higher temperature of 23.5°C. According to Becker and Sallans data (1955), an increase in D_{cc} by a factor of 1.246 would be expected because of this higher temperature.)

1st 40 minute run

	moisture content (%)	
	1	2
m_o	8.2069	8.3061
$\bar{m}$	7.6497	7.7403
$\bar{M}$	0.89174	0.89218

2nd 40 minute run

	moisture content (%)	
	1	2
m_o	9.0624	9.1120
$\bar{m}$	8.3524	8.3779
$\bar{M}$	0.88172	0.87869

An assessment of the accuracy of the weighing operation showed an uncertainty of ±0.0005 g, and, assuming such errors for each weighing to be accumulative, possible error spreads were calculated.

The surface moisture content, m_e, was based on two samples, with a mean value of 3.06%, a maximum of 3.13% and a minimum of 2.99%. The following tables used these values.

The abbreviated column headings in the tables have these interpretations:

orig wt	original weight
after t wt	weight after drying in the apparatus for t minutes
dry wt	weight after oven drying
orig m/c	calculated original moisture content
after t m/c	calculated moisture content after drying in the apparatus for t minutes
Mbar	calculated value of $\bar{M}$
Max Mbar	maximum value of $\bar{M}$, calculated on the basis of weighing errors and spread of values for m_e
Min Mbar	minimum value of $\bar{M}$, calculated as for Max Mbar
min om/c	minimum calculated value of original moisture content
min tm/c	minimum calculated value of moisture content after drying in the apparatus for t minutes
max om/c	maximum calculated value of original moisture content
max tm/c	maximum calculated value of moisture content after drying in the apparatus for t minutes

Table 7.5.1

t = 20 minutes

orig wt	after t wt	dry wt	orig m/c	after t m/c
22.6620	22.5770	20.9614	8.116824	7.711316
24.1417	24.0538	22.3502	8.015508	7.622303
21.9417	21.8252	20.0842	9.248563	8.668505
21.1085	20.9999	19.3421	9.132410	8.570941

Mbar	Max Mbar	Min Mbar	min om/c	min tm/c	max om/c	max tm/c
0.919809	0.922827	0.916782	8.111860	7.706362	8.121788	7.716271
0.920638	0.923585	0.917680	8.010934	7.617658	8.020241	7.626948
0.906269	0.908964	0.903583	9.243354	8.663310	9.253772	8.673700
0.907537	0.910330	0.904750	9.127004	8.565549	9.137816	8.576332

Table 7.5.2

t = 40 minutes

orig wt	after t wt	dry wt	orig m/c	after t m/c
21.2645	21.155	19.6517	8.206923	7.649719
20.4835	20.3765	18.9126	8.306102	7.740342
21.4601	21.3204	19.6769	9.062403	8.352433
20.7626	20.6229	19.0287	9.112025	8.377871

Mbar	Max Mbar	Min Mbar	min om/c	min tm/c	max om/c	max tm/c
0.891740	0.895198	0.888286	8.201626	7.644436	8.212221	7.655003
0.892156	0.895618	0.888697	8.300595	7.734850	8.311610	7.745834
0.881719	0.884807	0.878649	9.057090	8.347139	9.067715	8.357728
0.878692	0.881845	0.875559	9.106531	8.372396	9.117520	8.383346

As a result of these inaccuracies, the possible spread of values for $\bar{M}$ is as follows:

1st 20 minute run
$\bar{M}$ from 0.916782 to 0.923585

2nd 20 minute run
$\bar{M}$ from 0.903583 to 0.910330

40 minute runs
$\bar{M}$ from 0.875559 to 0.895818

The right hand side of equation (7.5.1) was calculated by computer for various values of D_{∞}/r_o^2, for t = 1200 secs and 2400 secs. Those corresponding to the values of $\bar{M}$ set out above are:

1st 20 minute run
D_{∞}/r_o^2 from 4.42 to 5.28×10^{-7}

2nd 20 minute run
D_{∞}/r_o^2 from 6.14 to 7.12×10^{-7}

40 minute runs
D_{∞}/r_o^2 from 4.20 to 6.03×10^{-7}

In order that the results for the second twenty minute run should be comparable with the others, the value of D_{∞}/r_o^2 may be reduced by a factor of 1.246 as mentioned above:

2nd 20 minute run (corrected)

D_∞/r_o^2 from 5.14 to 5.71 × 10^{-7}

The total spread, then, of values over the four runs, using eight samples, and allowing for possible weighing inaccuracies is:

D_∞/r_o^2 from 4.20 to 6.03 × 10^{-7}

r_o is the radius of a sphere in some sense equivalent to a kernel or bean from the point of view of diffusion. Becker and Sallans (1955) used a sphere of equal volume to the individual wheat kernel, and, although the cocoa bean is further from spherical in shape and more varied in size, this approach will be used here.

The cocoa beans used in the intra-particle diffusion experiments varied in size and shape, but a typical bean measured 2 × 1 × 0.7 cm in extreme dimensions, a rectangular volume of 1.4 cm^3. The actual volume of the bean may be calculated from the difference between the bulk and grain densities, a factor of 0.56 to 0.61, and a further allowance for the denser packing in the bulk than would be the case if each bean occupied its rectangular volume. Taking an overall factor of 0.45, then, the real volume of this typical bean would be 0.63 cm^3, and the radius of an equal volume sphere:

$$r_o = \sqrt[3]{\frac{0.63\times3}{\pi\times4}} = 0.532 \text{ cm}$$

and $r_o^2 = 0.283$

The range of values for D_{cc} found experimentally are:

0.119 to 0.171×10^{-6} cm^2sec^{-1}
or 0.119 to 0.171×10^{-10} m^2sec^{-1}

rather than that found by Becker and Sallans for wheat at a similar temperature of 0.069×10^{-6} cm^2sec^{-1}.

In order to convert this into a value for D_{cp}:

from section 7.2,

$$D_{cp} = D_{cc} \frac{\partial C}{\partial p}$$

and, in order to use the equilibrium curve for cocoa, graph 8.5.2.11, at a constant temperature,

$$\frac{dC}{dp} = \frac{dC}{dRH} \frac{dRH}{dp}$$

and
$$\frac{dC}{dRH} = \rho \frac{dw}{dRH}$$

The equilibrium curve in section 8 yields a value of dC/dRH of 0.47 at 75% RH, for the bulk density of 580 kgm^{-3}, rather than the bean density of 950 kgm^{-3}; for the bean, then,

$$\frac{dC}{dRH} = \frac{950}{580} 0.47 = 0.77$$

By the definition of relative humidity:

$$RH = 100 \frac{p}{p_{sat}}$$

with $p_{sat} = 2338$ Pa at 20°C

whence

$$\frac{dRH}{dp} = \frac{100}{2338} = 0.0428$$

and

$$\frac{dC}{dp} = 0.0329$$

and, for intra-particle diffusion in the cocoa bean:

$$D_{cp} = 3.92 \text{ to } 5.63 \times 10^{-13} s$$

rather than the coefficient for wheat:

$$6.8 \times 10^{-13} s$$

7.6 CONCLUSIONS

Given the heterogeneous nature of cocoa beans with respect to size, to shape, and to equilibrium moisture content, a macroscopic experiment of the nature described would be unlikely to yield a narrower spread of results.

Since the diffusion coefficient, D_{cp}, for water vapour in air is more than three hundred times the maximum value for cocoa calculated above, however, these results are sufficient to support the required deduction that the rate of diffusion of moisture through cocoa beans in bulk is determined by the rate of diffusion through the inter-particle air spaces.

8. THE CLOSED TUBE EXPERIMENT

8.1 INTRODUCTION

In order accurately to measure the bulk diffusion coefficient of cocoa, a series of experiments using the thick walled aluminium tube of the first series of experiments was carried out. Both ends of the tube were sealed, and the temperature gradient applied was nearly linear, because of the high rate of conduction through the tube, and, in comparison, the low rate of heat loss to the ambient air.

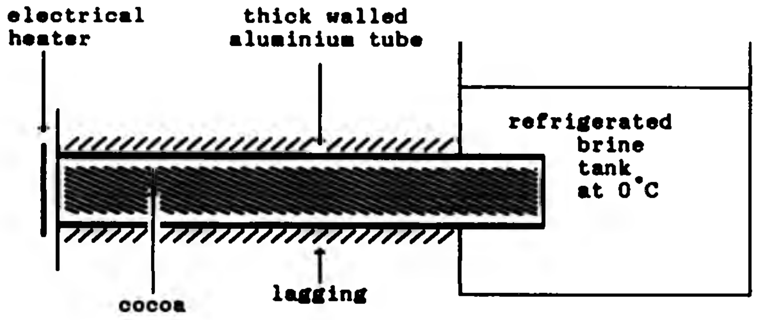
Griffiths (1964) arranged a similar experiment for wheat, using the temperature gradient set up between two plates by, at least initially, unsteady state conduction through the wheat. The experiment described in this section was intended to be an improvement, as, rather than this unsteady state gradient equilibrating to linear, which limits the length over which diffusion is measured, the aluminium tube provided a near linear temperature gradient very soon after the experiment was started, even over the 1.07 metre length used.

Whereas Griffiths was able to use hygrometer probes to monitor the redistribution of moisture, this was not possible in the case of cocoa, because of the contamination of the sensors by substances released by the cocoa bean. In order to avoid the difficulty of measuring consistently the small changes of moisture content of samples taken from various positions along the tube, it was decided to insert pre-weighed samples in nylon bags into the tube at the various positions, and measure the actual weight gain or loss.

8.2 EXPERIMENTAL APPARATUS

The aluminium tube used in the experiments described in section 5 was employed in these experiments. The hot end, however, rather than being open to a constant humidity chamber, was closed by an aluminium plate with an electric heater attached, connected to an electronic proportional temperature controller. The cold end was closed and protruded 50mm into a refrigerated brine tank, yielding an effective length of 1020mm. After the first run, with brine in the refrigeration tank, the aluminium tube was badly corroded, and, for the second run, an automobile antifreeze solution was substituted.

Twelve sample points of 25mm diameter were drilled, tapped, and fitted with threaded stoppers at intervals along the tube, in order to enable a more detailed picture of the changes in moisture content to be built up. Owing to difficulty in insertion and extraction of the samples, large gauge rigid steel mesh tubes of length 85mm, with monofilament nylon net linings were made to contain the samples.



8.3 RESULTS

The closed tube experiment was run twice, the first time for 29 days, the second being stopped after 27 days, when the thermostat on the refrigeration unit started to operate only intermittently.

The results of the two runs were very similar:

no.	x (mm)	moisture change (%) (dry base) 1st run	 2nd run
1	50	-2.42	-2.44
2	135	-1.03	-1.10
3	185	-0.17	-0.37
4	255	0.02	0.10
5	318	0.38	0.42
6	380	0.30	0.30
7	440	0.51	0.20

8	500	0.31	0.30
9	585	0.25	0.23
10	715	0.12	0.14
11	852	0.05	0.12
12	955	0.10	0.12

Sample no.7 was anomalous on both runs for no apparent reason.

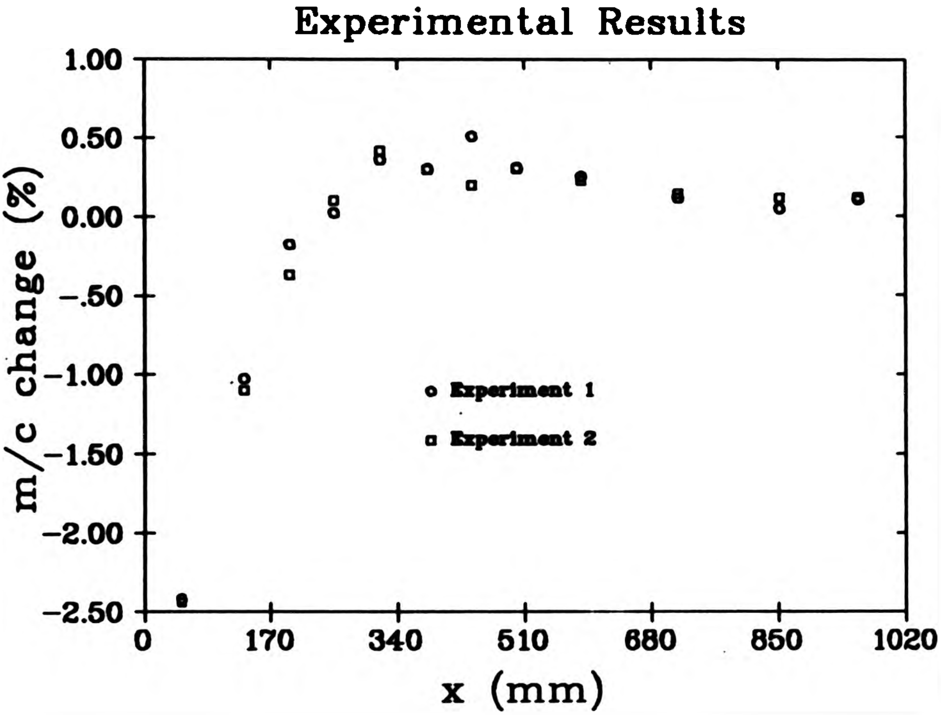
Conditions for the two runs were not identical:

	1st run	2nd run
duration	29 days	27 days
cold end temp	2.1°C	0.7°C
hot end temp	42.6°C	41.6°C
initial m/c	9.314%	9.625%

The differences, however, seem to have cancelled each other out; i.e. although the time was shorter in the second run, the initial moisture content was higher, causing a steeper initial vapour pressure gradient, and, although the maximum temperature was lower in the second run, the temperature range was greater.

Graph 8.3.1 plots the results of both experiments for comparison.

Graph 6.3.1


Experimental Results
1.00
0.50
0.00
-.50
-1.00
-1.50
-2.00
-2.50
m/c change (%)
0
170
340
510
680
850
1020
x (mm)
○ Experiment 1
□ Experiment 2

8.4 ANALYSIS OF ERRORS

The possible errors in measuring these changes in moisture content were calculated using a spreadsheet program.

Allowances were made for:

a. a range of initial moisture contents, measured on a series of samples taken from the batch used in the experiment while loading the tube.

In experiment 1, these ranged from 9.17 to 9.53%,
with an average of 9.314%,

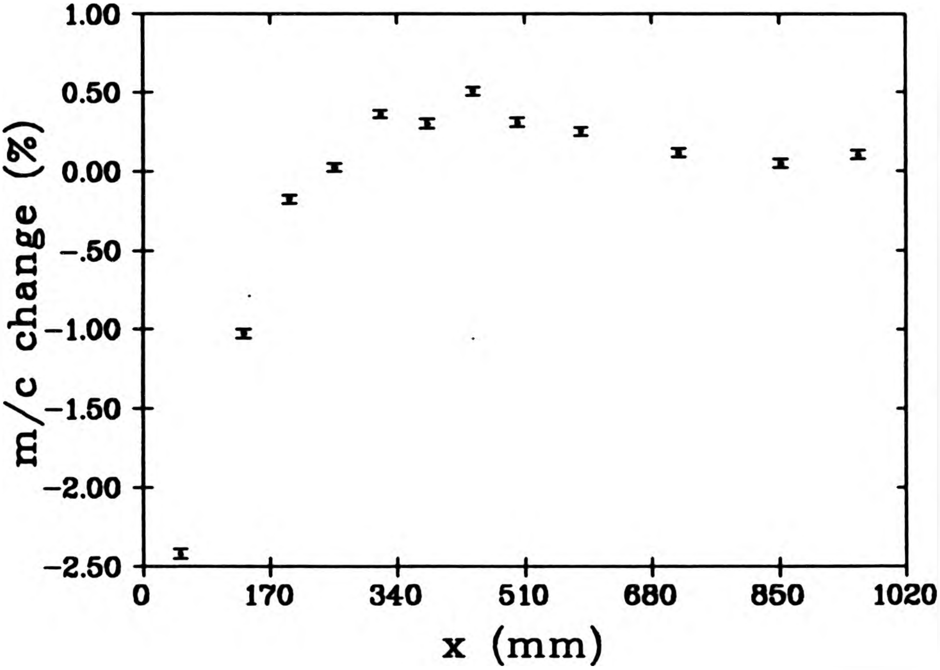
in experiment 2, these ranged from 9.41 to 9.89%,
with an average of 9.625%.

b. in calculating weight change, four accumulative weighing errors of ±0.0005 g (tare1, original weight, tare2, final (post-experiment) weight), total error allowance being ±0.002 g.

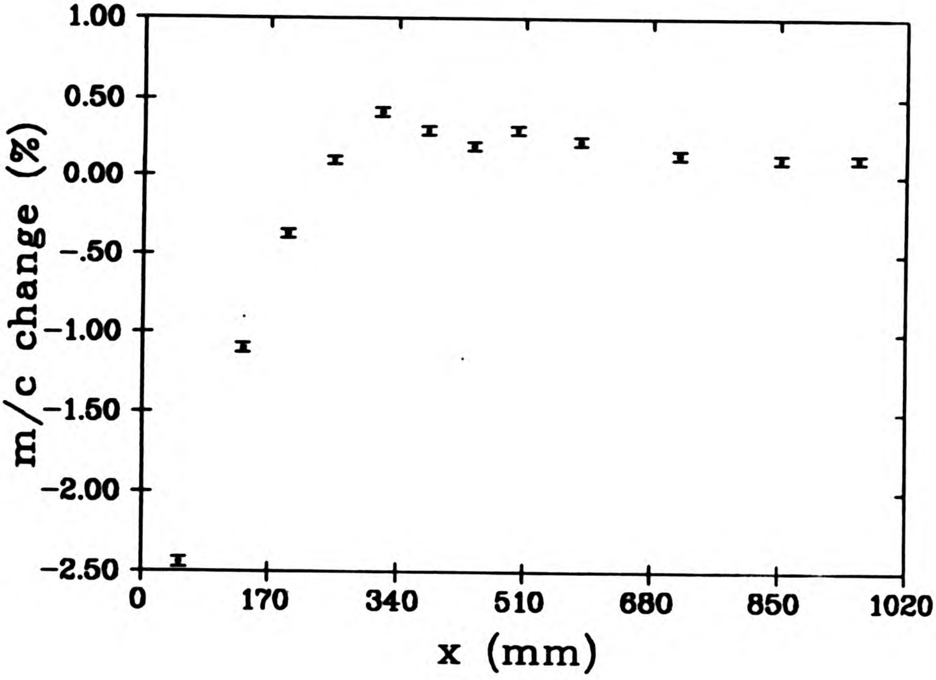
c. in calculating dry weight, two accumulative weighing errors of ±0.0005 g (tare1, original weight), total error allowance being ±0.001 g, in addition, of course, to the original moisture content range of item a..

The possible error spread, minimised by the design of the experiment, is shown by the error bars on the following graphs (8.4.1 and 8.4.2), the maximum error being ±0.03%.

Graph 8.4.1   Experiment 1



Graph 8.4.2 Experiment 2



8.5 THE NUMERICAL METHODS USED AND THE RESULTING COMPUTED CURVES

8.5.1 General Considerations

Several features of the physical system were considered when deciding the most suitable method of approximate solution of the modified diffusion equation:

$$\frac{\partial C}{\partial t} = D' \frac{\partial^2 p}{\partial x^2}$$

a. Under the conditions of the experiment, there was no initial transient, and, thus, no quasi infinite gradients. The thickness and high thermal conductivity of the aluminium tube ensured that the heating of the hot end and the cooling of the cold end did not create large thermal gradients at these ends, and the closed nature of the system did not require any instantaneous relative humidity changes to be applied at the ends.

b. Diffusion does not exhibit "discontinuous behaviour", as found, for example, in fluid flow, where the discrete change from laminar flow to turbulence may depend on minute changes in the system or complex interrelationships.

c. Diffusion is a "slow" process with respect to the time scale of the experiment and the vapour pressure gradients imposed by the constant temperature gradient. Whereas the latter had reached a steady state within two hours of the start of the experiment, the calculated curves show that, even at the end of the experiment, this was very far from the case with the diffusion process.

(In the calculated curves with a constant D′, a factor $\frac{D' \, \delta t}{(\delta x)^2}$ is extracted as a constant multiplier at each time step. Obviously, an increase in D′ (as shown in the appended graphs where D′ = 3.946, 6.0, and 8.0 × 10^{-8}) may be interpreted as a constant D′ and an increase in δt and, therefore, the sum of the δt's, in the same ratio.)

d. At the macroscopic level examined here, the diffusion process is entirely deterministic.

As these factors all suggested that this was a relatively undemanding application for any numerical method suitable for stiff parabolic partial differential equations, various finite difference methods were examined.

8.5.2 Implicit Methods

Most implicit methods, including that of Crank and Nicolson (1947), were immediately judged unsuitable, as their application to a non-linear equation of the form:

$$f(p)\,\frac{\partial p}{\partial t} = D' \,\frac{\partial^2 p}{\partial x^2}$$

where, in this case, $f(p)$ is $\frac{\partial C}{\partial p}$, required the solution of a set of non-linear equations at each time step.

An implicit method was found without this disadvantage, using a three time level method studied by Lees (1966) and discussed in Mitchell and Griffiths (1987); this method is outlined below.

Unfortunately, an expression for $\partial C/\partial p$ or $\partial p/\partial C$ is an intrinsic part of the rearrangement of the diffusion equation into a form usable by an implicit method. While a polynomial approximation to the equilibrium curve is sufficiently accurate for simply converting C to p, if this polynomial is differentiated in the calculation of $\partial p/\partial C$, small errors in value may be converted into large errors of slope. The results of the application for constant D' and D' varying with temperature (i.e. with x) were graphed and show the wide disparity between results calculated using fourth and fifth degree polynomials to represent the cocoa equilibrium curve (graphs (8.5.2.1) to 8.5.2.8)).

To convert the form of Fick's second law that applies to the closed tube experiment

$$\frac{\partial C}{\partial t} = D' \frac{\partial^2 p}{\partial x^2}$$

into a form suitable for the application of an implicit method:

$$\frac{\partial C}{\partial p}\frac{\partial p}{\partial t} = D' \frac{\partial^2 p}{\partial x^2} \qquad \text{......(8.5.2.1)}$$

or

$$\frac{\partial C}{\partial p}\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[D'(x) \frac{\partial p}{\partial x} \right] \qquad \text{......(8.5.2.2)}$$

The second form allows for a residual temperature dependency of D'. An expression for D_{cc} for water vapour in free air, quoted in Thorpe (1981), is:

$$\frac{k \times T^{2.5}}{(T+245.18)}$$

k being a constant and T being absolute temperature (K).

D' or D_{cp} would then approximate to:

$$\frac{D_{cc}}{RT} = \frac{k' \times T^{1.5}}{(T+245.18)}$$

and, according to Thorpe's theory, D' for bulk cocoa should be a proportion of this.

In fact, the change of D_{cc} and D' over the temperature range 0 to 40°C was calculated, and a reduction in the spread from 31% for D_{cc} to 14% for D' was noted.

As stated above, the method used is described in Mitchell and Griffiths (1987), p.98 ff, and the finite difference equation will be set out first using their notation, then translated to the present applications.

The general form of the equation to be approximated is:

$$b(u)\frac{\partial u}{\partial t} = \frac{\partial}{\partial x}\left[a(u)\frac{\partial u}{\partial x}\right] \qquad (a(u) > 0,\ b(u) > 0)$$

The simplest approximation to this would be:

$$b(U_m^n)\,\frac{1}{2k}\,(U_m^{n+1} - U_m^{n-1}) = \frac{1}{h^2}\,\delta_x(a(U_m^n)\,\delta_x)U_m^n$$

......(8.5.2.3)

where:

the upper indices range over discrete values of t, n×k,

the lower indices range over discrete values of x, m×h,

δ_x is the usual central difference operator; see the expansion below.

Unfortunately, for a(u) = b(u) = 1, this difference method is unconditionally unstable. Following a method that stabilises this in the linear constant coefficient case, equation (8.5.2.3) is expanded and rewritten as:

$$b(U_m^n)(U_m^{n+1} - U_m^{n-1}) =$$

$$2r(a(U^n_{m+1/2})(U^n_{m+1} - U^n_m) - a(U^n_{m-1/2})(U^n_m - U^n_{m-1}))$$

where

$$r = \frac{k}{h^2}$$

and the r.h.s. is the usual central difference approximation.

U^n_{m+1}, U^n_m, and U^n_{m-1} are then replaced by

$$1/3(U^{n+1}_{m+1} + U^n_{m+1} + U^{n-1}_{m+1}),$$

$$1/3(U_m^{n+1} + U_m^n + U_m^{n-1}),$$

and

$$1/3(U_{m-1}^{n+1} + U_{m-1}^n + U_{m-1}^{n-1})$$

respectively, leading to the formula:

$$b(U_m^n)(U_m^{n+1} - U_m^{n-1}) =$$

$$2/3r(\alpha^+((U_{m+1}^{n+1} - U_m^{n+1})+(U_{m+1}^n - U_m^n)+(U_{m+1}^{n-1} - U_m^{n-1}))$$

$$- \alpha^-((U_m^{n+1} - U_{m-1}^{n+1})+(U_m^n - U_{m-1}^n)+(U_m^{n-1} - U_{m-1}^{n-1}))),$$

where

$$\alpha^+ = a(U_{m+1/2}^n)$$

and

$$\alpha^- = a(U_{m-1/2}^n)$$

These latter expressions may be further simplified to use values of U at grid points, but for the present purpose this is unnecessary and will be omitted.

To apply this schema to the equations (8.5.2.1) and (8.5.2.2):

Equation (8.5.2.1), constant D', yields a considerable simplification:

$$\left|\frac{\partial C}{\partial p}\right|_m^n (p_m^{n+1} - p_m^{n-1}) =$$

$$2/3rD'\ ((p_{m-1}^{n+1} - 2p_m^{n+1} + p_{m+1}^{n+1})+(p_{m-1}^n - 2p_m^n + p_{m+1}^n)$$

$$+(p_{m-1}^{n-1} - 2p_m^{n-1} + p_{m+1}^{n-1}))$$

where

p_m^n is the vapour pressure at time $n\delta t$ at position $m\delta x$.

The conditions, that there should be no flow at the ends, was ensured by forcing $\delta p/\delta x$ to 0 at the ends, that is by modifying the above equation at $m=0$ to:

$$\left|\frac{\delta C}{\delta p}\right|_m^n (p_m^{n+1} - p_m^{n-1}) =$$

$$4/3rD' \, ((p_{m+1}^{n+1} - p_m^{n+1})+(p_{m+1}^{n} - p_m^{n})+(p_{m+1}^{n-1} - p_m^{n-1}))$$

and at $m=x/\delta x$ to:

$$\left|\frac{\delta C}{\delta p}\right|_m^n (p_m^{n+1} - p_m^{n-1}) =$$

$$4/3rD' \, ((p_{m-1}^{n+1} - p_m^{n+1})+(p_{m-1}^{n} - p_m^{n})+(p_{m-1}^{n-1} - p_m^{n-1}))$$

Equation (6.5.2.2), allowing for a D' varying with temperature in the way described above, uses the unsimplified formula, which is adapted to:

$$\left|\frac{\delta C}{\delta p}\right|_m^n (p_m^{n+1} - p_m^{n-1}) =$$

$$2/3r(D'(m+1/2)((p_{m+1}^{n+1} - p_m^{n+1})+(p_{m+1}^{n} - p_m^{n})+(p_{m+1}^{n-1} - p_m^{n-1}))$$

$$- D'(m-1/2)((p_m^{n+1} - p_{m-1}^{n+1})+(p_m^{n} - p_{m-1}^{n})+(p_m^{n-1} - p_{m-1}^{n-1}))),$$

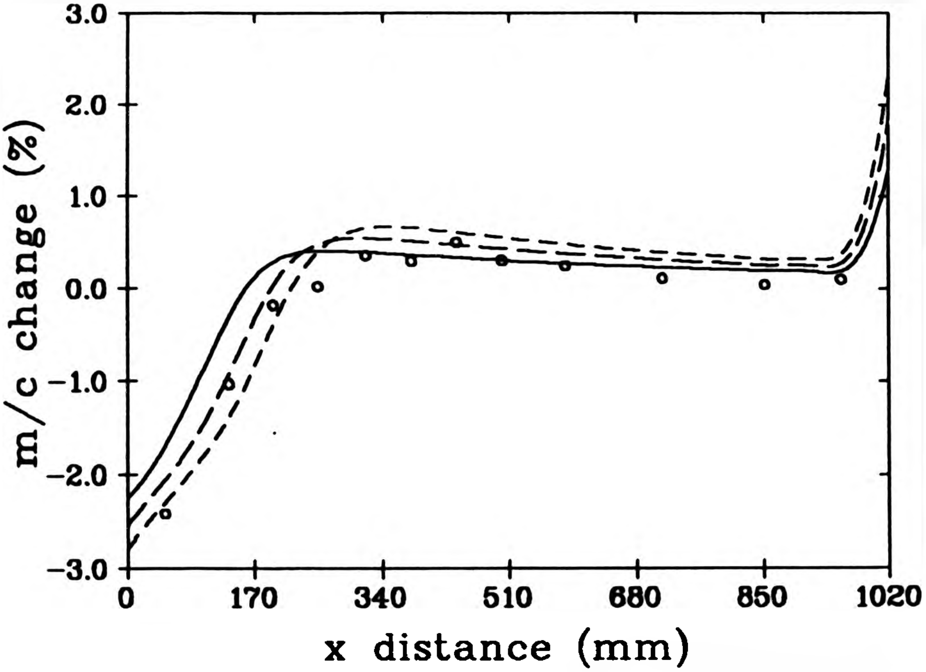
where

D'(m+1/2) is the value of D' at a point mid way between $m\delta x$ and $(m+1)\delta x$, and D'(m-1/2) similarly.

Using the above implicit formulae in a computer program involves the calculation of a matrix of coefficients of the terms p^{n+1}_{m-1}, p^{n+1}_{m} and p^{n+1}_{m+1}, and the numerical calculation of the remaining terms, those in p^{n} and p^{n-1} having numerical values. The resulting tridiagonal matrix with a numerical right hand side term is then solved in the usual way, the whole process being repeated for each time step. Of course, initial values for p were needed not only for t=0, but also for $t=\delta t$. These were provided by the explicit method described below, using 10,000 time steps to subdivide the first time interval of some 40 minutes (1000 time steps were used in calculations using the implicit method).

The following graphs (for, in each case, a D' of 3.846, 6.0 and 8.0 × 10^{-8}, at a reference temperature of 20°C for those using a variable D') show the above mentioned wide disparity caused by polynomials of different degree approximating the cocoa equilibrium curves, which effectively swamps any effect of the temperature dependency of D'. The curves relevant to the $\delta C/\delta p$ expression are graphs 6.5.2.11 and 6.5.2.12.

Graph 8.5.2.1



Experiment 1

• experimental results

—— $D' = 3.946 \times 10^{-11}s$

— — $D' = 6.0 \times 10^{-11}s$

- - - $D' = 8.0 \times 10^{-11}s$

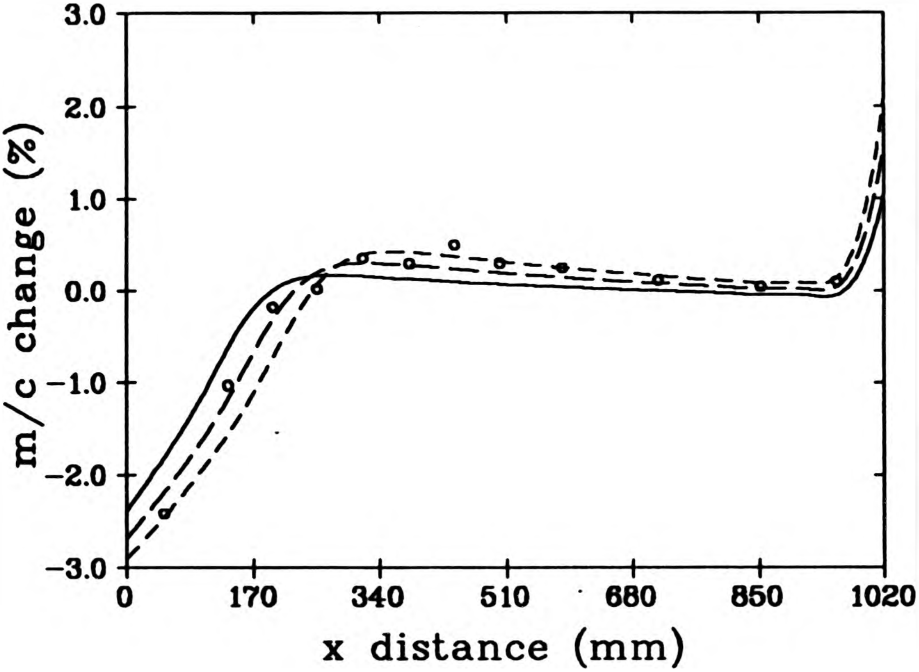
➡ Curves calculated by the implicit method

➡ D' constant (i.e. not corrected for residual temperature dependency)

➡ Degree 4 polynomial approximation of the ERH/moisture concentration function

➡ Moisture content change calculated on a dry weight basis

Graph 8.5.2.2



Experiment 1

•	experimental results
———	D′ = 3.946 × 10^{-11}s
— —	D′ = 6.0 × 10^{-11}s
- - -	D′ = 8.0 × 10^{-11}s

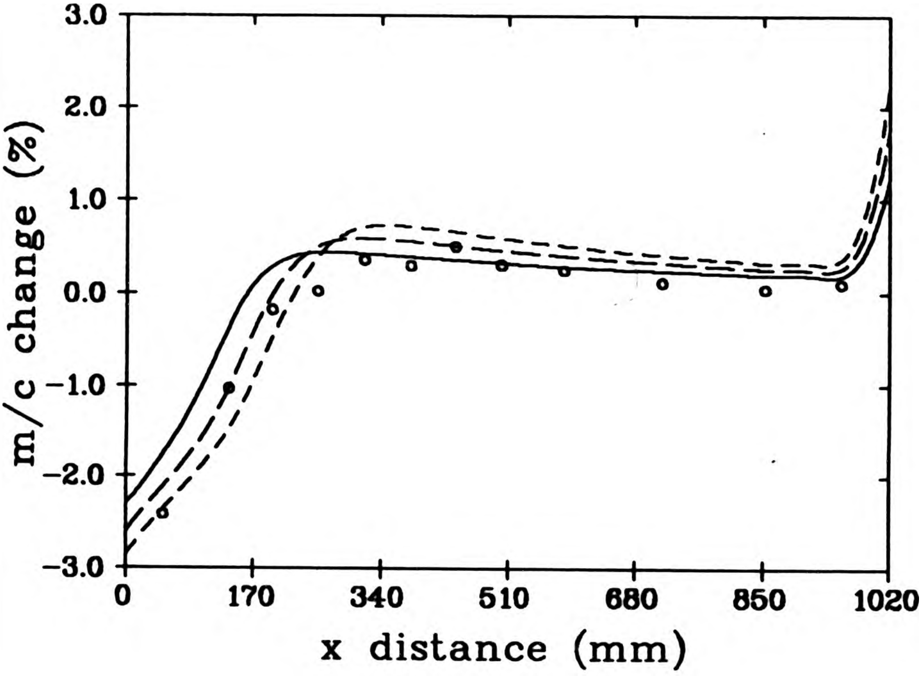
➡ Curves calculated by the implicit method

➡ D′ constant (i.e. not corrected for residual temperature dependency)

➡ Degree 5 polynomial approximation of the ERH/moisture concentration function

➡ Moisture content change calculated on a dry weight basis

Graph 8.5.2.3



Experiment 1

• experimental results

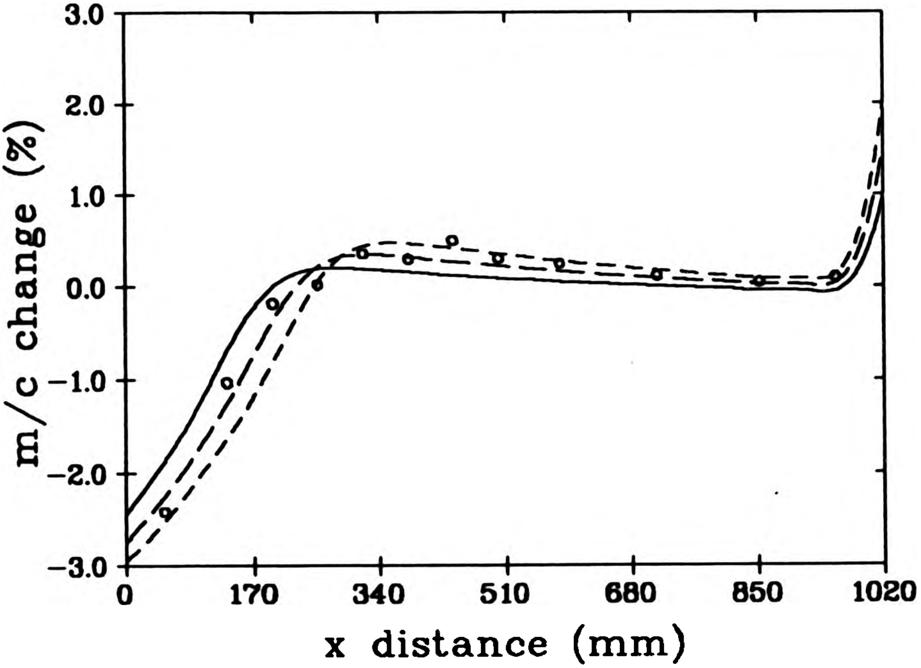
—— D' = 3.946 × 10^{-11}s

— — D' = 6.0 × 10^{-11}s

- - - D' = 8.0 × 10^{-11}s

- Curves calculated by the implicit method
- D' variable (i.e. corrected for residual temperature dependency)
- Degree 4 polynomial approximation of the ERH/moisture concentration function
- Moisture content change calculated on a dry weight basis

Graph 8.5.2.4



Experiment 1

▪ experimental results

—— $D' = 3.946 \times 10^{-11}$s

— — $D' = 6.0 \times 10^{-11}$s

- - - $D' = 8.0 \times 10^{-11}$s

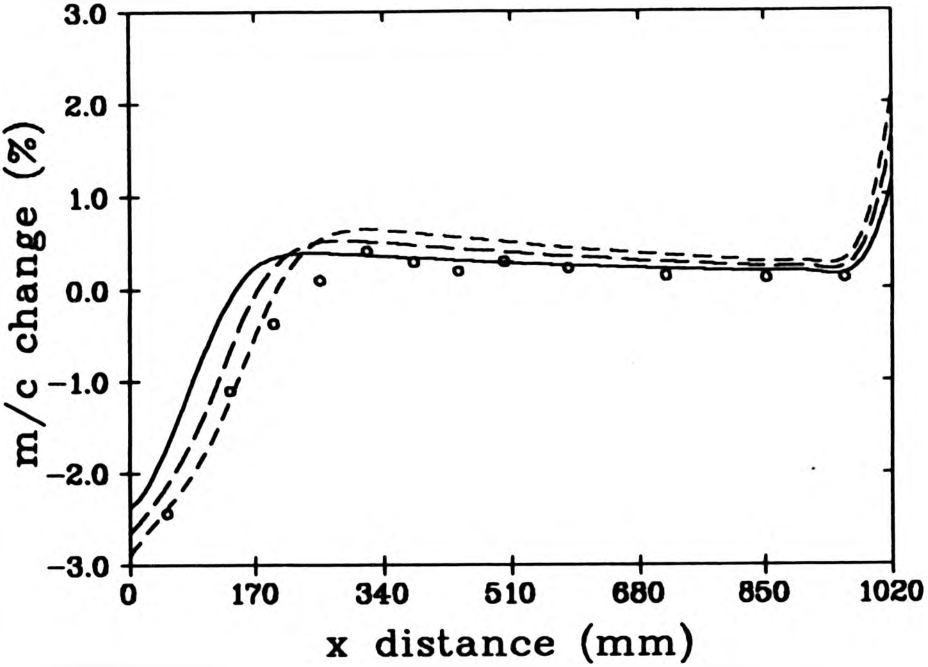
➔ Curves calculated by the implicit method

➔ D' variable (i.e. corrected for residual temperature dependency)

➔ Degree 5 polynomial approximation of the ERH/moisture concentration function

➔ Moisture content change calculated on a dry weight basis

Graph 8.5.2.5



Experiment 2

•	experimental results
——	$D' = 3.846 \times 10^{-11}s$
— —	$D' = 6.0 \times 10^{-11}s$
- - -	$D' = 8.0 \times 10^{-11}s$

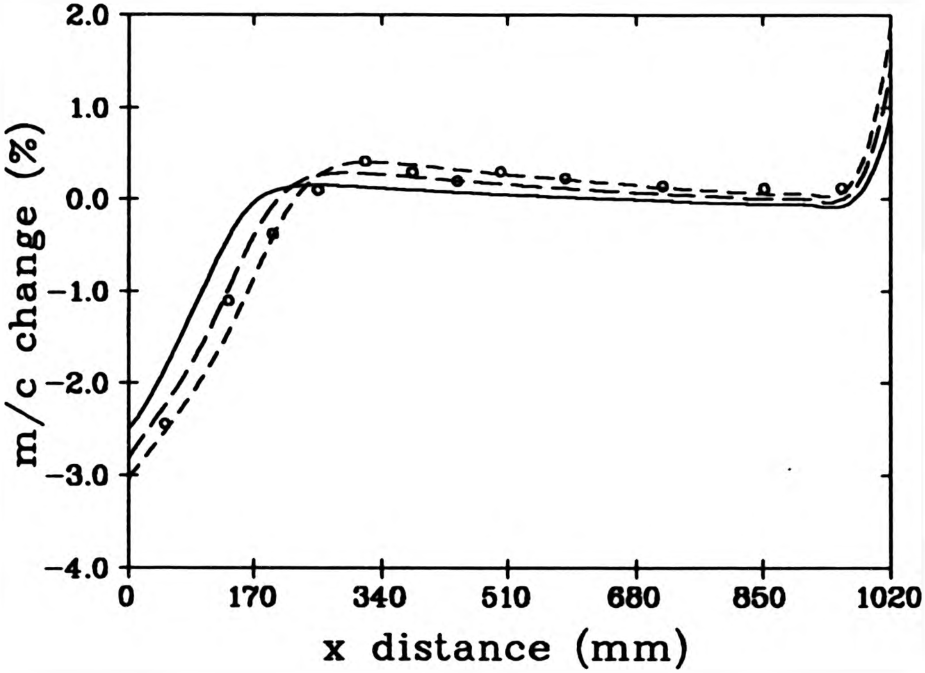
➡ Curves calculated by the implicit method

➡ D' constant (i.e. not corrected for residual temperature dependency)

➡ Degree 4 polynomial approximation of the ERH/moisture concentration function

➡ Moisture content change calculated on a dry weight basis

Graph 6.5.2.6



Experiment 2

•	experimental results
———	D′ = 3.946 × 10^{-11}s
— —	D′ = 6.0 × 10^{-11}s
- - -	D′ = 8.0 × 10^{-11}s

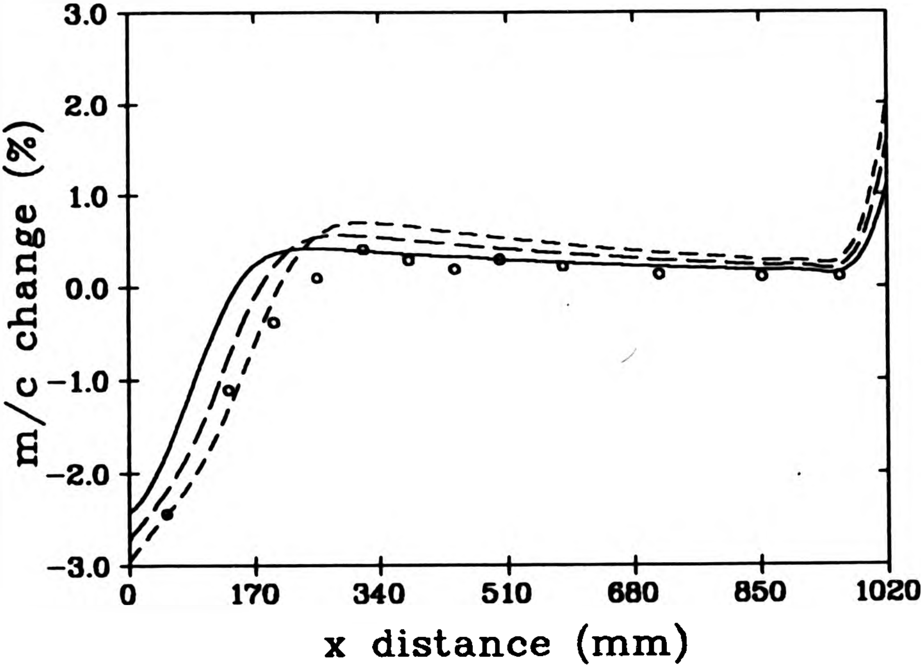
➡ Curves calculated by the implicit method

➡ D′ constant (i.e. not corrected for residual temperature dependency)

➡ Degree 5 polynomial approximation of the ERH/moisture concentration function

➡ Moisture content change calculated on a dry weight basis

Graph 8.5.2.7



Experiment 2

• experimental results

—— $D' = 3.946 \times 10^{-11}s$

— — $D' = 6.0 \times 10^{-11}s$

- - - $D' = 8.0 \times 10^{-11}s$

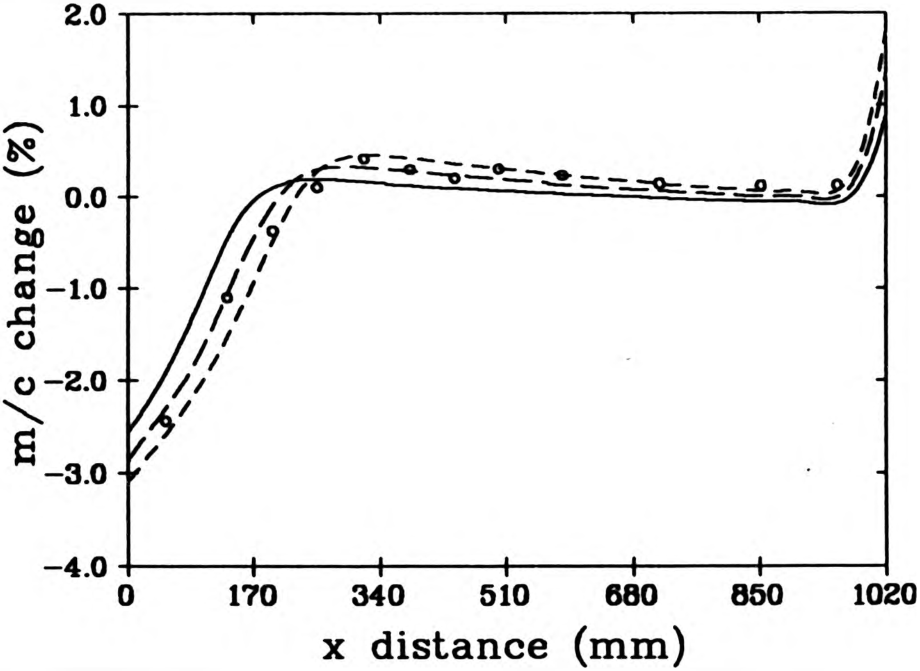
➡ Curves calculated by the implicit method

➡ D' variable (i.e. corrected for residual temperature dependency)

➡ Degree 4 polynomial approximation of the ERH/moisture concentration function

➡ Moisture content change calculated on a dry weight basis

Graph 8.5.2.8



Experiment 2

•	experimental results
——	$D' = 3.946 \times 10^{-11}s$
— —	$D' = 8.0 \times 10^{-11}s$
- - -	$D' = 8.0 \times 10^{-11}s$

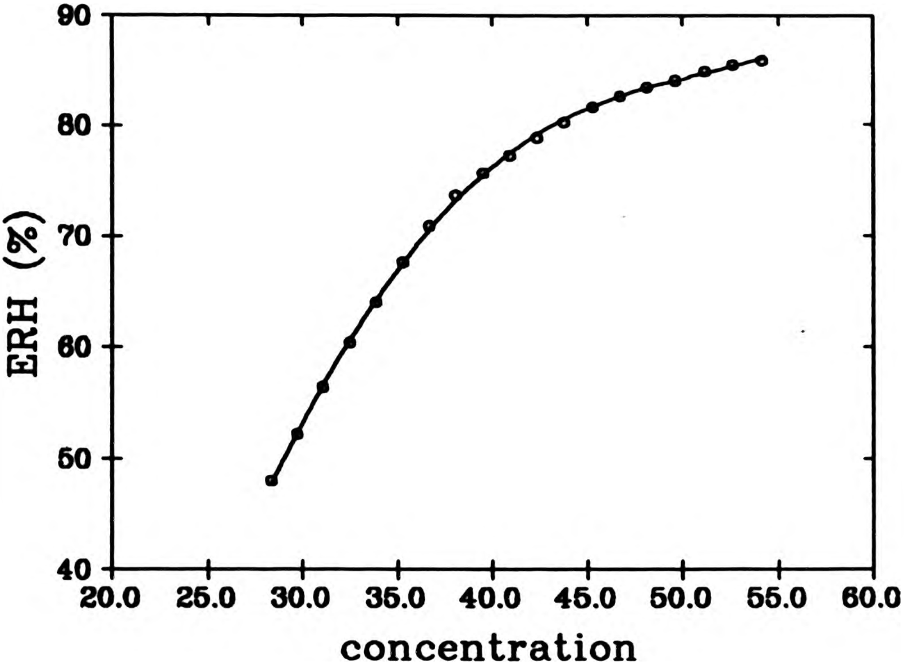
➡ Curves calculated by the implicit method

➡ D' variable (i.e. corrected for residual temperature dependency)

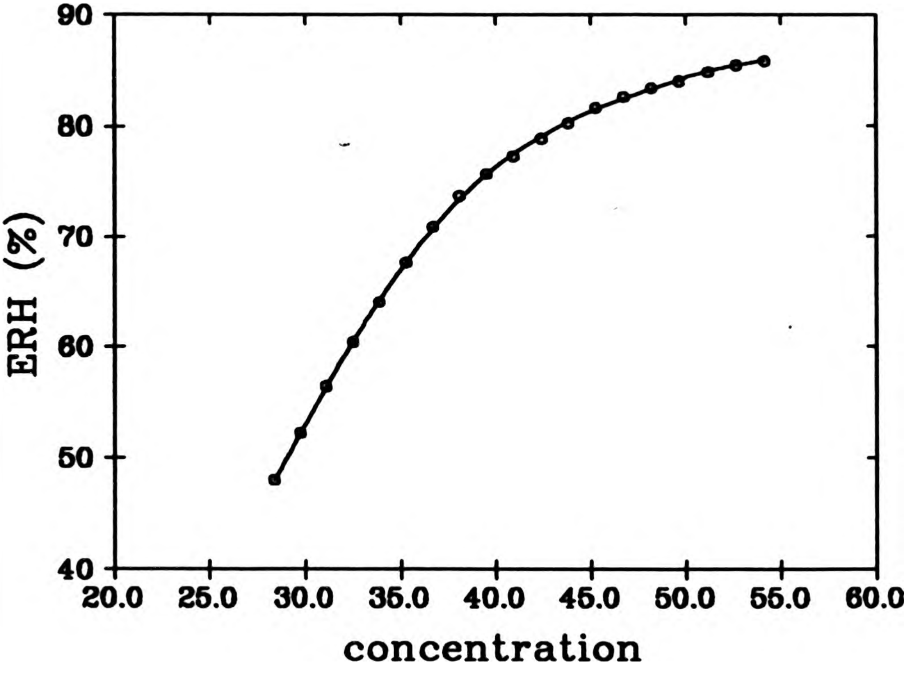
➡ Degree 5 polynomial approximation of the ERH/moisture concentration function

➡ Moisture content change calculated on a dry weight basis

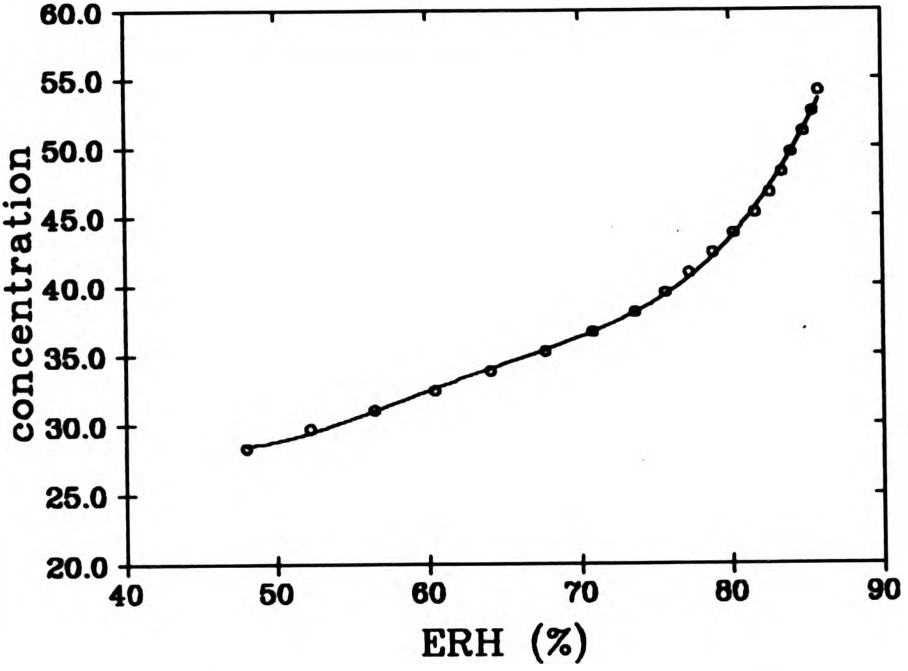
Graph 8.5.2.9 ERH/Concentration data
Degree 4 polynomial fit



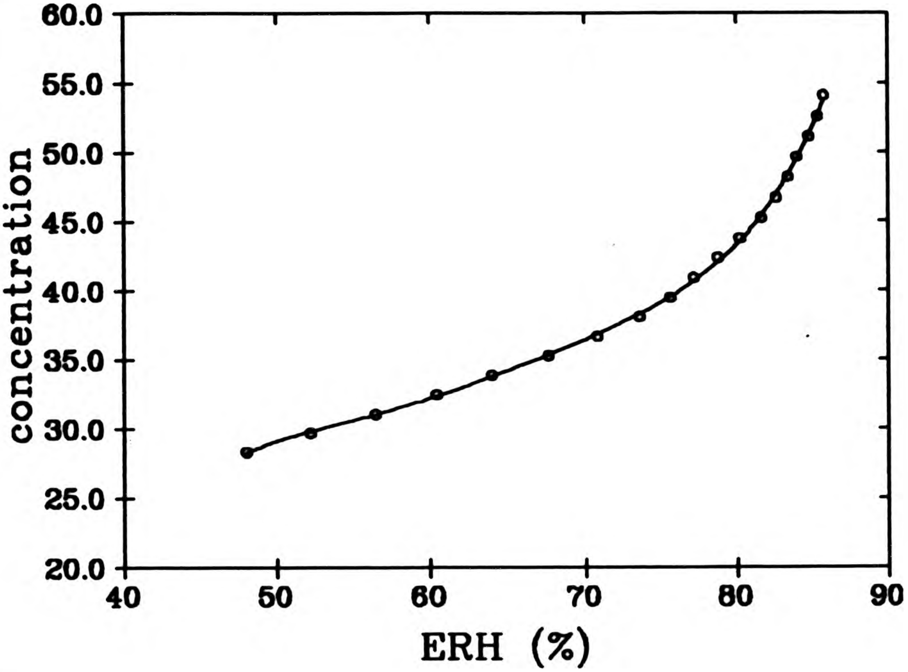
Graph 8.5.2.10 ERH/Concentration data
Degree 5 polynomial fit



Graph 8.5.2.11 Concentration/ERH data
Degree 4 polynomial fit



Graph 8.5.2.12 Concentration/ERH data
Degree 5 polynomial fit



8.5.3 Explicit Methods

Explicit methods are those which use only information from an earlier timestep to define the change to the present timestep, that is the finite difference equation has the general form:

$$U_m^{n+1} - U_m^n = f(U^n)$$

Since $f(U^n)$ has a definite numerical value at each timestep, matrix methods are not required, and the method is easily modified to:

$$C_m^{n+1} - C_m^n = f(p^n)$$

where, at each timestep the new C^{n+1} values are converted back into p values using the Equilibrium Relative Humidity curves and the value of p_{sat} at each particular point. This avoids problems with the large range of values for $\delta C/\delta p$, though introducing the disadvantage of lack of stability if the time intervals, δt, are too large and the space intervals, δx, are too small. For the linear difference equation :

$$\delta C = \frac{D\delta t}{(\delta x)^2}\,(C(x-\delta x)-2C(x)+C(x+\delta x))$$

the stability requirement is that $\frac{D\delta t}{(\delta x)^2} \leq \frac{1}{2}$. For the case where

$$\delta C = \frac{D'\delta t}{(\delta x)^2}\,(p(x-\delta x)-2p(x)+p(x+\delta x))$$ the position is

not so clear, though if it is reformulated as

$$k\delta p = \frac{D\delta t}{(\delta x)^2}((x-\delta x)-2p(x)+p(x+\delta x)),$$ where k is the "conversion factor" between concentration and pressure at the particular value of time and position, one could argue that, if k_{min} is the minimum value of k reached at any time or position, then, as long as

$$\frac{D'\delta t}{k_{min}(\delta x)^2} \le \frac{1}{2},$$ one would probably not encounter stability problems. Intuitively, the stability requirement may be formulated as the requirement that the time steps should be small enough that the process does not affect more than the neighbouring space points within the time interval.

In addition to the criterion in the preceding paragraph, the computer program was run with various values of time interval for the twenty space intervals used, to discover whether there was any obvious point where instability became a problem. Some results follow (Table (8.5.3.1)) and it may be seen that there is an oscillation of values at the hot end when the number of time intervals is reduced to five. As accuracy had suffered before this point, and the computation time was small, 10,000 time intervals were used for calculating all the graphed results using this method, a δt of some four minutes.

Table 8.5.3.1

"numt" is the number of time intervals into which the total time is divided for that calculation.

```
numt = 100000

initial m/c =   9.63          D prime =   3.946E-0009
minimum temp =  0.70          maximum temp =   41.60

moisture content changes at t = 38880 mins

 -2.42
 -1.66   -0.76   -0.02    0.27    0.31    0.30    0.28    0.25    0.23    0.21
  0.19    0.17    0.16    0.14    0.13    0.12    0.10    0.10    0.14    1.11

numt = 10000


 -2.42
 -1.66   -0.76   -0.02    0.27    0.31    0.30    0.28    0.25    0.23    0.21
  0.19    0.17    0.16    0.14    0.13    0.12    0.10    0.10    0.14    1.11

numt = 1000


 -2.42
 -1.66   -0.76   -0.02    0.27    0.32    0.30    0.28    0.25    0.23    0.21
  0.19    0.17    0.16    0.14    0.13    0.12    0.10    0.10    0.14    1.11
```

Table 8.5.3.1 (cont.)

```
numt = 100

initial m/c =   9.63            D prime =  3.946E-0009
minimum temp =  0.70            maximum temp =  41.60

moisture content changes at t = 38880 mins

 -2.42
 -1.66   -0.77   -0.02    0.27    0.32    0.30    0.28    0.25    0.23    0.21
  0.19    0.17    0.16    0.14    0.13    0.12    0.10    0.10    0.14    1.11


numt = 10

 -2.45
 -1.70   -0.78    0.02    0.30    0.32    0.30    0.28    0.25    0.23    0.21
  0.19    0.17    0.16    0.14    0.13    0.12    0.10    0.10    0.13    1.12

numt = 5

 -6.04
  1.15   -1.97    0.13    0.32    0.33    0.30    0.28    0.25    0.23    0.21
  0.19    0.17    0.16    0.14    0.13    0.12    0.10    0.10    0.13    1.13
```

Table 8.5.3.1 (cont.)

```
numt = 3

initial m/c =    9.63            D prime =  3.946E-0009
minimum temp =  0.70             maximum temp =  41.60

moisture content changes at t = 38880 mins

-24.18
 18.52  -10.56    0.39    0.36    0.33    0.30    0.27    0.25    0.23    0.21
  0.19    0.17    0.16    0.14    0.13    0.12    0.10    0.09    0.13    1.14


numt = 2


 25.57
-17.33    0.42    0.39    0.35    0.33    0.30    0.27    0.25    0.23    0.21
  0.19    0.17    0.16    0.14    0.13    0.12    0.10    0.09    0.12    1.15
```

8.6 DISCUSSION OF RESULTS

All calculations used twenty x intervals (δx = 51mm), which were expanded to two hundred using a spline under tension before graphing.

The employment of a numeric processor and a programming language able to use numbers with a dynamic range of 1.9×10^{-4951} to 1.1×10^{4932} and with 19 to 20 significant digits ensured the minimisation of rounding errors.

Although it had been expected that the lagged thick-walled aluminium tube would force a linear temperature gradient, it was found that there was a slight deflection of the gradient towards the ambient temperature (at the time of the experiments, near to 0°C). The effect of a non-linear temperature gradient was investigated, using gradients derived as follows (with x normalised to 0 - 1):

a. linear

$$y = (1 - x) \qquad \text{......(8.6.1)}$$

b. concave

$$y = (1 - x) - 0.5x(1 - x) \qquad \text{......(8.6.2)}$$

and $$y = (1 - x) - 0.25x(1 - x) \qquad \text{......(8.6.3)}$$

c. convex

$$y = (1 - x) + 0.5x(1 - x) \qquad \text{......(8.6.4)}$$

and $$y = (1 - x) + 0.25x(1 - x) \qquad \text{......(8.6.5)}$$

with $$\theta_x = \theta_i + (\theta_o - \theta_i)\ y$$

where θ_x is the temperature at point x
θ_0 is the temperature at x = 0 (the hot end)
θ_1 is the temperature at x = 1 (the cold end)

These yielded a maximum mid-point distortion of 5 and 2.5°C, the actual distortion found being rather less than the latter, in a concave direction.

The effect of a different equilibrium curve was also investigated. Calculations were performed using those published by Finn-Kelcey and Hulbert (1957), Riley (1961) and a composite of the Riley curve with that of Scott (1926), in addition to a curve which was drawn as the average of these published results; the curves are titled respectively ERA, Riley, Riley/Scott and "the original composite curve" in the equilibrium graph, (8.6.5). The results (graphs (8.6.8) to (8.6.13)) showed a subtle shift, with no one set of calculated curves fitting the data especially closely.

As these calculated results suggested a value of D' rather higher than that found in wheat by Thorpe (6 rather than 3.946×10^{-11}s), the possibility that this increase was due to a lower packing density/higher porosity, which also implies a lower tortuosity was considered.

As set out in section 7.2, Thorpe's value of D' of 3.946×10^{-11}s is derived from D' for water vapour in free air reduced by a factor:

$\alpha = 0.212$,

made up of $\epsilon = 0.4$, the porosity,

and $\gamma = 0.53$, the tortuosity,
where $\alpha = \varepsilon\gamma$

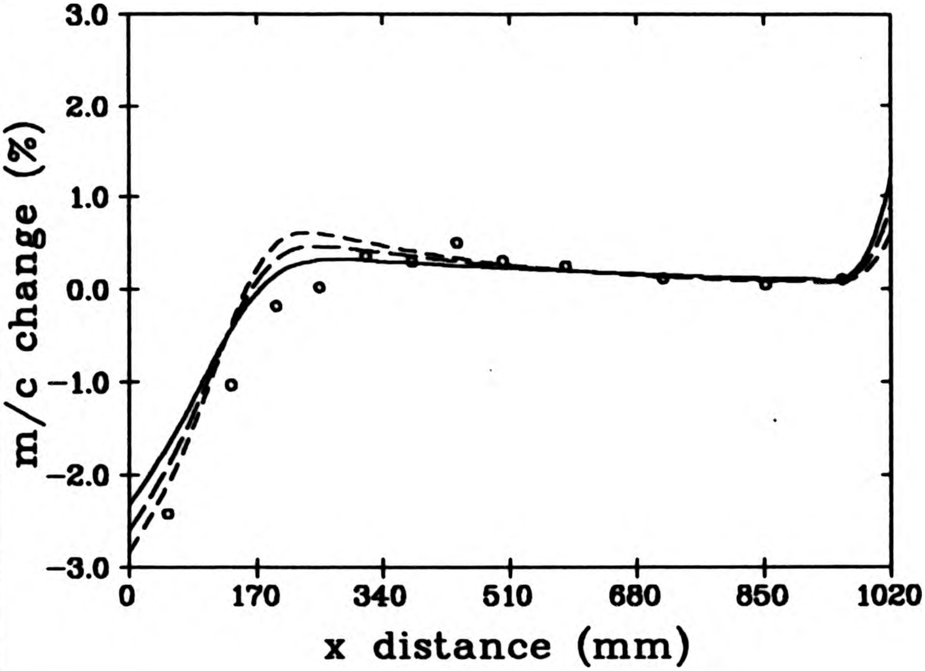
The weight of the contents of the tube used in the second run was added to that of the extracted samples, giving a total weight of 2.487 kg, in the tube volume of 4.66×10^{-3}, and bulk density of 533.6 kg m^{-3}. As the bean density was about 950 kg m^{-3},

$$\varepsilon = 1 - \frac{\text{bulk density}}{\text{grain density}} = 0.44$$

The increase in γ ("inverse tortuosity") is rather more difficult to estimate. As the porosity becomes greater so the inter-bean air paths become more direct but not necessarily in a linear relationship. Similarly, the granule size (cocoa bean against wheat grain) may have an influence on the tortuosity of the air path. For D' to rise, on this account, to 6×10^{-11}s, as providing a reasonable fit to the experimental data, γ would have to be some 38% higher for the cocoa in this experiment than for the wheat in Pixton and Griffiths' experiment (0.73 rather than 0.53). According to the results of Bennett and Bolch (1971), in the case of packed glass spheres such an increase is not found to occur.

The closest fit was obtained by calculating on the basis of the tube length being 1000 mm rather than 1020 mm, with the experimental results being shifted 20 mm towards the hot end, with a value of D' of 5×10^{-11}s (graphs (6.6.14) to (6.6.17)). It is difficult to see any justification for this.

Graph 8.8.1



Experiment 1

Concave Temperature Gradients

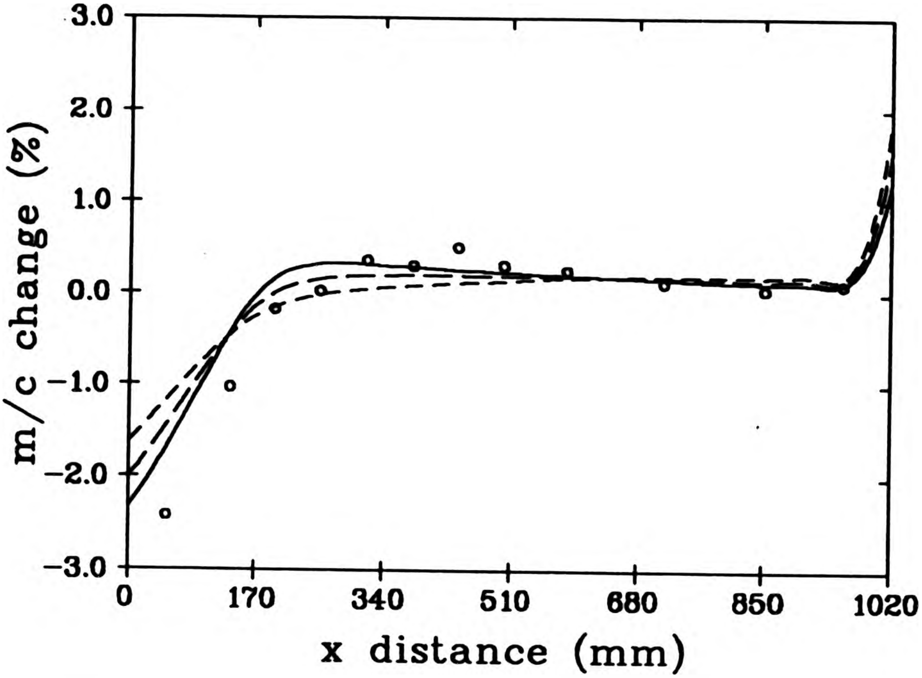
- • experimental results
- ——— linear temperature gradient (eqn 8.8.1)
- — — concave temperature gradient (eqn 8.8.3)
- - - - concave temperature gradient (eqn 8.8.2)

➡ Curves calculated by the explicit method

➡ $D' = 3.948 \times 10^{-11} s$

➡ Moisture content change calculated on a dry weight basis

Graph 8.6.2



Experiment 1

Convex Temperature Gradients

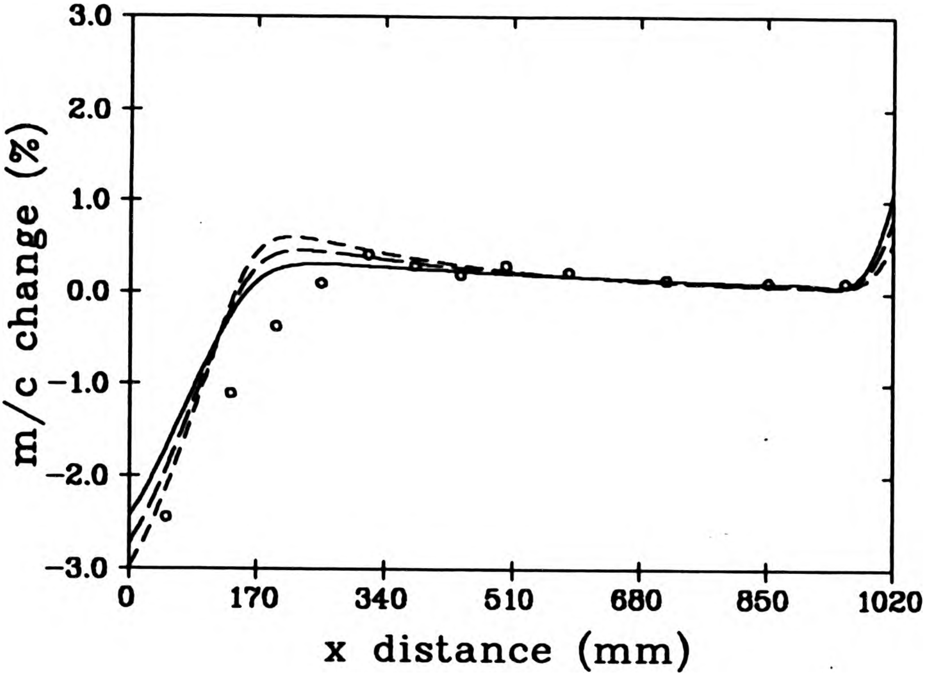
•	experimental results
———	linear temperature gradient (eqn 8.6.1)
— —	convex temperature gradient (eqn 8.6.5)
- - -	convex temperature gradient (eqn 8.6.4)

➨ Curves calculated by the explicit method

➨ $D' = 3.948 \times 10^{-11}s$

➨ Moisture content change calculated on a dry weight basis

Graph 8.6.3



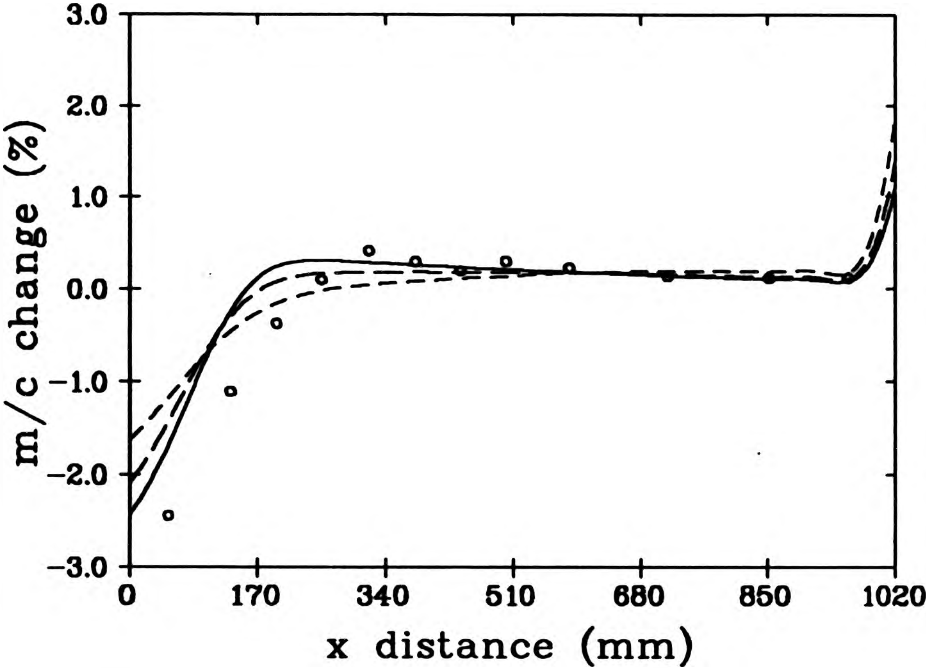
Experiment 2

Concave Temperature Gradients

•	experimental results
———	linear temperature gradient (eqn 8.6.1)
— —	concave temperature gradient (eqn 8.6.3)
– – –	concave temperature gradient (eqn 8.6.2)

- Curves calculated by the explicit method
- $D' = 3.946 \times 10^{-11}$s
- Moisture content change calculated on a dry weight basis

Graph 8.6.4



Experiment 2

Convex Temperature Gradients

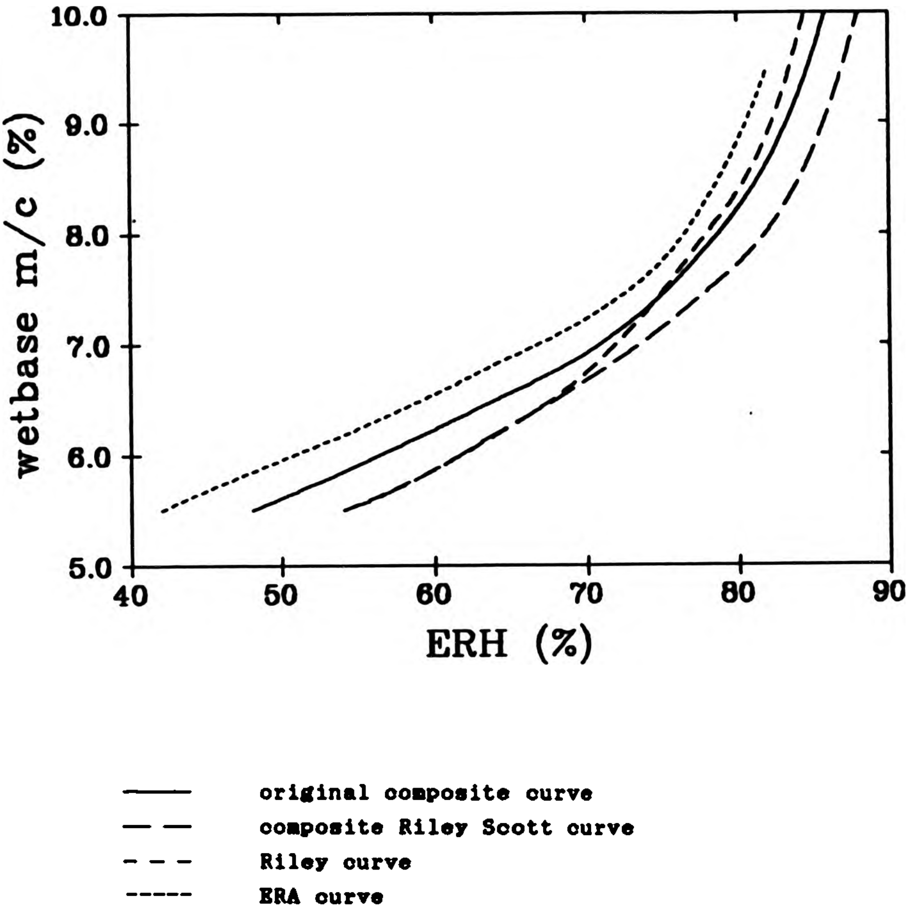
- • experimental results
- ——— linear temperature gradient (eqn 8.6.1)
- — — convex temperature gradient (eqn 8.6.5)
- - - - convex temperature gradient (eqn 8.6.4)

➡ Curves calculated by the explicit method

➡ $D' = 3.948 \times 10^{-11} s$

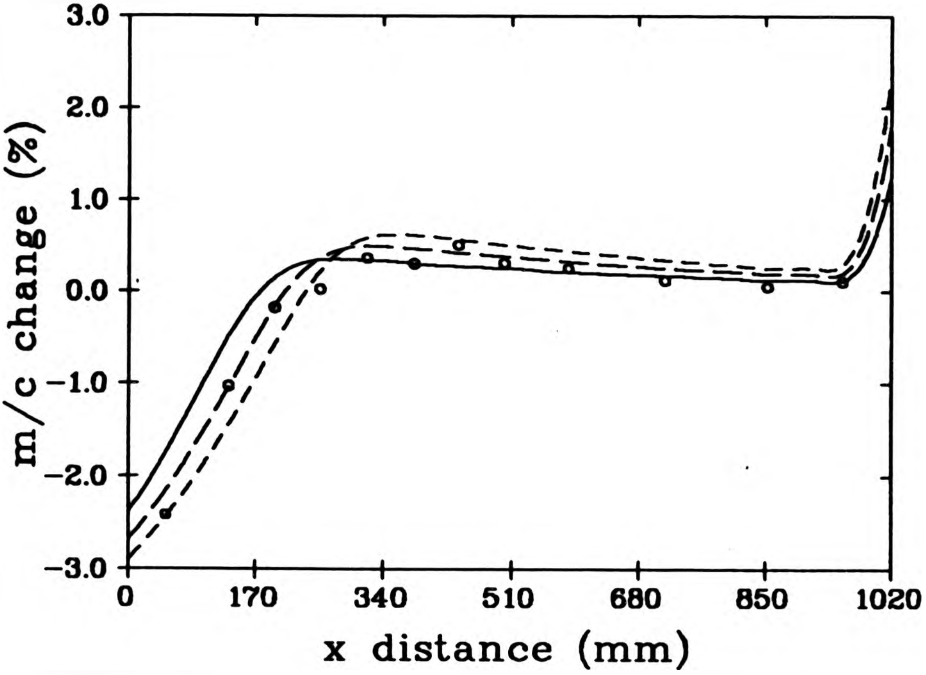
➡ Moisture content change calculated on a dry weight basis

Graph 8.6.5 Some Published Equilibrium Curves



(the "original composite curve" was drawn as an average of the other curves.)

Graph 8.6.6



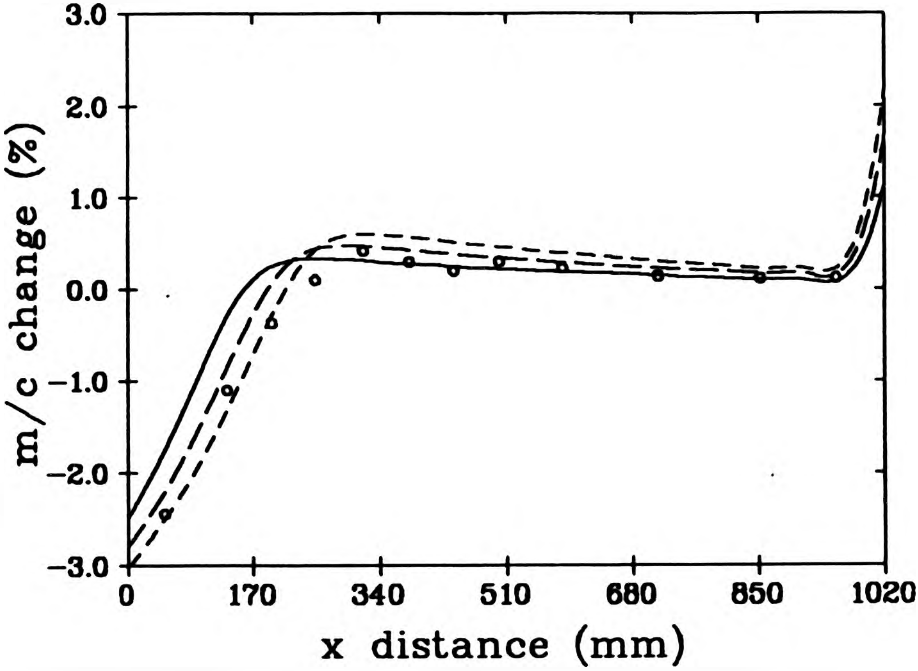
Experiment 1
using Original Composite Equilibrium Curve

•	experimental results
———	D' = 3.946 × 10^{-11}s
— —	D' = 6.0 × 10^{-11}s
- - -	D' = 8.0 × 10^{-11}s

➜ Curves calculated by the explicit method

➜ Moisture content change calculated on a dry weight basis

Graph 8.6.7

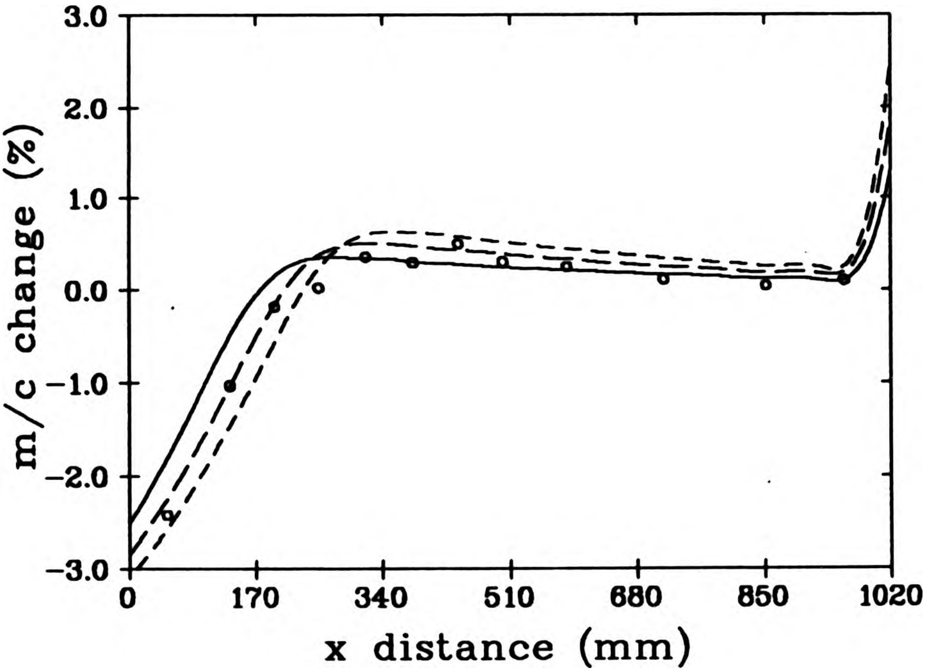


Experiment 2
using Original Composite Equilibrium Curve

•	experimental results
———	D' = 3.946 × 10^{-11}s
— —	D' = 6.0 × 10^{-11}s
- - -	D' = 8.0 × 10^{-11}s

➡ Curves calculated by the explicit method
➡ Moisture content change calculated on a dry weight basis

Graph 8.6.8



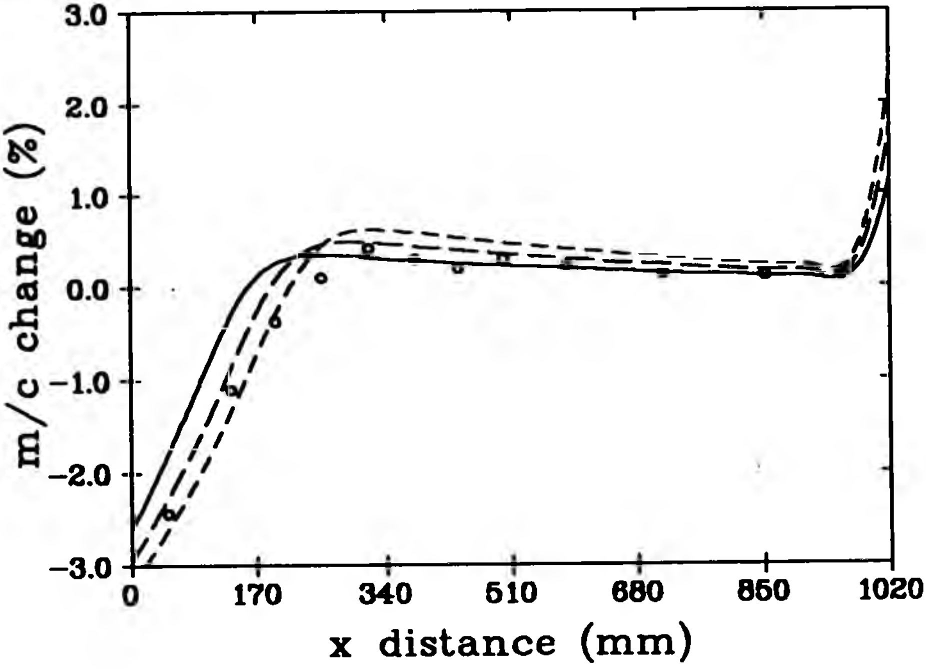
Experiment 1
using Riley Scott Equilibrium Curve

• experimental results
——— $D' = 3.946 \times 10^{-11}$s
— — $D' = 6.0 \times 10^{-11}$s
- - - $D' = 8.0 \times 10^{-11}$s

➡ Curves calculated by the explicit method

➡ Moisture content change calculated on a dry weight basis

Graph 8.6.9



Experiment 2

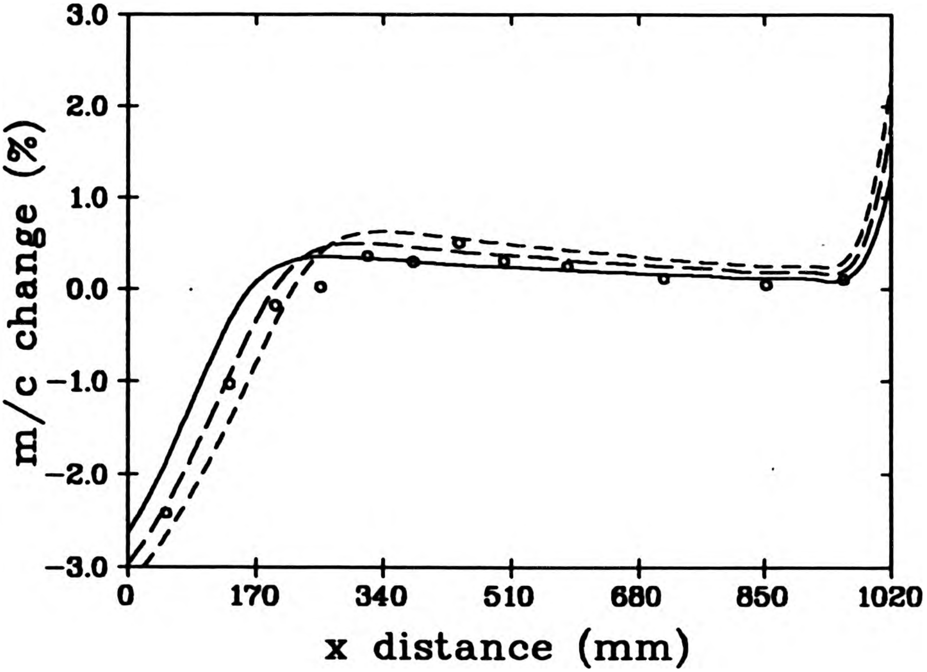
using Riley Scott Equilibrium Curve

•	experimental results
———	$D' = 3.946 \times 10^{-11}s$
— —	$D' = 6.0 \times 10^{-11}s$
- - -	$D' = 8.0 \times 10^{-11}s$

→ Curves calculated by the explicit method

→ Moisture content change calculated on a dry weight basis

Graph 8.6.10

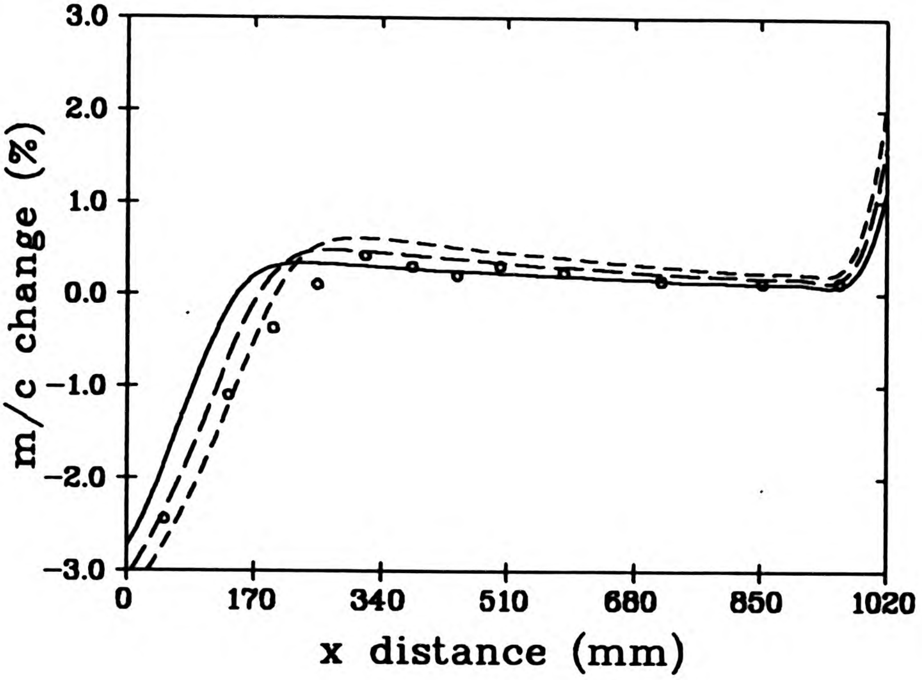


Experiment 1
using Riley Equilibrium Curve

•	experimental results
——	D′ = 3.946 × 10^{-11}s
— —	D′ = 6.0 × 10^{-11}s
- - -	D′ = 8.0 × 10^{-11}s

- Curves calculated by the explicit method
- Moisture content change calculated on a dry weight basis

Graph 8.6.11



Experiment 2

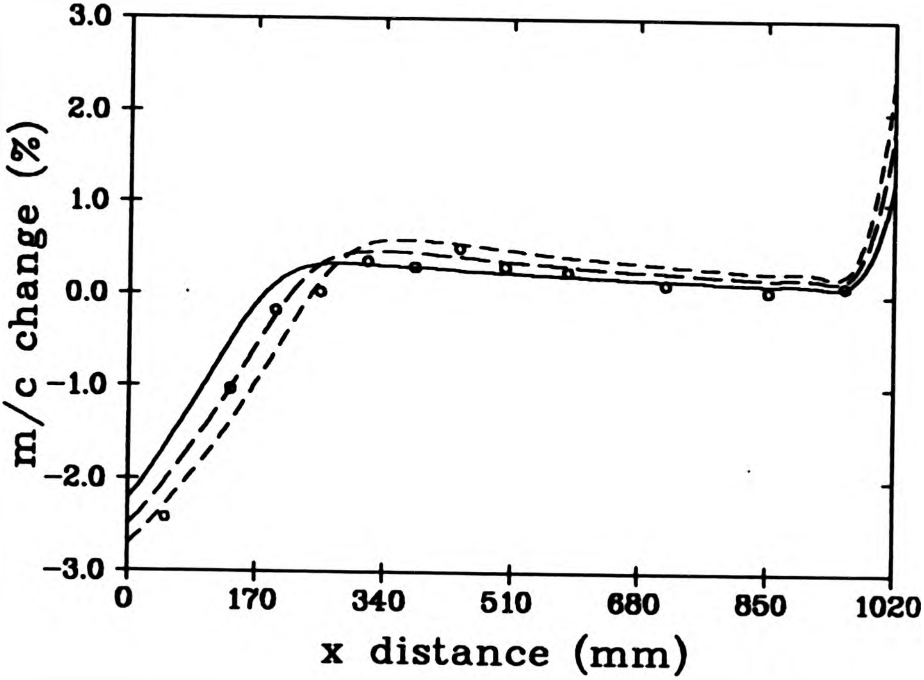
using Riley Equilibrium Curve

•	experimental results
———	$D' = 3.946 \times 10^{-11}s$
— —	$D' = 6.0 \times 10^{-11}s$
- - -	$D' = 8.0 \times 10^{-11}s$

➡ Curves calculated by the explicit method

➡ Moisture content change calculated on a dry weight basis

Graph 8.6.12



Experiment 1

using ERA Equilibrium Curve

• experimental results

——— D' = 3.946 × 10^{-11}s

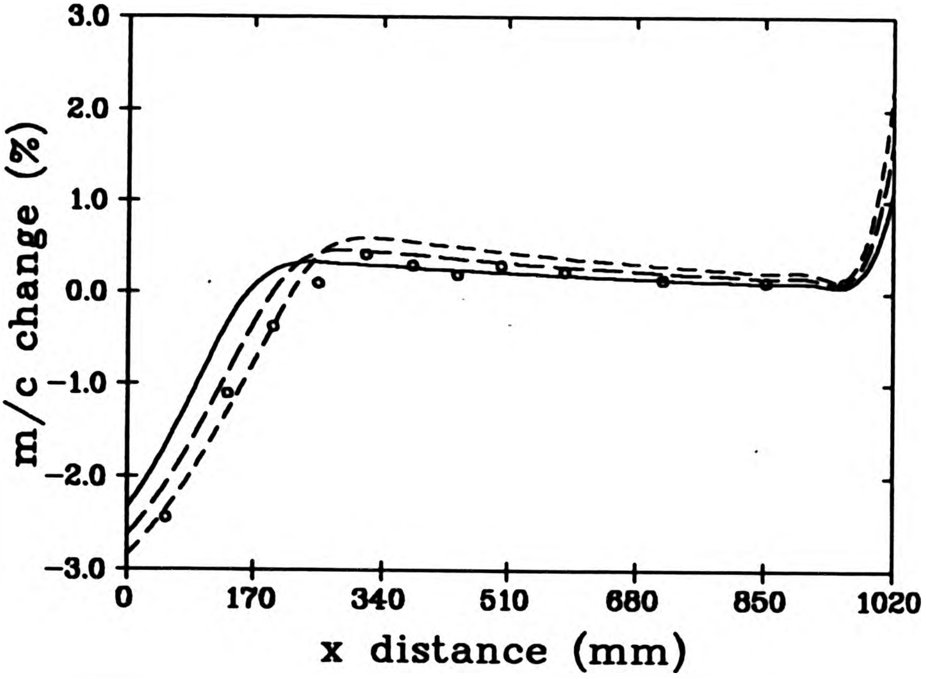
— — D' = 6.0 × 10^{-11}s

- - - D' = 8.0 × 10^{-11}s

➡ Curves calculated by the explicit method

➡ Moisture content change calculated on a dry weight basis

Graph 8.6.13



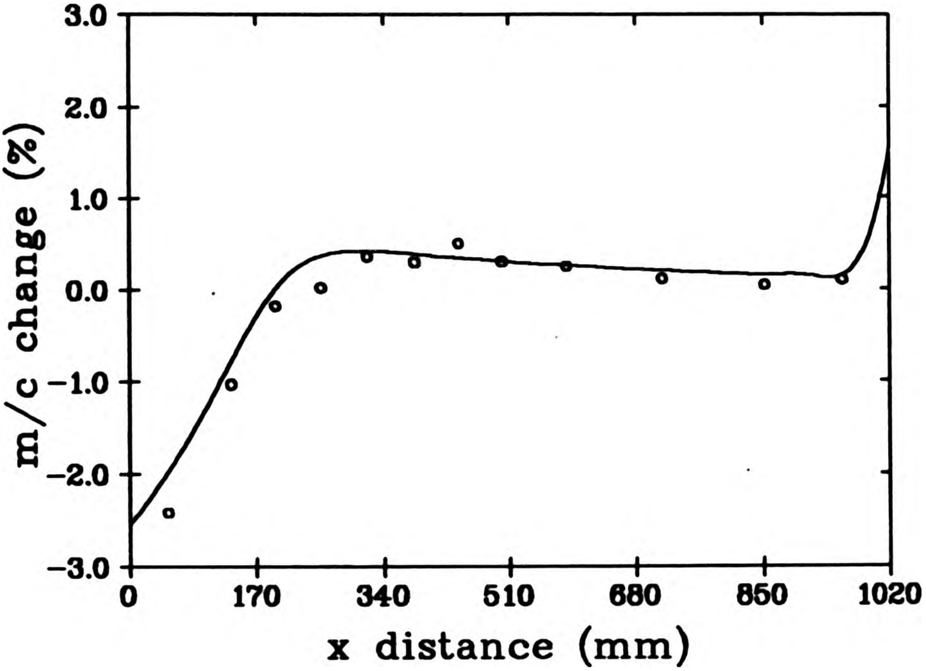
Experiment 2
using ERA Equilibrium Curve

•	experimental results
——	$D' = 3.946 \times 10^{-11}s$
— —	$D' = 6.0 \times 10^{-11}s$
- - -	$D' = 8.0 \times 10^{-11}s$

➔ Curves calculated by the explicit method

➔ Moisture content change calculated on a dry weight basis

Graph 8.6.14



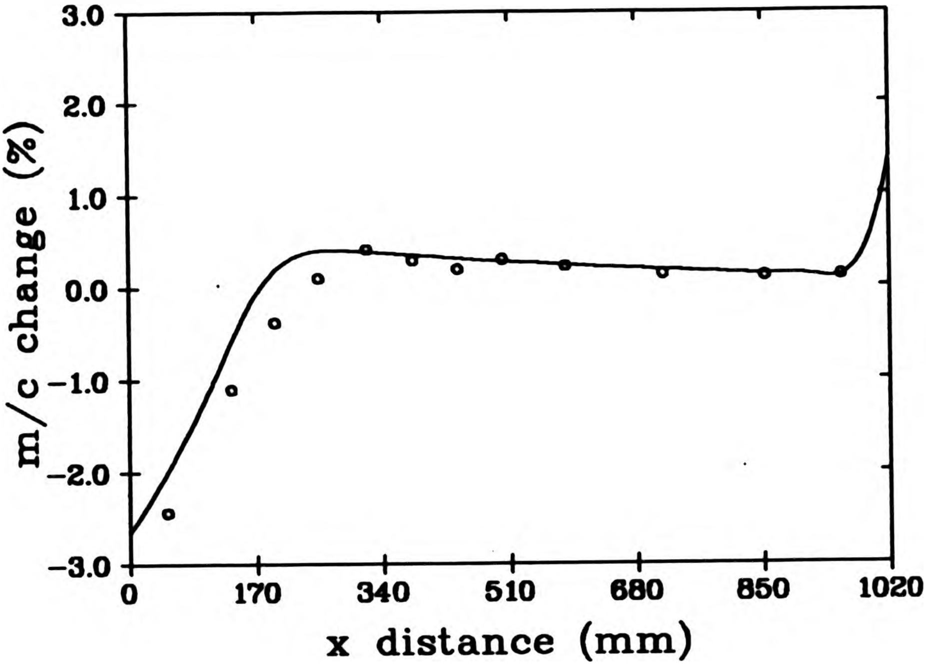
Experiment 1

using Original Composite Equilibrium Curve

- • experimental results
- —— $D' = 5 \times 10^{-11}s$

- ➧ l = 1020 mm
- ➧ Curve calculated by the explicit method
- ➧ Moisture content change calculated on a dry weight basis

Graph 6.6.15



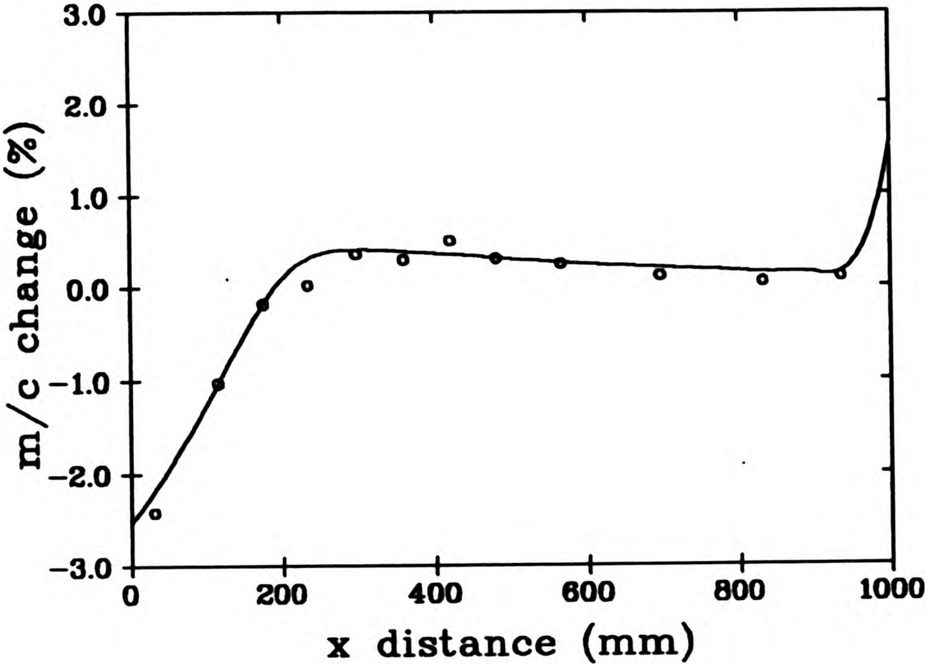
Experiment 2
using Original Composite Equilibrium Curve

• experimental results

——— $D' = 5 \times 10^{-11}s$

- l = 1020 mm
- Curve calculated by the explicit method
- Moisture content change calculated on a dry weight basis

Graph 6.6.16



Experiment 1

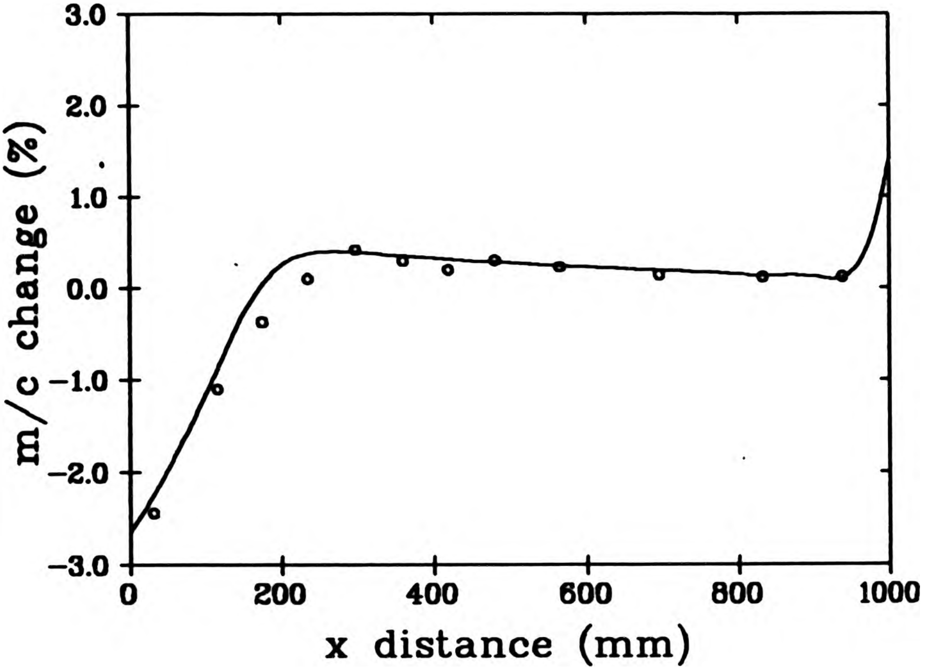
using Original Composite Equilibrium Curve

• experimental results

—— $D' = 5 \times 10^{-11}$s

- l = 1000 mm
- Curve calculated by the explicit method
- Moisture content change calculated on a dry weight basis

Graph 8.6.17



Experiment 2
using Original Composite Equilibrium Curve

- • experimental results
- —— $D' = 5 \times 10^{-11}s$

- 1 = 1000 mm
- Curve calculated by the explicit method
- Moisture content change calculated on a dry weight basis

8.7 CONCLUSIONS

Given the extreme variability of the properties of cocoa beans relevant to the experiments carried out, size, shape, equilibrium moisture content, and, probably as a result, the variability of the published equilibrium curves, it is not surprising that an exact figure cannot be determined for the intra-particle and bulk diffusion rates.

What has been determined, however, is that

a. the intra-particle diffusion rate is less than one three hundredth that of water vapour in air.

b. the bulk rate may, therefore, be deduced to be governed by the rate for water vapour in free air, reduced by a composite tortuosity/porosity factor.

c. this deduction has been confirmed by the results of the closed tube experiment. Whatever the value for D' chosen as yielding the closest fit to the results, it is certainly less than 18.61×10^{-11}s, the value for water vapour in free air.

9. DISCUSSION

Having determined that the bulk diffusion coefficient of cocoa is of the order of 6×10^{-11}s, the remaining question of those raised in the introduction is whether moisture migration in a ventilated stow of cocoa would produce as much condensation as convection in an unventilated hold.

9.1 CONVECTION IN AN UNVENTILATED HOLD

A bagged cargo is carried in a "dunnaged" hold, that is, a hold with battens or plywood to keep the cargo away from the shell plating and the floor of the hold. In the case of a warm cocoa cargo being carried into colder ambient conditions without ventilation, convective circulation arises because of the difference in density between the warm air in the interstices of the cargo and the cooled air in the the surrounding air space.

Assuming a cargo temperature of 25°C and an external air temperature of 5°C, typical winter conditions for a cocoa cargo carried from West Africa to Northern Europe, the average temperature of the air in the space between the shell plating and the side dunnage would be some 10°C, and its relative humidity 100%. The cargo would be loaded at a moisture content in equilibrium with air of about 70% relative humidity.

At 10°C, 100% relative humidity
humid volume is 0.824 m^3kg^{-1} of dry air
moisture content is 7.73×10^{-3} $kgkg^{-1}$ of dry air

and total density is $(0.824)^{-1} \times 1.00773$ kgm^{-3}
$= 1.223$ kgm^{-3}

At 25°C, 70% relative humidity
humid volume is 0.877 m^{3}kg^{-1} of dry air
moisture content is 14.10×10^{-3} kgkg^{-1} of dry air

and total density is $(0.877)^{-1} \times 1.0141$ kgm^{-3}
$= 1.156$ kgm^{-3}

If the height of the stow is h m, the difference in mass of the two air columns, that in the stow and that in the space between the dunnage and the shell plating, per m^{-2} of air cross section is

$$0.067\, h \text{ kg}$$

and the resultant pressure drop over the height of the stow is

$$0.067\, h\, g = 0.657\, h \text{ Pa}$$

or 0.657 Pa per m height of stow

Since there are no available values for airflow through bagged cocoa as a result of a pressure difference of this order, two methods of approximate assessment will be compared.

Coulson and Richardson (1980) provide a formula, an elaboration of Darcy's Law, for low velocities, where the flow is laminar:

$$u = \frac{B(-\Delta P)}{\mu l}$$

where $-\Delta P$ is the pressure drop across the bed,
l is the thickness of the bed,
u is the average velocity of flow of the fluid, defined as $(1/A)(dV/dt)$,
A is the total cross-sectional area of the bed,
V is the volume of fluid flowing in time t,
μ is the viscosity of the fluid, and
B is the permeability coefficient, depending only on the properties of the bed.

Values of B for various geometrical shapes of various sizes are tabulated in Coulson and Richardson, though for rather smaller sizes than are of interest here. Some values are:

	B
Spheres:	
1/8 in ⌀ (3.175 mm)	$9.4 \times 10^{-9}\ m^2$
1/4 in ⌀ (6.35 mm)	$4.9 \times 10^{-8}\ m^2$
5/16in ⌀ (7.94 mm)	$9.4 \times 10^{-8}\ m^2$
Cylinders:	
1/8 in ⌀ × 1/8 in (3.175 × 3.175 mm)	$1.1 \times 10^{-8}\ m^2$
1/8 in ⌀ × 1/4 in (3.175 × 6.35 mm)	$1.2 \times 10^{-8}\ m^2$
1/4 in ⌀ × 1/4 in (6.35 × 6.35 mm)	$4.6 \times 10^{-8}\ m^2$

Given the irregular shape of the cocoa bean, with its rough surface, and the diameter of a sphere of equal volume of some 10mm (section 7.5), a value for B of $0.1 \times 10^{-6}\ m^2$ has been used in the following calculations.

Substituting, then, a value of μ for air at 25°C of 18×10^{-6} Nsm^{-2}, and the previously derived values into the above equation,

$$u = 3.65 \times 10^{-3}\ m^{3}m^{-2}s^{-1}$$

or

$$4.18 \times 10^{-3}\ \text{kg of dry air}\ m^{-2}s^{-1}$$

A graph setting out the resistance to airflow of various grains and seeds is provided by Hall (1964). By extrapolation values of air velocity for a rate of pressure drop of 0.657 Pam^{-1} (= 8.042×10^{-4} in water ft^{-1}) may be read for various commodities.

Values from graph:

product	average velocity	
	$ft^{3}ft^{-2}min^{-1}$	$m^{3}m^{-2}s^{-1}$
clean ear corn	8.0	0.041
peanuts	2.75	0.014
ear corn (as harvested)	0.85	4.3×10^{-3}
value calculated above		*3.65×10^{-3}*
shelled corn	0.16	0.81×10^{-3}
wheat	0.04	0.20×10^{-3}

Two factors affecting resistance are apparent from these values, particle size and surface roughness. Ear corn as harvested would have the green leafy covering and the hairy tassel still attached, and this must be responsible for the difference of nearly ten times between the value for this product and that for clean ear corn. From these considerations, one might expect the velocity for cocoa to be nearer that for peanuts than that for ear corn as harvested, as approximated theoretically above. As, however, the theoretical value is conservative with respect to the argument of this section, the smaller value will be used in the following calculations.

At 25°C, 70% RH, air contains

14.1×10^{-3} kg water per kg dry air

At 5°C, 100% RH, the temperature of the deckhead, on which condenation would form, air contains

5.47×10^{-3} kg water per kg dry air

The difference is the quantity of moisture per kilogram of dry air available to condense:

8.93×10^{-3} kg water per kg dry air,

and the condensation rate is, then:

$$4.16 \times 8.93 \times 10^{-6} \text{ kg water } m^{-2}s^{-1}$$

$$= 37.15 \times 10^{-6} \text{ kg water } m^{-2}s^{-1}$$

or

$$3.21 \text{ kg water } m^{-2} \text{ per day}$$

Assuming a stowage density of 580 kgm^{-3}, the top 25 mm layer would weigh 14.5 kgm^{-2}. With a wet base moisture content of 7.5%, the dry matter would be 13.49 kgm^{-2}, and, after the addition of one day's condensation, the weight of moisture would be 4.22 kgm^{-2}. The resultant moisture content for this 25 mm layer would be

$$\frac{4.22}{4.22 + 13.49} \times 100 = 23.8\% \text{ wet base}$$

or

31.3% dry base.

The situation for a cargo of grain bulk loaded into the frames, without dunnage, is rather different, even under similar initial conditions, external air at 5°C, grain at 25°C, in equilibrium with 70% RH, head space air at 10°C.

It is assumed that the convecting air descends through a cross-sectional area, situated around the periphery of the stow, equal to that in the centre where the air ascends. The descending air flow at the periphery may be initiated by cooling by conduction through the plating, but, given the low thermal conductivity of grain, the depth from the sides to which appreciable cooling has occurred by conduction alone is too small to yield the equal cross-sectional area situation assumed above. It is likely that the air flow initiated by this cooling cools the surrounding area, and, thus, increases the cooled area until the steady state, from the flow aspect, of equal areas is attained.

The descending air column will not have a constant temperature, but rather increase from 10°C at the surface to some 20°C at the bottom of the stow, an average of 15°C. The ascending air column is assumed to be at 25°C.

At 15°C, 100% relative humidity

humid volume is 0.843 m^3kg^{-1} of dry air

moisture content is 10.79 × 10^{-3} $kgkg^{-1}$ of dry air

and total density is $(0.843)^{-1} \times 1.01079$ kgm^{-3}

$= 1.199$ kgm^{-3}

At 25°C, 70% relative humidity

total density is 1.156 kgm^{-3}

If the height of the stow is h m, the difference in mass of the two air columns per m^{-2} of air cross section is

$$0.043\ h\ \text{kg}$$

and the resultant pressure drop over the height of the stow is

$$0.043\ h\ g = 0.422\ h\ \text{Pa}$$

In this case, however, the path length subject to the resistance to air flow of the grain is $2 \times h$, yielding a rate of pressure drop of

0.211 Pa per m.

or

2.58×10^{-4} in water per ft

From the graph

product	average velocity	
	$ft^3 ft^{-2} min^{-1}$	$m^3 m^{-2} s^{-1}$
shelled corn	0.045	0.23×10^{-3}
wheat	0.011	0.056×10^{-3}

For maize, then, the air flow is

$$0.266 \times 10^{-3} \text{ kg of dry air } m^{-2} s^{-1}$$

At 25°C, 70% RH, air contains

$$14.1 \times 10^{-3} \text{ kg water per kg dry air}$$

At 5°C, 100% RH, the temperature of the deckhead, on which condenation would form, air contains

$$5.47 \times 10^{-3} \text{ kg water per kg dry air}$$

The difference is the quantity of moisture per kilogram of dry air available to condense:

$$8.93 \times 10^{-3} \text{ kg water per kg dry air,}$$

and the condensation rate is, then:

$$0.266 \times 8.93 \times 10^{-6} \text{ kg water } m^{-2} s^{-1}$$

$$= 2.375 \times 10^{-6} \text{ kg water } m^{-2} s^{-1}$$

or

$$0.21 \text{ kg water } m^{-2} \text{ per day}$$

For wheat the air flow is

$$0.0647 \times 10^{-3} \text{ kg of dry air } m^{-2}s^{-1}$$

As before, the quantity of moisture per kilogram of dry air available to condense is:

$$8.93 \times 10^{-3} \text{ kg water per kg dry air,}$$

and the condensation rate is, then:

$$0.0647 \times 8.93 \times 10^{-6} \text{ kg water } m^{-2}s^{-1}$$

$$= 0.5778 \times 10^{-6} \text{ kg water } m^{-2}s^{-1}$$

or

$$0.050 \text{ kg water } m^{-2} \text{ per day}$$

The various quantities of moisture, then, available to condense as "ship sweat", as a result of convection in an unventilated hold are:

cocoa	**3.21 kgm^{-2} per day**
maize	**0.21 kgm^{-2} per day**
wheat	**0.050 kgm^{-2} per day**

(Cocoa being carried in bags, wheat and maize in bulk)

This difference between cocoa and grain tallies with experience; bulk carriers generally have a rudimentary and ineffective ventilation system, and the cargo is loaded into the coamings where the head space is not ventilated, yet damage is usually limited to a thin

caked surface crust, which is easily skimmed off and discarded. "Ship sweat" condensation has, however, been a problem with shipments of cocoa, where ventilation has been limited, either intentionally or because of bad weather.

9.2 MOISTURE MIGRATION IN A VENTILATED HOLD

Moisture movement due to convection in a ventilated hold would be rather greater than in the unventilated case, because the air in the head space would be at 5°C rather than 10°C, but the ascending warm air from the stow would be exhausted by the ventilation rather than form condensation on the deck head.

In addition, the ventilating air, by penetrating the stow to a degree, would remove moisture condensed on the cooled surface of bags in the stow, and, by cooling to a greater depth than that predicted on the basis of thermal conduction alone, would reduce the steepness of the thermal gradient. As the exact depth of this penetration is uncertain, however, the stow is considered in this section as impermeable by ventilating air, allowing the simplifying assumptions of a thermal gradient solely the result of thermal conduction, and the availability of all migrating moisture to condense on the cargo surface. These assumptions are conservative to the argument, since they maximise the potential effect of moisture migration.

Two simplified cases will be considered, that where the temperature gradient occurs over a depth of 1m, and that over a depth of 2m. The gradient is assumed to be linear.

Vapour pressure at 25°C, 70% RH
22.17 mb

Vapour pressure at 5°C, 70% RH
6.11 mb

(The surface material is cooled by the ventilating air, but still is in equilibrium with 70% RH.)

Vapour pressure difference
16.06 mb

The simplified linear vapour pressure gradient is, then, in the two cases:

$16.06\ \mathrm{mbm}^{-1}$

and

$8.03\ \mathrm{mbm}^{-1}$

The bulk moisture diffusion coefficient for cocoa was found to be some 6×10^{-11}s, or

$6 \times 10^{-9}\ \mathrm{kgm}^{-1}\mathrm{mb}^{-1}\mathrm{s}^{-1}$

For the two cases, the moisture arriving at the surface will be:

$96.4 \times 10^{-9}\ \mathrm{kgm}^{2}\mathrm{s}^{-1}$

$48.2 \times 10^{-9}\ \mathrm{kgm}^{2}\mathrm{s}^{-1}$

or

$$8.33 \times 10^{-3}\ \mathrm{kgm}^{-2}\ \text{per day}$$

$$4.16 \times 10^{-3}\ \mathrm{kgm}^{-2}\ \text{per day}$$

compared with 3.21 kgm^{-2} per day as a result of convection in an unventilated hold, a factor of 385 and 770 in the two cases.

The conjecture, then, that ventilation of a hold containing bagged cocoa might produce as much damaging condensation as witholding it is shown to be mistaken.

10. SUMMARY AND CONCLUSIONS

The aim of the research has been to determine experimentally the bulk moisture diffusion coefficient for cocoa, and, by quantifying it, to investigate the contribution of such diffusion to wetting and mould damage that has occurred on the surface of cargoes during shipment from West Africa to Northern Europe.

Theory for the analysis of experimental results and for the application of the coefficient to real situations has been developed by the modification of the Fick diffusion equations to allow their scope to include:

a. diffusion as the result of a thermal gradient,

b. the peculiar nature of hygroscopic porous materials, distinguishing between moisture concentration in the inter-particular airspaces, and in the bulk material, and

c. the difference in diffusion rates through the inter-particle airspaces and through the beans themselves.

Simplifications to the general theory (including the neglect of changes in concentration over the region of diffusion, the imposition of a linear temperature gradient or a gradient constant with respect to time, and the application of a constant temperature to the surface) applicable both to particular experiments and to real situations have been developed, and have enabled the approximate solution of the resulting equations by finite difference methods.

Initial experiments, where a constant temperature gradient was imposed upon a cocoa bean filled tube, with a constant humidity at the open, hot end, consistently yielded at each measurement point a bulk coefficient for cocoa many times higher than that for rice, maize and wheat. Attempts to repeat the experiment, however, were unsuccessful, with no pattern to the changes in moisture content discernible on the basis of the theory developed up to that time.

A second series of experiments was undertaken using a larger diameter insulated, sealed tube, with one end cooled, leading to an unsteady state temperature profile, and mimicking the conditions experienced by a cocoa stow during a voyage. The results were consistent with a diffusion coefficient similar to that of wheat. Unfortunately, practical difficulties were experienced both with the insulation of the tube, as the thermal conductivity of the cocoa was lower than predicted and more than negligible radial heat flow occurred, and with variation in moisture content between beans equilibrated to the same relative humidity.

This latter problem was initially attributed to shortcomings in the method of moisture content measurement, but none more consistent was found during trials of other methods (including the use of a vacuum oven, ground and whole beans, and various drying temperatures). Variability in actual moisture content, to a degree similar to that reported by Henderson

(1984), was encountered, attributable to the the wide disparity between the moisture contents of the husk and kernel of the cocoa bean, probably inversely related to their difference in oil content, and the variation in husk to kernel weight ratio from bean to bean. The variability is, then, inherent in the bean, rather than due to a failing of the measurement method.

The deeper understanding of the relationship between diffusion rates into the bean itself, through the inter-particle airspaces, and through the bulk material, obtained from theoretical analysis and published results for wheat, suggested the importance of experimentally determining the first of these. Samples of cocoa beans were isothermally dried using silica gel desiccant, the results being analysed by the same method as that used by Becker and Sallans (1955) for direct comparison with their results for wheat. The intra-particle diffusion rate was found to be of similar magnitude to that for wheat, and many times less than that for water vapour in free air. This allowed the prediction that the bulk diffusion rate would be determined by the rate of diffusion through the inter-particle air-spaces.

The final series of experiments used a thick walled aluminium tube, filled with cocoa beans and closed at both ends. After a short period, the thermal gradient was constant with respect to time, and nearly linear. Twelve cocoa samples were distributed along the tube, and weighed before and after the experiment. These experimental results were compared with values calculated by implicit and explicit finite difference methods, and, whilst a perfect fit was not obtained, the diffusion coefficient was found to lie between the value for wheat and double that value.

To summarise these results, then:

for cocoa:

D' intra-particle	3.9 to 5.6×10^{-13}s
D' bulk	4 to 8×10^{-11}s

which may be compared with published results:

for water vapour in free air:

D'	16.61×10^{-11}s

for wheat:

D' intra-particle	6.78×10^{-13}s
D' bulk	3.946×10^{-11}s

Applying this result to a practical situation during a cocoa voyage, the moisture migrating as a result of the thermal gradient in a ventilated hold was compared with that reaching the surface as the result of convection in an unventilated hold. In the latter case, the difference in convection rate and, consequently, in the rate of moisture transfer to the stow surface between that occurring during the bulk carriage of wheat and maize, and that during the bagged carriage of cocoa was investigated. This yielded an explanation of the successful carriage of grain in bulk carriers, with their ineffectual ventilation systems, whilst bagged cocoa cargoes are damaged by limitation of ventilation.

Under similar conditions, cargo loaded at 25°C and in equilibrium with 70% relative humidity, outside air at 5°C, the moisture carried by convection and available to condense on the deckhead as "ship sweat" in an unventilated hold would be:

bagged cocoa	3.21 kgm^{-2} per day
bulk maize	0.21 kgm^{-2} per day
bulk wheat	0.050 kgm^{-2} per day

Under the same conditions of temperature and equilibrium relative humidity, assuming linear thermal gradients of one and two metres depth, the moisture arriving at the stow surface as a result of moisture migration in a ventilated hold would be:

1 metre thermal gradient

bagged cocoa	8.33×10^{-3} kgm^{-2} per day

2 metre thermal gradient

bagged cocoa	4.16×10^{-3} kgm^{-2} per day

The hypothesis that ventilation of a hold containing bagged cocoa might stimulate the production of a quantity of condensation greater than that occurring in an unventilated hold is thus shown to be mistaken.

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12 APPENDIX

DERIVATION OF A DIFFUSION COEFFICIENT FOR MAIZE FROM THE RESULTS OF AN EXPERIMENT DESCRIBED IN MILTON ET AL (1969)

This appendix is an extract from a report prepared by Arthur Suddaby for Messrs. Holman, Fenwick and Willan in 1977.

The Milton results for maize were obtained in an experiment in which maize was contained in an insulated column 4ft high and 1ft^2 cross sectional area. The column was heated to 40°C at 0.25ft from the bottom. After 30 days when a temperature of 30°C was reached at a distance of about 20 inches from the heat source, the moisture had risen by 0.3% (above the initial value of 13.6%) at a distance of 2ft from the bottom. The moisture content in the vicinity of the heat source was reduced by 3.1%. At 3ft above the bottom there was no change in moisture content but 1ft from the bottom the moisture content was raised by 0.1%. A plot of these figures suggests that the maximum moisture content was 0.33% above the original value, at a distance of 1.45ft from the heat source.

From the area under the plotted curve it can be calculated that this represents a transfer per square foot area of 0.1969 lbs of moisture over a distance of 1.45ft (taking maize as 50 lbs/cu ft). This transfer was carried out as the result of a vapour pressure difference which was initially as follows:

dist. (ft)	temp. (°C)	mois. cont. (%)	equil. R.H. (%)	vap. press (mb)	v.p. diff. (mb)
0.25	40	13.6	76	56.07	40.8
1.7	20.8	13.8	62	15.27	
	(Heat source at 0.25ft)				
and finally (after 32 days)					
0.25	40	10.5	54	39.84	9.7
1.7	30	13.9	71	30.14	

The average difference was therefore

$$\frac{40.6 + 9.7}{2} = 25.25 \text{ mb}$$

Thus 0.1969 lbs was transferred 1.45 ft in 32 days by a vapour pressure difference of 25.25 mb for 1 sq ft of cross sectional area.

Therefore the transfer rate is

$$\frac{0.1969}{25.25 \times 32} \times 1.45 = 0.000353 \text{ lbs ft}^{-2}\text{day}^{-1} \text{ per mb ft}^{-1}.$$

TITLE AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE MIGRATION OF MOISTURE IN COCOA BEANS

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