A MATHEMATICAL MODEL OF SIMULTANEOUS HEAT AND MASS TRANSFER IN A RIGID POROUS MATERIAL DURING THE FALLING RATE PERIOD OF DRYING

A Thesis submitted for the degree of Doctor of Philosophy

by

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March 1983
SUMMARY

A mathematical model of the drying process in porous media has been developed. When translated into a computer model written in Fortran code it displayed good agreement with published experimental work. Numerical algorithms were devised to overcome certain problematical features of the model equations. The model proved capable of describing the variation with respect to time of temperature, pressure and moisture content throughout a rigid homogeneous semi-infinite porous slab subjected to identical boundary conditions on each of its two sides. Unlike the simple diffusion model which predicts parabolic moisture content profiles, the model predicts s-shaped moisture content profiles; these are reported in the literature for a wide variety of porous materials.

Migration of moisture to the surface has been assumed to take place only in the vapour phase. The model is therefore limited to the falling rate period, by which time liquid phase transport has become extinct. The gaseous phase is treated as binary mixture of two constituents, water vapour and air. The flux of each of these components is described by the dusty gas model which has been the subject of recent improvement by a number of workers in the USA.

This work has demonstrated that the dusty gas model may be applicable to porous media when the void fraction is continually changing, though it is recognised that experimental verification is required before this can be stated categorically. An experiment is suggested which would address itself to this question, it would also resolve the controversy
surrounding the somewhat ambiguous definition of the porous medium inherent in the dusty gas model itself.

The suitability of the model as a basis for a computer study in optimal dryer design was evaluated. The most rigorous optimisation method - the classical variational technique - is an iterative procedure wherein the control strategy is improved stepwise over each major iteration forwards and backwards in time. A given control strategy determines a forward trajectory in the real system, a slightly improved strategy is then determined by working backwards in time given the complete history of the forward trajectory. Repetition of this procedure eventually produces an optimal control strategy. The model proved too large, requiring excessive computer storage for a complete history of the forward trajectory. Moreover, the application of the variational technique is complicated enormously by non-linear partial derivatives, and it is clear that its use is limited to fairly simple systems of equations.
DEDICATION

This thesis is dedicated to my son Kevin, who is a continuing source of happiness and amusement to those around him, and my wife Morelia, who typed the equations and kept Kevin out of the way.

"Not what they want but what is good for them"

"Paucioribus, sed intentior, et fida oratione"
ACKNOWLEDGEMENTS

The author would like to thank:

Doctor R Litchfield, whose supervision guided me through some seemingly intractable problems

The Science Research Council and the department of chemical engineering, who provided me with a grant

Andy Tate and Bruce Carter, whose knowledge and understanding of the more obscure features of Prime software proved invaluable

Sue Byron and Morelia, who did the typing; and BS&B for the use of their word processor
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CHAPTER 1

INTRODUCTION
INTRODUCTION

The most common objective in a theoretical study of the drying process is the prediction of the average moisture content in response to a given set of drying conditions. Recently, greater attention than usual has been focussed on this particular area because it has considerable economic significance, especially since the rapid rise in energy costs witnessed over the last decade. Drying is both energy and capital intensive and plays an integral part in the manufacture of a wide range of porous materials. Considerable benefit will ensue when increased understanding of the drying process is utilised at the equipment design stage as well as during operation.

There are several possible reasons why there is a requirement for the attainment of a specific moisture content. Subsequent product storage may dictate the objective for many materials have a maximum moisture content at which they may be stored without degradation occurring. Often, a much lower moisture content is desired. Costs may be substantially reduced by transporting some bulk porous materials in dehydrated form. Others have their handling properties enhanced by maintaining a strict specification on final product moisture content. In the paper industry, the manufacturer is interested in extremely precise control, for many grades of paper are sold by weight. All such requirements on final moisture content can only be met by automated control; that is, by constantly monitoring certain key process variables and taking appropriate control action.

Increased sophistication in the control of drying operations can now be justified from the energy conservation standpoint as well. The
pressures brought to bear on dryer manufacturers have led to a demand for improved modelling capability since the traditional method of design improvement, wherein design innovations arise solely from observations on existing installations, is too slow a process for the rapid rate of technological change we are currently experiencing.

Since the vast majority of porous materials readily adsorb moisture, they can be fully dried only by exposing them to an atmosphere devoid of any water vapour. Porous materials which readily adsorb moisture are described as hygroscopic, and it is this affinity for water which frustrates efforts to dry them. The extent to which hygroscopic materials contain water is dependent upon the moisture content of the surrounding air; when a sample of a porous material is exposed to air of constant humidity adsorption or desorption will take place depending upon its original condition. Eventually, the total mass of the sample will cease to vary, and the sample is then considered to have achieved dynamic equilibrium with the surrounding air. Some hygroscopic porous materials exhibit hysteresis over a limited range of relative humidity, that is, they possess two equilibrium moisture contents depending on whether they adsorbed or desorbed moisture in the process of reaching equilibrium. In the drying of materials which exhibit hysteresis, we are concerned exclusively with desorption, corresponding always to the higher of the two equilibrium moisture contents. Modelling aspects of equilibrium moisture content are dealt with in Chapter 2.

The loss of moisture which takes place during the convective drying of a rigid porous material occurs initially at an approximately constant rate. As soon as liquid moisture disappears completely from the surface of the material, the rate of moisture loss falls and continues to do so until equilibrium is reached. As the latter period is by far
the longer of the two, the dynamics of the falling rate period are among the more important factors in determining the overall drying time. The importance of the falling rate period has led to the development of several models described in Chapter 3. Chapter 3 also deals with vapour diffusion - the dominant mechanism of moisture transport during the falling rate period.

The essential feature of convective drying is that the removal of excess moisture is brought about by supplying heat causing its evaporation. The heat is usually supplied not directly to the material, but rather to the surrounding air, which must also have the capacity to absorb and transport away the evaporated moisture. With slab materials, a characteristic of this process is the opposing direction in which heat and mass transfer must take place within the porous medium. Heat must be transferred in one direction in order to evaporate the liquid; the resulting vapour must migrate in the opposite direction in order for it to be removed. Though liquid transport is never completely extinct, its contribution diminishes rapidly in comparison to vapour phase diffusion, once the surface becomes dry. Clearly, therefore, developments and advances in the theory of gaseous diffusion in porous media must be of application in the development of drying models.

The nature of diffusion of gases in capillary porous media is conveniently divided into three categories. The behaviour of the gas molecules is of paramount concern; the most important factor being the object or objects against which the majority of gas molecules collide. Either under high pressure or within large diameter pores, the molecules will collide predominantly with each other, whereas under considerably reduced pressure or within very small diameter pores, they will collide exclusively with the pore walls. In between these extremes, an analysis
of the situation requires both types of collisions be taken into account.

Analysis of the first category is simplified because as far as the fluxes are concerned the existence of the porous solid is immaterial. The problem is reduced to the mechanics of the interaction of gaseous molecules, a subject exhaustively studied for well over a century. Well established continuum theory is adequate for modelling purposes.

At the other extreme, where gas molecules collide predominantly with the wall, the theory is also well developed: Knudsen's analysis at the turn of this century left little scope or requirement for further advancement.

The intermediate regime, where both types of collisions are significant, presents a more intractable problem. It is best covered by the dusty gas model, which provides a means of predicting vapour fluxes in this region. The expression 'dusty gas' accurately describes the manner in which the porous material is incorporated into the model. The porous solid is represented by an assembly of large stationary dust 'molecules'. It suffers from a degree of ambiguity in its characterisation of the porous structure, and with certain less common types of pore size distribution, it is inaccurate in predicting the fluxes. Though the incorporation of the relatively compact dusty gas model for describing the fluxes in an overall model increases considerably the complexity of the partial differential equation system, (which is non-linear and requires large amounts of computing resources for its solution) models containing a more realistic picture of the porous network are subject to even more severe drawbacks. Generally, such models tend to be highly cumbersome; they also require extensive
experimentation in order to characterise the porous material.

The progression of general drying theory has, in the main, comprised the advancement of several simple models which subsequently were shown to be at worst inadequate, at best applicable only to a very limited number of cases. The loss of moisture of a porous material under the full range of drying conditions occurs as a result of a number of time dependant transport mechanisms. The very existence, the time variance and total flux contribution of a particular transport mechanism is dependant not only upon the nature and severity of the appropriate driving force, but also upon many of the physical characteristics and properties of the porous material.

Thus, the variety of possible conditions, together with the number of material properties relevant to a proper analysis, precludes the widespread application of a simple model applicable to all possible circumstances. An example of this sort of misapplication is the diffusion model proposed by Sherwood in 1929\textsuperscript{3,4}. Sherwood demonstrated that the diffusion model can be adjusted to fit an average moisture content trajectory. Subsequently Ceaglske and Hougen\textsuperscript{5} proved that this correlation was on too superficial a basis, for a diffusion type equation requires parabolic concentration profiles, yet the vast majority of systems exhibit s-shaped concentration profiles whilst in the process of being dried.

Many more sophisticated analyses are fundamentally flawed by employing an inappropriate mass transport potential. This fashion has gained considerable ground behind the Iron Curtain, encouraged by the dearth of computing resources and the emphasis placed upon theoretical solutions to drying problems. The most prominent result is a widely acclaimed
analysis by Luikov\textsuperscript{6}, which considers the normalised liquid content as a mass transport potential. There are parallel schools in the West employing substantially the same method of analysis, but no fundamental basis exists for this approach. On the contrary, it is employed because it is conceptually simple and appears to offer a short cut solution. The mass transfer coefficient is a complicated unknown function of local microscopic conditions and can vary over several orders of magnitude as drying proceeds. Most work adopting the normalised liquid content as a transport potential conveniently assumes that the transport coefficients are constant, so that the resulting set of differential equations can be solved. Increasingly complicated boundary conditions\textsuperscript{7} extend further the scope for publication. Without exception no explicit expression is available to describe the manner in which the mass transfer coefficient varies. Furthermore, its determination by independant experimental means is acknowledged as being extremely difficult and time consuming.

Some penetrating observations into published literature on mass transfer in convective drying are to be found in a critical article by J. van Brackel\textsuperscript{8}. Van Brackel has observed that for almost any conclusion based on empirical data for a particular system, it is possible to find in the literature empirical data on the same system contradicting that conclusion. Even more disconcerting, he has proposed that to obtain a better insight into the nature of the transport mechanism careful experimentation will be more successful than fitting complicated mathematics models to unreliable and/or very limited data. It is certainly true that much published experimental data is incomplete and of dubious value. An analysis of Harmathy's work\textsuperscript{9,10} revealed some alarming inconsistencies, as shown in Chapter 6.
1.1 Scope of the Work.

This research is intended to develop an accurate fundamental model of the drying of porous media during the falling rate period which will be capable of predicting the performance of a material and, therefore, of use in dryer design. The model will take into account Knudsen and Fickian diffusion within the pores and the interaction between heat and mass transfer in the porous solid.

1.2 Definition of the Porous Solid and the Scope of the Model.

The theoretical model developed in this work (Chapter 4) is concerned with the batchwise drying of a slab of porous material. The physical scheme corresponds to a flat vertical slab in the y-z plane, with identical boundary conditions on either side of the slab. The air flows parallel to the slab in the y-z plane. Moisture transfer is considered to occur in the x-direction only; on the left hand side of the slab this will be towards the surface at x=0.

Only half of the material need be considered in the mathematical analysis because the profiles will be symmetrical about the centre line of the slab (due to assumed identical boundary conditions on either side).

The model applies to the secondary drying stage, generally known as the falling rate period, that is from the time at which the surface first appears dry with no observable wet patches.

The work is based upon the following assumptions:
(a) The porous solid is classified as a hygroscopic capillary porous medium, the defining criteria for which are:

(i) a clearly recognisable pore space (macropores and/or micropores) with a relatively narrow range of pore size distribution. The latter is not a necessary limitation, however, the dusty gas model, which is employed to describe the vapour fluxes, is known to be inaccurate when the pore size distribution deviates from the simple Gaussian distribution norm,

(ii) isotropic pore orientation,

(iii) significant amounts of physically bound moisture even at low relative humidities.

(b) Shrinkage and swelling is insignificant.

(c) The gaseous phase may be analysed exclusively in terms of an ideal gas mixture.
(d) Liquid transport is extinct.

(e) Evaporation occurs throughout the material (the implication is that there is no evaporation zone or front).

(f) The heat of desorption is negligible.

(g) There is always local equilibrium between all three phases.

(h) The temperature is moderate, much less than the boiling point of the liquid phase (water).
CHAPTER II

EQUILIBRIUM MOISTURE CONTENT
2.1 INTRODUCTION

For modelling applications, the variation of equilibrium moisture content with temperature and humidity cannot be predicted accurately by theoretical means. It is necessary to resort to a suitable semi-empirical relationship.

A saturated porous material, on commencement of drying, will present at the boundary a virtually flat gas/liquid interface, the solid phase being completely covered by a thin liquid film. Mass transfer at the interface is largely unaffected by the presence of the underlying solid phase, giving rise to a constant rate of drying. The depletion of water becomes manifest by the retreat of the gas/liquid interface into the largest capillaries. Also, dry patches start to appear on the surface. The rate of moisture loss does not respond to these changes until a substantial proportion of the surface is dry; this is due to the effects of the laminar boundary layer immediately above the surface.

Thermodynamic considerations of a curved liquid surface in a capillary lead to two conclusions. Firstly, the vapour pressure of water in a capillary is always less than the equilibrium vapour pressure at the same temperature and pressure (the equilibrium vapour pressure being that experienced above a flat gas/liquid interface).

Secondly, there exists a certain pore radius within which a gas/liquid interface can be said to be only just stable, in pseudo-mechanical equilibrium with the imposed vapour pressure. At smaller pore radii all gas/liquid interfaces are inherently stable, while at greater pore radii all such interfaces are unstable, resulting in evaporation. This
phenomenon attains mathematical expression in the familiar Kelvin equation\textsuperscript{12}. It can form the basis of an equilibrium moisture content model at high relative humidities. The precise effect of temperature variation may be incorporated by empirical equations which reflect the dependance of saturated water vapour pressure and surface tension on temperature. Both these variables appear in the basic Kelvin equation.

The last traces of moisture removed during the drying process at low relative humidities will be bound adsorptively to the surfaces of the solid. Adsorption phenomena are well understood due to their relevance to catalyst behavior. Adsorptively bound moisture differs from that located in relatively large quantities located away from the pore walls within the capillaries for there are weak forces binding the water molecules to the surface of the solid. These forces have been categorised by Valchar et al\textsuperscript{13}. Usually, the extra energy required to strip away adsorptively bound water molecules is an unknown factor. Associated with adsorption is the hysteresis effect, mentioned previously, wherein a higher equilibrium moisture content is displayed if moisture is desorbed than if moisture is adsorbed. This non-reversibility is probably due to wetting effects. The existence of hysteresis need not be of concern when considering drying applications provided it is established that all experimental measurements of equilibrium moisture content were arrived at via a process of desorption. In practical terms, this means that for the determination of a single isotherm the first measurement is made when the relative humidity is unity and subsequent measurements are taken progressively until the air surrounding the material is completely dry.

Langmuir\textsuperscript{14} considered adsorptively bound moisture as being comprised of a single layer of molecules. Brunauer et al\textsuperscript{15,16} extended the Langmuir
mechanism to second and multiple layers. Rounsley\textsuperscript{17} refined the concept of multiple layer adsorption further by considering that the layers are dismantled in an orderly fashion as the relative humidity decreases. Each layer is complete only when the air is saturated, however, as the relative humidity falls, the rate at which each layer disassembles varies. Layers further removed from the surface are dismantled more rapidly than layers closer to the surface until low humidities are experienced. (The first layer is 50\% complete after the humidity has decreased to 11\%, whereas the second layer by this stage is only 13\% complete.)

El-Sabaawi and Pei\textsuperscript{18} have combined the mechanisms of capillary evaporation and multiple molecule layer adsorption into a model of equilibrium moisture content. Both the Kelvin equation and Rounsley's model are employed. When combined with data on pore size distribution derived from mercury porosimetry measurements the model has the capability to cover the entire range of moisture content. The Kelvin equation differentiates between those capillaries which still contain liquid and those from which the water has evaporated. The mercury porosimetry data enables the volume of water within the pores still containing liquid to be deduced; Rounsley's model accounts for the moisture adsorbed onto the surface of the material in those pores containing only vapour.
2.2 THE EL-SABAAWI-PEI MODEL

The El-Sabaawi-Pei model assumes that the controlling factor in the equilibrium moisture content of a porous material is the stability of the interface between the gaseous and liquid phases at the entry necks of the pores within the material.

Since the drying process effectively imposes a set of conditions, the Kelvin equation can be rearranged and used to calculate a pore radius which corresponds to the imposed conditions. An interface sited within a pore of the calculated radius or smaller is deemed to be stable, while at any larger radius, an interface is unstable. It is assumed that as soon as the gas-liquid interface in the pore-neck becomes unstable, evaporation will proceed as long as the pore radius is greater than the calculated stable value. Once a smaller radius is encountered (the pore neck of another capillary) evaporation will not proceed until conditions change sufficiently so as to make it unstable. Since an adsorbed layer of moisture is present on the surface of the pore neck, a slightly modified form of the Kelvin equation is needed in order to differentiate between the stable and unstable gas-liquid interfaces.

The El-Sabaawi-Pei model requires some knowledge of the pore size distribution of the porous material under study. This is best obtained from mercury porosimetry, which, strictly speaking, enables the cumulative pore volume distribution of a material to be determined. It is based on the known relationship between the pressure (that required to force mercury into the pore) and the pore entry neck radius. The method is entirely consistent with the assumed equilibrium moisture content and drying mechanisms.
The expression linking the mercury pressure and pore radius is given by Moelwyn-Hughes\textsuperscript{19} as:

\[ p = \frac{2\gamma_{\text{Hg}} \cos \phi}{r} \]  \hspace{1cm} (2.1)

The experimental techniques involved in mercury porosimetry are comparatively simple. A pre-evacuated porous sample of known voidage and overall volume is completely immersed in mercury. As the pressure is increased, the volume of mercury taken up by the sample is accurately measured. For each pair of measurements, the pore radius can be deduced from equation (2.1), and the total volume of all pores with entry neck radii smaller than the calculated value is equal to the voidage times the overall volume minus the volume of mercury taken up. Hence, the \( \Theta(r) \) relationship can be deduced down to the pore radius corresponding to the maximum pressure attainable by the experimental apparatus. \( \Theta \) is given by the expression:

\[ \Theta = \frac{\varepsilon V_t - V_{\text{Hg}}}{\varepsilon V_t} \Xi - \frac{m}{\varepsilon} \]  \hspace{1cm} (2.2)

\( V_t \) is the total sample volume, \( V_{\text{Hg}} \) is the volume of mercury taken up by the sample under pressure.

A generalised form of the \( \Theta(r) \) relationship is shown in figure 2.1.

The El-Sabaawi-Pei model is developed from the Kelvin equation, which takes the form:

\[ \log_e \left( \frac{p}{p_0} \right) = - \frac{2\gamma_{\text{M}} M \cos \phi}{\rho \lambda RT} \]  \hspace{1cm} (2.3)
Cosφ is assumed to be unity since φ for most water/solid systems approaches zero (particularly if there are minute concentrations of impurities dissolved in the liquid phase).

The left hand side of equation (2.3) is the logarithm of the relative humidity:

\[ \psi = \frac{p_w}{p^o_w} \]  \hspace{1cm} (2.4)

It is necessary to replace \( r \) by \( (r-Z) \), where \( Z \) is the thickness of the adsorbed moisture layer in cm.

Rearrangement of equation (2.3) yields:

\[ r = Z - \frac{2\gamma_w M_w}{\rho_w R T \ln \psi} \]  \hspace{1cm} (2.5)

The value of \( Z \) is deduced from Rounsley's model\(^{17} \) which is expressed by the equation:

\[ \frac{X_e}{X_m(T)} = \frac{c(T)\psi}{1+(c(T)-1)\psi} \cdot \frac{1-\psi^n(T)}{1-\psi} \]  \hspace{1cm} (2.6)

El-Sabaawi and Pei proposed that \( Z \) is the product of \( n(T) \) - the number of molecular layers that must be considered in the Rounsley model - and the diameter of the water molecule.

Certain temperature dependant parameters in equation (2.6) - \( X_m(T) \), \( c(T) \) and \( n(T) \) - are always determined experimentally by a least squares fit to each set of isothermal experimental data; \( n(T) \) is not restricted to an integer value. Other variables appearing in equations (2.5) and (2.6), such as \( \psi \) and \( \gamma_w \), are also functions of temperature, and are
often replaced by commonly used empirical equations \( c(T) \) can in fact be described by an empirical equation (Keey\textsuperscript{20}); however, in practice it is always determined experimentally).

Equation (2.6) predicts the equilibrium moisture content due to moisture adsorption of the whole porous sample and will include - unwanted in this case - moisture already accounted for in the liquid-filled pores. The adsorbed moisture not accounted for by consideration of capillary condensation will be the product of the value predicted by equation (2.6) times the vapour exposed fraction of the total surface area of the sample. The total surface area of the sample is the product of its total (dry) mass and its specific surface area. An estimate of specific surface area may be obtained from experimental data by an adsorption isotherm representing the completion of a monolayer (Everett\textsuperscript{21}). No experimental method has yet been devised enabling the determination of the cumulative surface area distribution of a porous material, but El-Sabaawi and Pei\textsuperscript{18} suggest the use of simplified relationship to circumvent the difficulty.

They suggest that the relationship between the surface area of a pore and its neck diameter is constant and independent of pore diameter. The following procedure is suggested:

(a) The \( \Theta(r) \) curve is divided into \( N \) divisions. From each division, the volume of pores \( \Delta V(r_i) \) whose neck radii lie between \( r_i \) and \( r_{i+1} \) can be deduced (\( r_i > r_{i+1} \)).

(b) Each division is treated as equivalent to one long cylindrical pore of volume \( \Delta V(r_i) \) and of radius \( (r_i+r_{i+1})/2 \).
(c) The length $L_{eq}$ of this long cylindrical pore is calculated from:

$$
L_{eq} = \frac{\Delta V(r_i)}{\pi \left( \frac{r_i + r_{i+1}}{2} \right)^2}
$$

(2.7)

(d) The surface area of this equivalent pore is obtained by:

$$
S_i = 2\pi \left( \frac{r_i + r_{i+1}}{2} \right) L_{eq}
$$

(2.8)

(e) The fraction $f_i$ of the surface area of the pores which have entry radii $\geq r_i$ will be given by:

$$
f_i = \frac{S_1 + S_2 + ... + S_{i-1}}{S_1 + S_2 + ... + S_{N-1}} = \frac{\sum_{j=1}^{i-1} S_j}{\sum_{j=1}^{N-1} S_j}
$$

(2.9)

The overall equation is then expressed as:

$$
X_{\psi_i} = \frac{\epsilon \theta(r_i) \rho_e}{(1-\epsilon) \rho_s} + f_{i-1} X_{si}
$$

(2.10)

$X_{\psi_i}$ is the equilibrium moisture content experienced upon lowering the relative humidity to any value $\psi_i$, $r_i$ is calculated from equation (2.5), $\theta(r_i)$ and $f_{i-1}$ are obtained from the mercury porosimetry data. $X_{si}$ is the value predicted by Rounsley's equation.

The El-Sabaawi-Pei model becomes identical to the Rounsley model at limiting (low) relative humidities.
Typically, results of adsorption measurements are presented in the form of a single isotherm. Although this may be of great use in the design of fixed temperature storage facilities, the drying process is not isothermal, and it is therefore necessary to incorporate empirical equations which reflect the temperature dependance of the parameters which already exist within the model equations. The Kelvin equation can be so treated. However, with the Rounsley model, the number of molecular layers that must be considered varies with temperature and it becomes necessary to determine experimentally a whole series of isotherms in order to cover the range of interest. This is usually impractical in terms of available resources; the determination of a single equilibrium moisture content at moderately high relative humidity often requires several days in order to reach equilibrium. However, Henderson\textsuperscript{22} has developed a simple relationship which requires only a single pair of experimental points to provide an equilibrium moisture content relationship.
2.3 THE HENDERSON MODEL

Henderson relates the energy of the interface between the solid and the adsorbing moisture to the pressure at the exposed surface:

\[
\frac{\partial \gamma}{\partial V} = -\left(\frac{\partial P}{\partial S}\right)_T
\]  

(2.11)

\(V\) is the volume of the adsorbed material held over a surface. By relating the 'osmotic' pressure \(P\) to the relative humidity, Henderson shows that:

\[-\log_e (1-\psi) = \frac{C_sRT}{\Delta \gamma}\]  

(2.12)

where \(C_s\) is the concentration of adsorbed moisture over a unit wetted surface (gm.cm\(^{-1}\)) and \(\Delta \gamma\) is the surface energy change accompanying adsorption. Equation (2.12) may be rewritten in the form:

\[x_e = \left(\frac{-\log_e (1-\psi)}{kT}\right)^{1/n}\]  

(2.13)
LIST OF SYMBOLS USED IN CHAPTER II

C  constant in equation (2.6)

k  constant in equation (2.13)

m  volumetric moisture content  \( (\text{cm}^3/\text{cm}^3) \)

M  molecular weight  \( (\text{gm/gm-mole}) \)

n  number of molecular layers to be considered in equation (2.6); constant in equation (2.13)

P  pressure  \( (\text{dyne/cm}^2) \)

\( P_w \)  equilibrium vapour pressure of water  \( (\text{dyne/cm}^2) \)

R  universal gas constant  \( (\text{erg/gm-mole.K}) \)

r  pore radius  \( (\text{cm}) \)

S  surface area  \( (\text{cm}^2) \)

T  temperature  \( (\text{K}) \)

V  volume  \( (\text{cm}^3) \)

X  moisture content  \( (\text{gm/gm solid}) \)

\( \gamma \)  surface tension  \( (\text{dyne/cm}) \)

\( \varepsilon \)  porosity  \( (\text{cm}^3/\text{cm}^3) \)

\( \Theta \)  relative saturation, defined by equation (2.2)

\( \rho \)  density  \( (\text{gm/cm}^3) \)

\( \phi \)  contact angle between solid and liquid surfaces

\( \psi \)  relative humidity, defined by equation (2.4)

Subscripts

e  equilibrium

Hg  mercury

\( \ell \)  liquid (water)
m monolayer

t total

w water vapour, water
CHAPTER III

CONVECTIVE DRYING DURING THE FALLING RATE PERIOD

GASEOUS DIFFUSION IN POROUS MEDIA
3.1 INTRODUCTION

There is no clearly defined point in time at which the falling rate period can be said to begin. The analysis of Suzuki and Maeda\textsuperscript{23}, in which evaporation from a surface comprising dry and wet patches is considered, indicates that amongst other less significant factors, a small ratio of boundary layer thickness to size of average pore space window at the surface will be instrumental in bringing about the disappearance of the constant rate period. In the subsequent discussion, the criteria set out in section 1.2 hold; specifically the falling rate period starts when the surface becomes dry.

The particular definition chosen here is consistent with the objective definition moisture migration exclusively in the vapour phase; by the time the surface becomes dry, in many systems, liquid phase mobility is so small that it can be ignored\textsuperscript{24,25,26,27}.

There are three possible explanations for the existence of a falling rate period.

(a) A continually decreasing drying rate may be observed because evaporation takes place at a front which retreats below the surface as drying proceeds.

(b) The same phenomenon will also be observed in cases where the front becomes so diffuse that evaporation - which takes place initially only at the surface - subsequently occurs simultaneously throughout the material (at differing rates). In this instance an evaporation front does not exist.

(c) A period of decreasing drying rate may also be observed when evaporation takes place in a thin surface layer.
The latter category is not significant and may be ascribed to the surface layer possessing different properties from the bulk of the medium. These differences may be due either to inhomogeneities or to the existence of dissolved solids which tend to migrate towards the surface and are deposited, so producing changes in the surface pore geometry and the wetting properties during the early stages of drying. The phenomenon is usually transitory and systems in which it occurs tend to resort eventually to one of the previous two categories, if drying continues.

The first category is really a special case of the second, which is by far the most common amongst hygroscopic capillary-porous media. There is evidence to suggest that the more strongly hygroscopic the material, the less the likelihood of a distinct evaporation front, particularly at low liquid contents. The occurrence of evaporation throughout the porous medium results in the formation of S-shaped concentration profiles (See Figures 6 and 14 in Appendix B) which have been reported in the literature for several different materials. Experimental moisture content curves virtually identical to those in Appendix 2 have been reported for clays, gypsum, insulation board, paper, roof tiles, and talcum powder.

The existence of S-shaped concentration profiles rules out models which assume that mass transfer inside all drying media is governed solely by a diffusion type equation. Sherwood's diffusion model predicts parabolic concentration profiles. Ceaglske and Hougen have shown that if Sherwood's diffusion equation fits drying data, it is generally coincidental.
In the drying literature, many references are made to the "schools" of Luikov, Krischer, and Philip and de Vries, with the implication that each employ a different approach. Obscured by the variations in symbolism and terminology, they, in fact, use similar descriptions of the system and can be dealt with together. Whitaker\textsuperscript{38,39}, although deriving volume averaged equations, uses the same approach.

Another school is composed of authors who make the assumption of a submerged evaporation front\textsuperscript{40,41,42,43}. Most of this work suffers from a rather severe deficiency; no explicit expression for the exact location of the front as a function of time can be found a priori; instead, an entirely empirical function is usually determined by superimposing model predictions onto experimental average moisture content data. The justification for this approach is not particularly well founded, especially in the light of the S-shaped curves found in the majority of systems.
3.2 THE MODELS OF LUIKOV, KRISCHER, AND PHILIP AND DE VRIES

Luikov\textsuperscript{6}, Krischer\textsuperscript{35}, and Philip and de Vries\textsuperscript{44} all use the normalised liquid content and temperature as transport potentials. The normalised liquid content is defined as:

\[ U = \frac{x - x_e}{x_i - x_e} \quad (3.1) \]

where

- \( x_i \) - initial liquid content of medium.
- \( x_e \) - equilibrium liquid content at the prevailing temperature.

Given the chosen transport potentials of normalised liquid content and temperature, the one dimensional form of the equation for mass flux within a porous material is of the form:

\[ N_w = \frac{\rho L}{m_w} \left( \beta_t \frac{\partial u}{\partial t} + \beta_t \frac{\partial T}{\partial x} + k \cos \phi \right) \quad (3.2) \]

the last term in equation (3.2) accounting for viscous flow due to gravity. Applying the law of conservation of mass:

\[ \frac{\partial u}{\partial t} = \frac{m_w}{\rho_L} \frac{\partial N_w}{\partial x} \quad (3.3) \]

The variation in liquid density as a function of temperature is usually ignored.
Luikov rarely includes the gravity term and often specifies $\beta_t$ as a product of $\beta_u$ and a "thermogradient coefficient". He sometimes acknowledges that $\beta_u$ may be split into liquid and vapour transfer parts.$^{45}$

Krischer usually omits both the gravity term and the mass transfer due to temperature gradients.

Both Krischer and Philip and de Vries split $\beta_u$ and $\beta_t$ into two parts, namely, transfer in the liquid phase, and transfer in the vapour phase.

Undoubtedly the progress that is made in drying is hampered considerably by the confusion and disarray to be found in the literature. Tensor and vector notation is employed$^{46}$, volume-averaged equations derived$^{38,39}$, but precious few insights result from such approaches. Adaptations of Sherwood's diffusion model still appear$^{47}$, no doubt due to the alluring simplicity of the mathematical treatment. Examples of superfluity are to be found due to the most distinguished of authors. Luikov$^{48,49,50}$ introduces a relaxation term to account for variation in the mass transfer coefficient. The basis for the incorporation of the relaxation term is purported to lie within the realms of irreversible thermodynamics, yet no detailed derivation has been published; furthermore, it is evident that the equations cannot be derived from irreversible thermodynamics alone.$^{51}$ The potential of the proposal can be judged by Luikov's$^{45}$ statement, "If use is made of the formal mathematical apparatus of irreversible thermodynamics, then such complicated systems of differential equations may be obtained, which are of no value for practical calculations..."
The essential feature of the majority of the mathematical models found in the literature is that the normalised moisture content is chosen as a transport potential. This is convenient and presents least conceptual difficulty from the drying viewpoint, but there is no fundamental justification for such an approach. The transfer coefficients that result are complicated unknown functions of local microscopic conditions. All too often they are assumed to be constant\textsuperscript{7}. The foregoing analysis is fundamentally flawed and has resulted in an enormous body of work that has added little to our understanding of the phenomena and diverted resources from areas much more deserving of attention. The published work of Harmathy\textsuperscript{10} with all its shortcomings, represents a real break with the established traditions of the discipline. For the first time, the mole fraction of water in the vapour phase, the pressure, and the temperature are considered to be the transport potentials. Such an approach is more in line with our fundamental appreciation of the phenomena involved.
3.3 GASEOUS DIFFUSION IN POROUS MEDIA

In the analysis of drying phenomena, the migration of moisture in the vapour phase has been exclusively analysed in terms of continuum theory. A basic assumption with this approach is that molecule-solid collisions (and molecule-liquid collisions) occur so infrequently that they may be ignored. This assumption can only be checked if both the drying conditions and the pore size distribution are known; only then can the diffusion regime be determined, depending upon the value of the Knudsen number. The Knudsen number is the ratio of mean free path to pore diameter:

\[ Kn = \frac{\lambda}{2\pi} \]  

(3.4)

\( \lambda \), the mean free path (the average distance a gas molecule travels before colliding with another gas molecule) is defined by the equation:

\[ \lambda = \frac{0.032\mu}{P} \sqrt{\frac{RT}{2\pi M}} \]  

(3.5)

The three diffusion regimes are given by Geankoplis as:

- Knudsen Diffusion : \( Kn > 10 \)
- Transition Region : \( 1/100 < Kn < 10 \)
- Molecular Diffusion : \( Kn < 1/100 \)

A good appreciation of the fundamental diffusion phenomena in all three regimes can be obtained by applying simple momentum transfer arguments
to a single pore. Though real porous media cannot be described by
simply scaling-up the final equations, the equations may be used in a
limited manner to develop arguments concerning certain features of the
dusty gas model.

Knudsen diffusion can be described by a simple flux equation of the
type:

\[ N_i^d = -K_i \frac{dC_i}{dx} \]  \hspace{1cm} (3.6)

The system may be analysed from two different viewpoints. Since the
partial pressure gradient of each species is entirely determined by
momentum transfer to the wall, the rate of momentum transfer can be
estimated and the flux relations determined quite simply\(^1\). For a tube
of circular cross section, the resulting expression for the Knudsen
diffusion coefficient is:

\[ K_i = \frac{\pi R T}{4 \sqrt{\pi M_i}} \]  \hspace{1cm} (3.7)

Alternatively, a more rigorous relationship can be obtained by the
application of kinetic theory. For the same system\(^5\):  

\[ K_i = \frac{2 \pi R T}{3 \sqrt{\pi M_i}} \]  \hspace{1cm} (3.8)

It is however, more convenient to express the Knudsen coefficient as:

\[ K_i = \frac{c_1 R T}{\sqrt{M_i}} \]  \hspace{1cm} (3.9)
The constant $c_1$ is clearly proportional to the mean pore radius. In isotropic media it should also be proportional to the void fraction and should contain a factor which takes account of the fact that the channels are not uniform cylinders, nor are they all aligned with the direction of flow. From these considerations, an expression for $c_1$ is obtained:

$$c_1 = \frac{2cT}{3\pi} \sqrt{\frac{8}{\pi}} \quad (3.10)$$

There are two separate mechanisms to be accounted for in the molecular diffusion regime.

Consideration of the viscous flow of species through a tube of circular cross section gives:

$$N_i^V = -\frac{r^2 P}{8\mu RT} \cdot \frac{\gamma_i}{dx} \quad (3.11)$$

It is more convenient to express this equation in the form that is usually attributed to d'Arcy:

$$N_i^V = -\frac{c_0 \gamma_i}{\mu RT} \cdot \frac{dP}{dx} \quad (3.12)$$

Clearly, $c_0$ - the permeability of the medium - is given by the equation:

$$c_0 = \frac{r^2}{8} \quad (3.13)$$
The second mechanism of the molecular diffusion regime is the exchange of momentum between pairs of unlike molecules. Treatment of this phenomena goes back to the work of Stefan\textsuperscript{55} and Maxwell\textsuperscript{56}. The relations which they derived reduces to the familiar Fickian equation when there are only two components:

\[ N^d_w = - CD^O_w, a \frac{dy_w}{dx} + y_w \left( N_w + N_a \right) \] \hspace{1cm} (3.14)

A similar equation may be written for \( N_a \). When the diffusion process described by Fick's equation takes place within a porous medium, the binary diffusivity coefficient must be replaced by an effective binary diffusivity coefficient:

\[ D^e_w, a = c_2 D^O_w, a \] \hspace{1cm} (3.15)

The constant \( c_2 \) is independant of pore size provided the latter is large compared with the mean free path. In an isotropic medium it is proportional to the void fraction and should reflect the restraints to molecular drift imposed by the orientation of the pores. It is often expressed by the equation:

\[ c_2 = \frac{\varepsilon}{\tau} \] \hspace{1cm} (3.16)

The simple analysis presented by equation (3.14) oversimplifies the situation considerably. For example, the influence of gradients in temperature and pressure are not accounted for. As with Knudsen diffusion, a complicated kinetic theory treatment of the molecular diffusion regime is necessary, such as that described by Chapman and Cowling\textsuperscript{57}. Such a treatment is used in the development of the dusty gas model itself.
In the transition region all three mechanisms described above are likely to be of comparable importance. Mason and Evans\textsuperscript{58} have shown that the Knudsen and Fickian diffusion components can be combined additively. They have also shown that the total flux may be arrived at by summing the viscous flux described by equation (3.12) with the combined diffusive flux.

For most gases at ordinary temperatures and pressures, one or both of the Knudsen numbers at the limits of the transition region fall within the range of pore radii encountered in a great many commercial catalysts\textsuperscript{59}. Hand calculations using the pore size distribution for a clay brick published by Harmathy\textsuperscript{10} reveal that his falling rate period starts within the transition region and proceeds toward the Knudsen diffusion regime. This indicates that the drying of clays, in particular the latter stages, cannot be modelled adequately using continuum theory. It also indicates the appropriateness of interpreting Harmathy's results from the viewpoint of a model which properly accounts for the phenomena of transition region diffusion.

There are two basically dissimilar approaches in the modelling of a porous medium for the purpose of predicting flux relations. The earliest of all models, due to Maxwell\textsuperscript{2}, has evolved into the dusty gas model. It is the sole example where the approach concentrates on the obstructive nature of the solid matrix to gaseous motion. In the other alternative approach, greater attention is focussed on the features of the pore network through which the gaseous species pass. The most articulate proponents of the latter approach are Feng and Stewart\textsuperscript{60}, whose comprehensive models are developed from the earlier work of Johnson and Stewart\textsuperscript{61}. 
When the porous solid is viewed as an inter-connected network of capillaries, the pore geometry must correspond to a smooth field model in order that the gas composition can be represented by a smooth function of position within the medium. Feng and Stewart represent the structure of the medium by a statistically specified network of pores, closely cross-linked so that the smooth field assumption is valid.

Though the Feng and Stewart model offers considerable freedom in the description of the pore network, the dusty gas model is simpler. Also the latter requires less extensive experimentation in order to complete the mathematical description of the porous medium. Though this may occasionally result in a discrepancy between predicted and experimental fluxes, it is generally not significant unless the material has an unusual pore size distribution.
3.4 THE DUSTY GAS MODEL

The basic concept for the formulation of the dusty gas model was first put forward by Maxwell in 1860. In the last twenty years, various workers have developed - in stages - the Dusty Gas model from its original concept63-67.

The essence of the model is the representation of the solid matrix by a dummy species known as the dust, which is composed of massive molecules held stationary by unspecified forces. A kinetic theory treatment similar to that given by Chapman57 is then applied to all the diffusing species present. It is apparent that the interaction between the gaseous species and the solid in the real system is represented by the interaction of the gas molecules with the dust in the model. At the initial level of analysis the volume of the dust is ignored. As a result, the final equations do not contain an explicit representation of the void fraction.

A derivation of the dusty gas equation has also been carried out by Gunn68, independently of Mason et al67. Though the form of the final equations are quite different, they are in fact, identical. For the purpose of this study, it is necessary only to quote the final form of Gunn's equation69:

\[
N_A = - \left[ \frac{c_2 D_{AB} K_A P}{c_2 D_{AB} + K_m P} \right] \nabla y_A - \left[ \frac{K_A \left( c_2 D_{AB} + K_B P \right)}{c_2 D_{AB} + K_m P} \right] \frac{c_0 P}{RT} \] (3.17)

The corresponding flux relation for component B is obtained by interchanging the subscripts A and B. (Expressions for some of the
The experimental determination of the constants $c_0$, $c_1$ and $c_2$ has its origins in a method first proposed by Buckingham\textsuperscript{70} in 1904. It appears that all investigations in the field employ substantially the same method\textsuperscript{69}. The constants $c_1$ and $c_2$ are determined via a series of binary isobaric diffusion measurements conducted in a diffusion cell apparatus. The constants $c_1$ and $c_0$ are determined via a series of permeability measurements with pure components (such as helium and nitrogen) in the same apparatus. Since $c_0$, $c_1$ and $c_2$ are independent of the flowing fluids, the value of $c_1$ obtained in the second experiment serves as a check on the value of $c_1$ obtained in the first experiment.

**Binary Isobaric Diffusion: Determination of $c_1$ and $c_2$.**

For one-dimensional isobaric diffusion of a binary system, equation (3.17) becomes:

\[
\left( y_A, o e^n - y_A, \lambda \right) \left( 1 - \frac{M_A}{M_B} \right) \left( e^n - 1 \right) = \left( \frac{c_2}{c_1} \right) \left( \frac{D_{AB}^0}{P} \right) \sqrt{\frac{M_A}{RT}} \]

where

\[
n = \frac{N_A}{c_2 D_{AB}^0} \sqrt{\frac{M_A}{M_B}} \]

If $c_2$ is known, a plot of the squared brackets on the left hand side of the equation (3.18) versus the squared bracket on the right hand side
yields a straight line of slope \((c_2/c_1)\) passing through the origin. Usually \(c_2\) is not known, and then several graphs are plotted with various assumed values for \(c_2\) until a straight line passing through the origin is obtained.

Pure Gas Permeability: Determination of \(c_0\) and \(c_1\).

One-dimensional flow of a pure gas subject to a pressure gradient gives a transport equation of the form:

\[
\frac{\sqrt{\frac{MRT}{\Delta P}}} = \frac{c_1}{L} + \frac{c_0}{L^2} \left[ \frac{\varphi L}{\mu\sqrt{RT}} \right]
\] (3.20)

The left hand side of equation (3.20) is the dimensionless flowrate, while the term in squared brackets on the right hand side is the dimensionless pressure. A plot of dimensionless flowrate versus dimensionless pressure yields a straight line of slope \((c_0/L^2)\) which intercepts the \(y\)-axis at \((c_1/L)\).

Criticism of the dusty gas model is concerned primarily with the characterisation of the porous medium in terms of only three parameters, \(c_0\), \(c_1\) and \(c_2\). It has been argued that the dusty gas equations are appropriate only for a medium with a single pore size or, at most, a narrow distribution of pore sizes\(^{59,60,71}\). Ornata and Brown observe deviations between predicted and experimental fluxes in isobaric diffusion experiments in bimodal porous media. Deviations were also observed in unimodal structure with pore sizes below \(5 \times 10^{-7}\) cm\(^{11}\). Correction factors have been proposed to account for variations in the contribution of two groups of coefficients in the flux equations. (The
whole of the coefficient of $\partial y_\delta/\partial x$ is sometimes called the diffusion-flow coefficient, while the two parts of the coefficient of $\partial P/\partial x$ are called the slip-flow and viscous-flow coefficients respectively.) Abed\textsuperscript{72} introduces an empirical parameter to correct the slip-flow term. Chen and Rinker\textsuperscript{71} propose simple correction factors for both the diffusion-flow and slip-flow coefficients.

The proponents of the dusty gas model do not have a really satisfactory argument to counter the specific criticism concerning the tenuous characterisation of the porous material. There can be little doubt that the argument that the dusty gas equations are appropriate for a medium with a narrow distribution of pore sizes is substantially correct. Deviations between predicted and experimental fluxes seem to be greater, the greater the maldistribution of pore sizes. Such deviations are due to the complicated manner in which the total flux in the pores varies as a function of pore radius, in response to an identical set of driving forces. It would be expected that the magnitude and relative contribution of the three types of flow - diffusive, slip and viscous - vary as a function of pore radius. Of all the parameters appearing in the simple isotropic equations for $c_0$, $c_1$ and $c_2$, it is known that tortuosity is a non-linear function of pore radius. There is considerable evidence indicating that smaller pores are more tortuous than larger ones\textsuperscript{73,74}. Not only does the proportion of dead end pores increase rapidly with decreasing pore radius, the length to diameter ratio increases in the same fashion. That the deviation between predicted and experimental fluxes is usually small is undoubtedly due to the relatively small net contribution of the small pores to the total flux.

The problem takes on an added dimension when we consider the use of the
dusty gas equations in a porous medium where there is a continually changing (though relatively small) amount of liquid present. It is worth noting, however, that the drying process is rarely pursued while there is no water vapour present at the boundary. The minimum humidity likely to be experienced will be that of the ambient air. Therefore, some moisture will still be present even when drying is terminated, and this will be contained within the smallest pores.

The existence of a temperature gradient provides an additional force for mass transfer; the phenomenon is known as the Soret effect. However, the contribution to the total flux is negligible when only small temperature gradients are present.
LIST OF SYMBOLS USED IN CHAPTER III

\[
\begin{align*}
\text{co} & \quad \text{relative d'Arcy flow permeability} & (\text{cm}^2) \\
\text{c1} & \quad \text{relative Knudsen flow permeability} & (\text{cm}) \\
\text{c2} & \quad \text{ratio of bulk diffusivity to free gas} \\
& \quad \text{bulk diffusivity} \\
\text{C} & \quad \text{molar concentration} & (\text{gm-mole/cm}^3) \\
\text{D}_{w,a} & \quad \text{free gas mutual diffusivity of} \\
& \quad \text{air/water mixture} & (\text{cm}^2/\text{sec}) \\
\text{D}_{w,a}^0 & \quad \equiv \text{D}_{w,a}p & (\text{dyne/sec}) \\
\text{k} & \quad \text{liquid flow permeability} & (\text{cm/sec}) \\
\text{K} & \quad \text{Knudsen diffusivity} & (\text{cm}^2/\text{sec}) \\
\text{Kn} & \quad \text{Knudsen number} \\
\text{L} & \quad \text{thickness of porous plug} & (\text{cm}) \\
\text{M} & \quad \text{molecular weight} & (\text{gm/gm-mole}) \\
\text{N} & \quad \text{molar flux} & (\text{gm-mole/} \\
& \quad \text{cm}^2.\text{sec}) \\
\text{P} & \quad \text{pressure} & (\text{dyne/cm}^2) \\
\text{P} & \quad \text{average pressure} & (\text{dyne/cm}^2) \\
\text{r} & \quad \text{pore radius} & (\text{cm}) \\
\overline{r} & \quad \text{average pore radius} & (\text{cm}) \\
\text{R} & \quad \text{universal gas constant} & (\text{erg/gm-mole.K}) \\
\text{t} & \quad \text{time} & (\text{sec}) \\
\text{T} & \quad \text{temperature} & (\text{K}) \\
\text{U} & \quad \text{normalised liquid content} \\
\text{x} & \quad \text{distance} & (\text{cm}) \\
\text{X} & \quad \text{moisture content} & (\text{gm/gm-solid}) \\
\text{y} & \quad \text{mole fraction} \\
\text{B} & \quad \text{mass transfer coefficient} & (\text{cm}^2/\text{sec})
\end{align*}
\]
\( \Delta \) nabla vector (mathematical operand)

\( \varepsilon \) voidage

\( \lambda \) mean free path (cm)

\( \mu \) viscosity (gm/cm\text{. sec})

\( \rho \) density (gm/cm\(^3\))

\( \tau \) tortuosity

\( \phi \) angle with the vertical (degrees)

Subscripts

\( a \) air

\( A \) component A

\( B \) component B

\( i \) initial; species i

\( e \) equilibrium

\( \ell \) liquid; position L

\( m \) mean

\( w \) water; water vapour

\( o \) position 0

Superscripts

\( d \) diffusive

\( e \) effective

\( v \) viscous
CHAPTER IV

THEORETICAL TREATMENT
4.1 EQUILIBRIUM MOISTURE CONTENT MODEL.

It is postulated that the rate controlling step in drying is the removal by diffusion of water vapour from the vicinity of the internal liquid and solid surfaces. It is assumed that on a local microscopic level, moisture content is always in equilibrium with the immediately adjacent vapour.

Variations in pressure, temperature and in water vapour content of the gaseous voids within the porous material therefore result in changes in local moisture content as if the material were in equilibrium with the immediately adjacent vapour the entire time. The equilibrium moisture content model can thus be used in conjunction with equations based on the conservation of mass and energy to construct an overall model.

The basic equation for the equilibrium moisture content is:

\[
x = \left( \log_e \left( \frac{1 - \frac{P_w}{P_w^0(T)}}{kT} \right) \right)^{1/n}
\]

Now

\[
P_w = y_w P
\]

and

\[
P_w^0(T) = P_{\text{atmos}} \exp \left( 70.4346943 - \frac{7362.6981}{T} + 6.952085 \times 10^{-3} T - 9 \log_e T \right)
\]
Equation (4.3) is due to Prausnitz et al. The relationship between $X$ and $m$ is simple and is derived from...

\[ X = \frac{m \rho_L}{(1-\varepsilon) \rho_S} \quad \text{(4.4)} \]

Substituting equations (4.2), (4.3) and (4.4) in equation (4.1) gives:

\[ m = k' \frac{(1-\varepsilon) \rho_S}{\rho_L} \left\{ \log_e \left( \frac{1}{1 - \frac{y_w^p}{p_w^o(T)}} \right) \right\}^{n'} \quad \text{(4.5)} \]

where

\[ k' = \left( \frac{9}{5} \right)^{1/n} \quad \text{(4.6)} \]

\[ n' = \frac{1}{n} \quad \text{(4.7)} \]

Equation (4.5) is an equation expressing the moisture content as a function of $y_w$, $P$ and $T$. It is clearly differentiable with respect to all three variables.

\[ \frac{\partial m}{\partial y_w} = k'n' \frac{(1-\varepsilon) \rho_S}{\rho_L} \frac{1}{T} \left\{ \log_e \left( \frac{1}{1 - \frac{y_w^p}{p_w^o(T)}} \right) \right\}^{n'-1} \]

\[ \frac{P}{\left\{ p_w^{o(T)} - y_w^p \right\}} \quad \text{(4.8)} \]
\[
\frac{\partial m}{\partial P} = \frac{\gamma_w \partial m}{P \partial y_w}
\]  
(4.9)

\[
\frac{\partial m}{\partial T} = k'n' \frac{(1-\varepsilon) \rho_s}{\rho_\lambda} \left\{ \log_e \left( \frac{1-\frac{y_w P}{p^\circ_w(T)}}{T} \right) \right\}^{n'-1}
\]

\[
\frac{\partial m}{\partial T} = k'n' \frac{(1-\varepsilon) \rho_s}{\rho_\lambda} \left\{ \log_e \left( \frac{1-\frac{y_w P}{p^\circ_w(T)}}{T} \right) \right\}^{n'-1}
\]

\[
\frac{1}{T^2} \log_e \left( \frac{y_w P}{p^\circ_w(T)} \right)
\]

where

\[
p^\circ_w(T) = \frac{\partial p^\circ_w(T)}{\partial T} = p^\circ_w(T). \left\{ \frac{7362.6981}{T^2} + 6.952085 \times 10^{-3} \right\}
\]

\[
\frac{g}{T}
\]

(4.11)

Equations (4.8) to (4.11) are required later in the solution of the equations representing the material model.

The assumption of local equilibrium means that the system is unambiguously defined if \(y_w, P\) and \(T\) are fixed. Equation (4.5) defines the moisture content as a function of these three variables. The variables \(y_w, P\) and \(T\) are defined for convenience as the state variables, and since there are three degrees of freedom, the requirement of the model is the provision of three independant equations.
4.2 THE POROUS MATERIAL MODEL

During the falling rate period, the migration of moisture towards the surface occurs predominantly in the vapour phase. The dusty gas model enables the accurate prediction of gaseous vapour fluxes for a wide range of the ratio of pore diameter to mean free path length. It is markedly superior to the only alternatives - capillary based models - with their multitudinous forms reflecting the nature of particular assumptions regarding the orientations, pattern of connections and size distribution of the pores. This is particularly true when the capillary diameter is comparable with free path lengths. Recently, other workers have realised the relevance of the dusty gas model to the falling rate period of drying.

The dusty gas model for diffusion in porous media yields the following expressions for the molar fluxes:

\[
N_w = \left( \frac{c_2 D_{w,a} K_p}{(c_2 D_{w,a} + K_m)RT} \right) \frac{\partial y_w}{\partial x} - \left( \frac{K_w (c_2 D_{w,a} + K_m) + c_o}{(c_2 D_{w,a} + K_m) + \mu_m} \right)
\]

\[
y_w \frac{\partial P}{RT} \frac{\partial x}{\partial x}
\]

\[
N_a = \left( \frac{c_2 D_{w,a} K_p}{(c_2 D_{w,a} + K_m)RT} \right) \frac{\partial y_a}{\partial x} - \left( \frac{K_a (c_2 D_{w,a} + K_m) + c_o}{(c_2 D_{w,a} + K_m) + \mu_m} \right)
\]

\[
y_a \frac{\partial P}{RT} \frac{\partial x}{\partial x}
\]

(4.12) (4.13)
The solid phase is considered as being composed of massive stationary molecules with the gaseous species flowing around them. In this hypothetical system the volume of free space is practically identical to the overall volume. There is, therefore, no explicit representation of the void fraction. This becomes something of a dilemma when the flux equations are applied to a real porous medium, and even more so when the void volume is continually changing - as would be the case when a porous material is drying out. Thus, there is a necessity for taking the fluxes described by the dusty gas model as being based on the proportion of cross-sectional area occupied by vapour.

Various terms within the flux equations may be expanded thus:

\[ D_{w,a}^0 = D_{w,a}^p \]  
\[ K_w = c_1 \left( \frac{RT}{M_w} \right)^{0.5} \]  
\[ K_a = c_1 \left( \frac{RT}{M_a} \right)^{0.5} \]  
\[ K_m = y_w K_a + y_a K_w \]  
\[ \text{Since } y_a = (1-y_w) \]  
\[ K_m = y_w (K_a - K_w) + K_w \]  
\[ \frac{\partial y_a}{\partial x} = - \frac{\partial y_w}{\partial x} \]
The coefficients \( c_1 \) and \( c_2 \) are geometric factors of the porous medium and are thus functions of its structure. They are virtually independent of the diffusing vapour.

The temperature dependance of the binary diffusivity is accounted for by considering \( D_{w,a} T^{-1.5} \) to be constant. Thus:

\[
D_{w,a} = c_3 T^{1.5}
\]  

(4.21)

Substituting this expression for \( D_{w,a} \) in equation (4.14) gives:

\[
D_{w,a}^0 = c_3 P T^{1.5}
\]  

(4.22)

It is convenient to define some subsidiary constants in order to simplify the expressions for the molar fluxes:

\[
c_4 = \frac{(\text{RM}_w)^{0.5}}{c_1}
\]  

(4.23)

\[
c_5 = \left(\frac{\text{m}_w}{\text{m}_a}\right)^{0.5}
\]  

(4.24)

\[
c_6 = c_5^{-1}
\]  

(4.25)

It is further convenient to define the following expressions:

\[
c_7 = c_4 T^{0.5} \frac{\text{RT}^{-0.5}}{c_2 c_3} (c_6 y_w + 1)
\]  

(4.26)

\[
c_8 = \frac{c_0 y_w^p}{u_m \text{RT}}
\]  

(4.27)

\[
c_9 = c_2 c_3 c_4 T^2 + \text{RT}(c_6 y_w + 1)
\]  

(4.28)
\[
C_{10} = C_2 c_3 1.5 + C_1 \left( \frac{RT}{M_a} \right)^{0.5} \tag{4.29}
\]

Altering the area basis of equation (4.12) and utilising the above constants and expressions, we arrive at a compact expression for \(-N_w\):

\[
-N_w = \left( \frac{\varepsilon (1-\Theta) P}{c_7} \right) \frac{\partial y_w}{\partial x} + \left( \frac{\varepsilon (1-\Theta) \left( \frac{c_{10} y_w}{c_g} + c_B \right)}{c_8} \right) \frac{\partial P}{\partial x} \tag{4.30}
\]

Here, \(\Theta\) is the relative saturation:

\[
\Theta = \frac{m}{\varepsilon} \tag{4.31}
\]

The continuity equations for the mobile gaseous constituents are:

\[
\frac{\partial (-N_w)}{\partial x} = \frac{\rho \varepsilon}{M_w} \frac{\partial \Theta}{\partial t} + \frac{\partial C_w}{\partial x} \tag{4.32}
\]

\[
\frac{\partial (-N_a)}{\partial x} = \frac{\partial C_a}{\partial t} \tag{4.33}
\]

Expressions for the molar concentrations are:

\[
C_w = \frac{\varepsilon (1-\Theta) y_w P}{RT} \tag{4.34}
\]

\[
C_a = \frac{\varepsilon (1-\Theta)(1-y_w) P}{RT} \tag{4.35}
\]

The next step in the derivation is to expand the continuity equations to produce coefficients of the general equation:
The first of three such equations \( k = 1 \) is obtained by expanding the continuity equation of water vapour. Equation (4.30) is differentiated with respect to \( x \) to provide the left hand side of equation (4.32) and hence, the coefficients \( A_1 \) to \( J_1 \). The right hand side of equation (4.32) is evaluated by substituting equation (4.34) into the second term; derivatives of \( \theta \) are evaluated using the chain rule i.e.

\[
\frac{\partial \theta}{\partial t} = \frac{1}{\epsilon} \frac{\partial m}{\partial t} + \frac{\partial m}{\partial m} \frac{\partial \gamma_w}{\partial \theta} + \frac{\partial m}{\partial P} \frac{\partial \gamma_w}{\partial P} + \frac{\partial m}{\partial T} \frac{\partial \gamma_w}{\partial T} \tag{4.37}
\]

(A similar equation may be written for the space derivative of \( \theta \).)

Expressions for the derivatives of the relative saturation with respect to the three state variables are linked closely with those already obtained for the moisture content (equations (4.8) to (4.10)) because of the simple relationship between \( \theta \) and \( m \) (equation (4.31)).

The coefficients of the first general equation are:

\[
A_1 = \frac{\epsilon(1-\theta)P}{c_7} \tag{4.38}
\]

\[
B_1 = \epsilon(1-\theta) \left( \frac{c_{10}}{c_9} \right) \gamma_w + c_8 \tag{4.39}
\]
\[ C_1 = 0 \]  
\[ (4.40) \]

\[ D_1 = \frac{\varepsilon p}{c_7} \left( \frac{\partial \Theta}{\partial y} + \frac{c_6 R(1-\Theta)}{c_2 c_3 c_7 T^{0 \cdot s}} \right) \]  
\[ (4.41) \]

\[ E_1 = \frac{\varepsilon c_8 (1-\Theta)}{p} - \varepsilon \left( \frac{c_{10}}{c_g} \right) y_w + c_B \left( \frac{\partial \Theta}{\partial p} \right) \]  
\[ (4.42) \]

\[ F_1 = 0 \]  
\[ (4.43) \]

\[ G_1 = \frac{\varepsilon (1-\Theta)}{c_7} - \frac{\varepsilon p}{c_7} \left( \frac{\partial \Theta}{\partial p} \right) + \frac{\varepsilon c_8 (1-\Theta)}{y_w} - \varepsilon \left( \frac{c_{10}}{c_g} \right) y_w + c_B \left( \frac{\partial \Theta}{\partial y_w} \right) \]  
\[ (4.44) \]

\[ H_1 = \frac{\varepsilon p}{c_7} \left( \frac{\partial \Theta}{\partial T} \right) - \frac{\varepsilon c_4 (1-\Theta)p}{c_7} \left( \frac{R(c_6 y_w + 1)}{2(c_7)^2 T^{0 \cdot s}} \right) \]  
\[ (4.45) \]

\[ J_1 = -\varepsilon \left( \frac{c_{10}}{c_g} y_w + c_B \right) \left( \frac{\partial \Theta}{\partial T} \right) + \frac{\varepsilon (1-\Theta)}{2c_g} \left( \frac{R}{3c_2 c_3 T^{0 \cdot s}} + c_1 \frac{R}{M_a T} \right) \]  
\[ (4.46) \]

\[ K_1 = \frac{\rho_k}{M_w} \left( \frac{\partial \Theta}{\partial y_w} \right) + \frac{\varepsilon p}{RT} \left( 1 - \Theta \right) \left( \frac{\partial \Theta}{\partial y_w} \right) y_w \]  
\[ (4.47) \]
\[ L_1 = \frac{\rho_L \varepsilon}{M_w} \left( \frac{\partial \theta}{\partial p} \right) \frac{\varepsilon y_w}{RT} \left( 1 - \frac{\partial \theta}{\partial p} \right) \]  

(4.48)

\[ M_1 = \frac{\rho_L \varepsilon}{M_w} \left( \frac{\partial \theta}{\partial T} \right) \frac{\varepsilon y_w \rho}{RT^2} \left( 1 - \frac{\partial \theta}{\partial T} \right) \]  

(4.49)

Before proceeding with the expansion of the continuity equation for air, it is necessary to define one more expression thus:

\[ c_{11} = c_2 c_3 T^{0.5} + c_1 \frac{RT}{M_w} \]  

(4.50)

Altering the area basis of equation (4.13), and utilising previously derived constants and expressions, we arrive at the following expression for \(-N_a\):

\[ -N_a = \left( \frac{\varepsilon (1-\theta)c_5 \rho}{c_7} \right) \frac{\partial y_w}{\partial x} + \left( \frac{\varepsilon (1-\theta)}{c_9} \right) \frac{c_5 c_{11} (1-y_w)}{c_9} \frac{1-y_w}{y_w} \left( \frac{\partial p}{\partial x} \right) \]  

(4.51)

Equation (4.51) when differentiated with respect to \(x\) provides for the left hand side of equation (4.33) and hence the coefficients \(A_2\) to \(J_2\) of the general equation. The equation for the molar concentration of air is substituted into the right hand side of equation (4.33); again, the chain rule (equation (4.37)) is utilised.
The coefficients of the second general equation are:

\[ A_2 = -c_5 A_1 \]  

(4.52)

\[ B_2 = \varepsilon (1-\Theta)(1-y_w) \frac{c_5 c_{11} c_8}{c_g y_w} \]  

(4.53)

\[ C_2 = 0 \]  

(4.54)

\[ D_2 = -c_5 D_1 \]  

(4.55)

\[ E_2 = \frac{\varepsilon c_8 (1-\Theta)(1-y_w)}{y_w} - \varepsilon (1-y_w) \frac{\partial\theta}{\partial \rho} \frac{c_5 c_{11} c_8}{c_g y_w} \]  

(4.56)

\[ F_2 = 0 \]  

(4.57)
\[
G_2 = \frac{\varepsilon c_5}{c_7} \left[ 1 - \theta - \frac{\partial \theta}{\partial p} \right] - \varepsilon (1 - y_w) \frac{\partial \theta}{\partial y_w} \left( \frac{c_s c_{1L} c_8}{c_g y_w} \right)
\]

\[
\frac{\varepsilon c_5 c_{1L} (1 - \theta)}{c_g} \left[ \frac{c_6 R T (1 - y_w)}{1 + c_g} \right] - \frac{\varepsilon c_8 (1 - \theta)}{y_w}
\]

(4.58)

\[
H_2 = -c_5 H_1
\]

(4.59)

\[
J_2 = \frac{\varepsilon c_5 (1 - \theta) (1 - y_w)}{2 c_g} \left( \frac{3 c_2 c_3 T^{0.5} + c_1 \left( \frac{R}{M_w T} \right)^{0.5} }{c_2 c_3 c_4 T + R (c_6 y_w + 1)} \right)
\]

\[
\frac{\varepsilon c_5 c_{1L} (1 - \theta) (1 - y_w)}{(c_g)^2} \left( \frac{c_2 c_3 c_4 T + R (c_6 y_w + 1)}{c_2 c_3 c_4 T + R (c_6 y_w + 1)} \right)
\]

(4.60)

\[
-\varepsilon (1 - y_w) \left[ \frac{\partial \theta}{\partial T} \right] \left( \frac{c_s c_{1L} c_8}{c_g y_w} \right) - \frac{\varepsilon c_8 (1 - \theta) (1 - y_w)}{y_w T}
\]

(4.61)

\[
K_2 = \frac{\varepsilon P}{RT} \left[ 1 - \theta + \frac{\partial \theta}{\partial y_w} (1 - y_w) \right]
\]
The third independent equation is obtained by applying to the system the law of conservation of energy. The starting point is that appropriate for a system with four constituents (solid, liquid, water vapour, air).

\[
\partial \frac{4}{\partial t} + \sum_{i=1}^{4} \left( \partial \frac{C_{i}H_{i}}{\partial t} + \nabla \cdot \left( \sum_{i=1}^{4} N_{i}H_{i} \right) \right) = \nabla \cdot \frac{k_{m} \nabla T}{\partial t} - (\tau \cdot \nabla \tau)
\]

The substantial time derivative may be replaced by the expression:

\[
\partial \frac{P}{\partial t} = \frac{\partial P}{\partial t} + \nu \nabla P
\]

Since the liquid and solid phases are stationary, \( N_{L} = N_{S} = 0 \). The mass average velocity \( \nu \) is negligible and also assumed to be zero. Hence, the one dimensional form of equation (4.64) applicable to the porous system is:

\[
\partial \left( k \frac{\partial T}{\partial x} \right) \frac{\partial}{\partial x} \left( \sum_{i=1}^{4} N_{i}H_{i} \right) = \frac{\partial}{\partial t} \left( C_{w}H_{w} + C_{a}H_{a} + C_{L}H_{L} + C_{S}H_{S} \right)
\]

The left hand side of equation (4.66) is the energy flux with respect to stationary co-ordinates and is the usual starting point for studies involving simultaneous heat and mass transfer. In neglecting the Dufour
and radiant energy fluxes, \( k_m \) is the instantaneous local thermal conductivity. A suitable empirical expression for \( k_m \) which accommodates for changing constituent volumes is given by Kingery

\[
k_m = \left( \left( k_g \right)^n \varepsilon (1-\varepsilon) + \left( k_l \right)^n \varepsilon \Theta + \left( k_s \right)^n (1-\varepsilon) \right)^{1/n}
\]  
(4.67)

The differential of \( k_m \) with respect to \( \Theta \) is:

\[
\frac{\partial k_m}{\partial \Theta} = \varepsilon \left[ \left( k_l \right)^n - \left( k_g \right)^n \right] \left( \frac{1}{n} \right) \left[ \left( \frac{1}{n} \right) - 1 \right]
\]
(4.68)

The exponent \( n \) is determined experimentally and is in the range \(-1 < n < 1\). The enthalpy change can be written as:

\[
dH = \frac{\partial H}{\partial \rho} + \frac{\partial H}{\partial P} + \frac{\partial H}{\partial T} + \frac{\partial H}{\partial \Theta} \frac{d\Theta}{dP} + \frac{dH}{dT} + \frac{dH}{d\Theta} \frac{d\Theta}{dT}
\]
(4.69)

for the gaseous constituents, whereas for the material of the solid \((\partial H/\partial \Theta)_{P,T} = 0\). For the liquid phase \((\partial H/\partial \Theta)_{P,T} = - (\partial Q/\partial \Theta)_{P,T}\) because of the relation:

\[
Q = H_w - H_k
\]
(4.70)

With the aid of familiar thermodynamic relations, the following expressions are obtained for the four constituents of the system:

\[
dH_w = M_w C_{p_w} dT
\]
(4.71)

\[
dH_a = M_a C_{p_a} dT
\]
(4.72)

\[
dH_s = \left\{ \frac{dP}{\rho_s} + C_{p_s} dT \right\}
\]
(4.73)
The last term of equation (4.74) is significant only when the very last traces of moisture are removed, and can therefore usually be neglected.

The molar concentration of the solid and liquid phases are respectively:

\[ C_s = \frac{\rho_s (1-\varepsilon)}{m_s} \quad (4.75) \]

\[ C_l = \frac{\rho_l \varepsilon \Theta}{m_w} \quad (4.76) \]

The derivation of the third general equation can now be carried out.

The continuity equations are used to replace the derivatives of the molar fluxes of the two gaseous constituents in equation (4.66).

Equations (4.71) to (4.74) are integrated and substituted into the same equation. Expressions for the molar concentrations - equations (4.34), (4.35), (4.75) and (4.76) - together with expressions for \( N_w \) and \( N_a \) from equations (4.30) and (4.51) respectively, are also substituted into equation (4.66). Because \( k_m \) varies with the relative saturation, the first term on the left hand side of equation (4.66) is evaluated using the chain rule i.e.

\[
\frac{\partial}{\partial x} \left( k_m \frac{\partial T}{\partial x} \right) = k_m \left( \frac{\partial^2 T}{\partial x^2} \right) + \left( \frac{\partial \Theta}{\partial y_m} \right) \left( \frac{\partial k_m}{\partial \Theta} \right) \left( \frac{\partial y_m}{\partial x} \right) \left( \frac{\partial T}{\partial x} \right)
\]

\[
+ \left( \frac{\partial \Theta}{\partial \rho} \right) \left( \frac{\partial k_m}{\partial \Theta} \right) \left( \frac{\partial T}{\partial \rho} \right) + \left( \frac{\partial \Theta}{\partial \rho} \right) \left( \frac{\partial k_m}{\partial \Theta} \right) \left( \frac{\partial T}{\partial \rho} \right)^2
\]

(4.77)
The use of one further expression simplifies the expressions for the coefficients of the third general equation.

\[
C_{12} = -\varepsilon \rho \frac{Q}{M_w} \left[ \frac{\partial \theta}{\partial \theta} \right] \quad (4.78)
\]

The coefficients of the third general equation are:

\[
A_3 = 0 \quad (4.79)
\]

\[
B_3 = 0 \quad (4.80)
\]

\[
C_3 = k_m \quad (4.81)
\]

\[
D_3 = 0 \quad (4.82)
\]

\[
E_3 = 0 \quad (4.83)
\]
\[ F_3 = \frac{\partial \phi}{\partial T} \left( \frac{\partial k}{\partial \theta} \right) \tag{4.84} \]

\[ G_3 = 0 \tag{4.85} \]

\[ H_3 = \left( \frac{\partial \theta}{\partial y_w} \right) \left( \frac{\partial k}{\partial \theta} \right) + \frac{\varepsilon (1-\Theta) P}{C_7} \left( M_w C_{pw} - c_5 M_a C_{pa} \right) \tag{4.86} \]

\[ J_3 = \left( \frac{\partial \theta}{\partial \rho} \right) \left( \frac{\partial k}{\partial \theta} \right) + \varepsilon M_w C_{pw} (1-\Theta) \left( \frac{c_{10}}{c_9} y_w + c_9 \right) \]

\[ + \varepsilon M_a C_{pa} (1-\Theta) (1-y_w) \left[ \frac{c_5 c_{11} c_8}{c_9} y_w \right] \tag{4.87} \]

\[ K_3 = c_{12} \left( \frac{\partial \theta}{\partial y_w} \right) \tag{4.88} \]

\[ L_3 = c_{12} \frac{\partial \theta}{\partial \rho} - \varepsilon (1-\Theta) \tag{4.89} \]

\[ M_3 = c_{12} \left( \frac{\partial \theta}{\partial T} \right) + \frac{P \varepsilon (1-\Theta)}{RT} \left( M_w C_{pw} y_w + M_a C_{pa} (1-y_w) \right) \]

\[ + \varepsilon \rho_L C_p \Theta + (1-\Theta) \rho_s C_p \tag{4.90} \]
4.3 THE SURFACE BOUNDARY CONDITIONS

Three independent equations must be defined which link the state variables at the surface to those in the bulk phase. Since the pressure at the surface must be identical to that in the bulk phase, the expression for $P$ at the boundary is:

$$P(s,t) = P(\infty,t) \quad (4.91)$$

The molar flux of water just above the surface of the porous material is given by the equation:

$$N_w = y_w (N_w + N_a) - (C_w + C_a) D_{w,a} \frac{\partial y_w}{\partial x} \quad (4.92)$$

The molar concentrations just above the surface are defined by the expression:

$$C_w + C_a = \frac{P}{RT} \quad (4.93)$$

Assuming $N_a$ is zero and substituting for the molar concentrations and for the binary diffusivity (equation 4.21), we arrive at the following expression for the molar flux of water vapour:

$$N_w = \left\{ \frac{c_3 B T^0 s}{R(1-y_w)} \right\} \frac{\partial y_w}{\partial x} \quad (4.94)$$

According to the film concept of mass transfer, the molar flux of water vapour may be defined by the expression:

$$N_w = -\alpha(y_{w,s} - y_{w,\infty}) \quad (4.95)$$
Equations (4.94) and (4.95) may be combined in order to eliminate \( N_w \) and give the following expression for the derivative of \( y_w \):

\[
\frac{\partial y_w}{\partial x} = \alpha \cdot \frac{R(1-y_w)}{c_3 P T_o \cdot s_0 \cdot (y_w, s - y_w, \infty)} \tag{4.96}
\]

The mass transfer coefficient \( \alpha \) can be determined from mass transfer correlations which are to be found in the literature \(^5\). These correlations are expressed in terms of dimensionless numbers, the most important of which is the Reynolds number, which indicates the degree of turbulence:

\[
Re = \frac{Bu_\infty D_{\infty}}{v_m} \tag{4.97}
\]

The density of air is given by the expression:

\[
\rho_\infty = \frac{1 - 0.37773 y_{w, \infty}}{2.8342 T_\infty} \tag{4.98}
\]

Other dimensionless numbers used in these correlations are the Schmidt and Prandtl numbers:

\[
Sc = \frac{\mu_m}{\rho_\infty D_{w, a}} \tag{4.99}
\]

\[
Pr = \frac{C_p_m v_m}{k_g} \tag{4.100}
\]

The dependance of \( D_{w, a} \) upon temperature is given by equation (4.42).

The value of \( C_p_m \) is given by the expression:

\[
C_p = C_p a + \left( C_p w \cdot \frac{y_{w, \infty}}{M_a(1-y_{w, \infty})} \right) \tag{4.101}
\]
The correlation for the convective mass transfer coefficient requires the introduction of another dimensionless factor, $J_D^{52}$

For $Re < 15000$

$$J_D = 0.664 \, Re^{-0.5} \quad (4.102)$$

for $15000 < Re < 300000$

$$J_D = 0.036 \, Re^{-0.2} \quad (4.103)$$

The convective mass transfer coefficient may be determined once the value of $J_D$ is known due to the following equation:

$$\alpha' = \frac{u_{\infty} J_D}{Sc^{2/3}} \quad (4.104)$$

$\alpha'$ is the mass transfer coefficient appropriate to equimolar counterdiffusion. The value of the mass transfer coefficient ($\alpha$) required is that applicable to water vapour diffusing through a stagnant air film. The relationship between $\alpha$ and $\alpha'$ is:

$$\alpha = \frac{\alpha' P}{R T y_{a,lm}} \quad (4.105)$$

where:

$$y_{a,lm} = \frac{y_{a,\infty} - y_{a,s}}{\log \left( \frac{y_{a,\infty}}{y_{a,s}} \right)} \quad (4.106)$$

Heat transfer across the boundary can also be adequately modelled using a derivative boundary equation:

$$\frac{\partial T}{\partial x} = - \frac{h}{k} \left( T_{\infty} - T_s \right) \quad (4.107)$$
The Chilton and Colburn J-factor analogy between heat and mass transfer enables the determination of the convective heat transfer coefficient once \( J_D \) is known. The analogy is characterised by the equation:

\[
J_D = J_H = \frac{p_r^{2/3}}{C_p}.
\]  

(4.108)

hence

\[
h_c = \frac{J_D C_p \rho_g u_\infty}{p_r^{2/3}} \tag{4.109}
\]

The overall heat transfer coefficient is the sum of the convective and radiative coefficients. The latter is of the form:

\[
h_r = \frac{\varepsilon \sigma (T_\infty^4 - T_s^4)}{(T_\infty - T_s)} \tag{4.110}
\]

so that the heat transfer coefficient in equation (4.102) is the sum of the convective and radiant coefficients, i.e.

\[
h = h_c + h_r \tag{4.111}
\]
4.4 SUMMARY OF THE MODEL EQUATIONS

The mathematical model described in the preceding sections of this chapter comprises essentially three equations of the form specified by equation (4.36).

The first equation is based upon the continuity equation of water vapour, and its coefficients are defined by equations (4.38) to (4.49). The second equation is based upon the continuity equation for air, and its coefficients are defined by equations (4.52) to (4.63). The third and final equation is essentially an expression of the law of conservation of energy. The coefficients of the last equation are given by equations (4.79) through (4.90).

Two subsidiary equations are required for the solution of the third equation. These are an expression for the local mean thermal conductivity - equation (4.67) and its derivative with respect to $\Theta$ - equation (4.68). The assumption of local equilibrium means that there are three degrees of freedom and therefore, with $y_{W}$, $P$ and $T$ defined, the rest of system parameters are fixed. The moisture content is then determined from equation (4.5). The derivative of the moisture content is required with respect to $y_{W}$, $P$ and $T$ (equations 4.8 to 4.10) while an empirical equation for the saturated vapour pressure of water vapour in air, and its derivative with respect to temperature, (equations (4.3) and (4.11)) are necessary in the solution of the three main equations mentioned previously.

The simultaneous solution of the three main equations yields values of $y_{W}$, $P$ and $T$ as a function of space and time. Their solution cannot be
achieved without appropriate boundary equations.

The surface boundary equations are not all of the same type while the three internal boundary equations are identical.

The definition of the system based on identical boundary conditions at both exposed surfaces means that a symmetry condition exists and there is no requirement for a solution of the system right the way across the slab. The boundary equations at the centre of the slab are characterised by the general equation:

\[
\frac{\partial s}{\partial x} = 0 \quad (4.112)
\]

where

\[
s = \begin{bmatrix} y_w \\ P \\ T \end{bmatrix} \quad (4.113)
\]

The surface pressure boundary condition is straightforward and described by equation (4.91). (Though when it comes to its expression in numerical terms it presents some difficulty.) The derivative boundary equations of (4.96) and (4.107) supply the boundary conditions for \( y_w \), \( P \) and \( T \) respectively. The value of the mass transfer coefficient is dependant upon the velocity of the air flowing over the surface, the physical properties of the bulk air, such as density - equation (4.98), and specific heat - equation (4.101), and also the Reynolds and Schmidt dimensionless numbers. Its value is determined using one of a pair of dimensionless correlations, the air velocity determining which correlation is to be employed (equations (4.102) and (4.103)). The determination of the heat transfer coefficient is based upon the Chilton
and Colburn analogy and requires only the definition of the Prandtl number once the calculation of the mass transfer coefficient has been carried out.
**LIST OF SYMBOLS USED IN CHAPTER IV**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>height of vertical surface</td>
<td>(cm)</td>
</tr>
<tr>
<td>c_0</td>
<td>relative d'Arcy flow permeability</td>
<td>(cm^2)</td>
</tr>
<tr>
<td>c_1</td>
<td>relative Knudsen flow permeability</td>
<td>(cm)</td>
</tr>
<tr>
<td>c_2</td>
<td>ratio of bulk diffusivity to free gas bulk</td>
<td>(cm)</td>
</tr>
<tr>
<td>c_3</td>
<td>empirical constant in equation (4.21)</td>
<td>(cm^2/sec.K^{1.5})</td>
</tr>
<tr>
<td>C</td>
<td>molar concentration</td>
<td>(gm-mole/cm^3)</td>
</tr>
<tr>
<td>Cp</td>
<td>specific heat capacity</td>
<td>(erg/gm.K)</td>
</tr>
<tr>
<td>D_{w,a}</td>
<td>free gas mutual diffusivity of air/water vapor mixture</td>
<td>(cm^2/sec)</td>
</tr>
<tr>
<td>D_{w,a}^0</td>
<td>= D_{w,a}P</td>
<td>(dyne/sec)</td>
</tr>
<tr>
<td>e</td>
<td>empirical constant in equation (4.110)</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>heat transfer coefficient</td>
<td>(erg/cm^2.sec.K)</td>
</tr>
<tr>
<td>H</td>
<td>partial molal enthalpy</td>
<td>(erg/gm-mole)</td>
</tr>
<tr>
<td>k</td>
<td>constant in equation (4.1); dimensionless thermal conductivity</td>
<td>(erg/cm.sec.K)</td>
</tr>
<tr>
<td>K</td>
<td>Knudsen diffusivity</td>
<td>(cm^2/sec)</td>
</tr>
<tr>
<td>m</td>
<td>moisture content</td>
<td>(cm^3/cm^3)</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight</td>
<td>(gm/gm-mole)</td>
</tr>
<tr>
<td>n</td>
<td>constant in equation (4.1)</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>molar flux</td>
<td>(gm-mole/cm^2.sec)</td>
</tr>
<tr>
<td>p</td>
<td>pressure</td>
<td>(dyne/cm^2)</td>
</tr>
<tr>
<td>Pr</td>
<td>Prandtl number</td>
<td></td>
</tr>
<tr>
<td>P_w</td>
<td>equilibrium vapour pressure of water</td>
<td>(dyne/cm^2)</td>
</tr>
<tr>
<td>q</td>
<td>conductive heat flux</td>
<td>(erg/cm^2.sec)</td>
</tr>
</tbody>
</table>
Q  molar latent heat of evaporation of water (erg/gm-mole)
R  universal gas constant (erg/gm-mole.K)
Re  Reynolds number
s  state vector
Sc  Schmidt number
t  time (sec)
T  temperature (K)
v  mass average velocity (cm/sec)
x  distance (cm)
X  moisture content (gm/gm.solid)
y  mole fraction in the vapour phase
α  mass transfer coefficient (gm-mole/cm².sec)
ε  voidage (cm³/cm³)
φ  relative saturation
μ  viscosity (gm/cm.sec)
ρ  density (gm/cm³)
σ  Stefan-Boltzman constant (gm/sec³.K⁴)
ζ  viscous stress tensor (gm/sec².cm)

Subscripts

a  air
i  species i
l  liquid (water)
m  mean
s  surface
w  water vapour, water
∞  bulk
Mathematical Operations

\( \nabla \) nabla vector

\( \frac{D}{DT} \) substantial time derivative
CHAPTER V

NUMERICAL SOLUTION OF THE MODEL EQUATIONS
5.1 FINITE DIFFERENCE REFORMULATION

Partial differential equations are solved by the approximation of the derivatives by finite differences using difference equations which may be divided into two broad categories; the comparatively simple explicit method which has serious drawbacks, and the more complicated implicit method. The starting point for difference equations is the discretization of space and time into a grid.

In an explicit method using the preferred central difference form of expressing the equation the value of \( s_{i,j+1} \) (the value of \( s \) - the dependant variable described by an unspecified partial differential equation - at time \( j+1 \) and point \( i \) in the space matrix) is determined by the values of \( s_{i-1,j}, s_{i,j} \) and \( s_{i+1,j} \). In an implicit method \( s_{i,j+1} \) is determined additionally by \( s_{i-1,j+1} \) and \( s_{i+1,j+1} \). The use of an explicit method can be seen to be quite straightforward. However, in order to solve for \( s_{i,j+1} \) using an implicit method, we require to know
the adjacent values $s_{i-1,j+1}$ and $s_{i+1,j+1}$ which are unknown. By writing the governing partial differential equation in terms of finite differences for all $n$ space points with an implicit method, it becomes necessary to solve $n$ simultaneous equations in $n$ unknowns ($s_1$, $s_2$, $s_3$...$s_n$) in order to proceed from one time level to the next. The implicit method, though more complicated in its calculation procedure, correctly accounts for the dependance of adjacent values of the dependant variable at the next time level. In other respects, regarding stability and accuracy, it has further advantages over the explicit method.

Of the many implicit techniques available, that of Crank-Nicholson has been shown to be superior in stability and execution time when applied to a similar set of equations. This method forms the basis for the solution of the model equations.
5.2 THE CRANK-NICHOLSON METHOD

The Crank-Nicholson method uses differences defined by:

\[
\frac{\partial^2 s_i}{\partial x^2} = \frac{1}{2} \left[ \frac{(s_{i+1,j} - 2s_i,j + s_{i-1,j})}{(\Delta x)^2} \right. \\
+ \left. \frac{(s_{i+1,j+1} - 2s_i,j + 1 + s_{i-1,j+1})}{(\Delta x)^2} \right]
\]  
\tag{5.1}

\[
\frac{\partial s_i}{\partial x} = \frac{1}{2} \left[ \frac{s_{i+1,j} - s_{i-1,j}}{2\Delta x} \right] + \frac{s_{i+1,j+1} - s_{i-1,j+1}}{2\Delta x}
\]
\tag{5.2}

\[
\frac{\partial s_i}{\partial t} = \frac{s_{i,j+1} - s_i,j}{\Delta t}
\]
\tag{5.3}

Using the Crank-Nicholson formulae, solution of a partial differential equation with one dependant variable is achieved by straightforward substitution and subsequent re-arrangement of the terms in each equation so that all the unknowns appear on the left hand side and a constant appears on the right. The requirement is then the repeated solution of a set of n simultaneous equations in n unknowns when a grid of n space points is used. In a system in which there are three dependant variables, a grid of n space points requires 3n equations. Each of the three model equations - at each point in the space matrix - is expressed
in finite difference form. Each equation therefore, contains nine unknowns; the future values of the state variables \( y_w, P \) and \( T \) at three adjacent points. (The boundaries are treated in a special way. They are dealt with later in this chapter.)

Every term in the three model equations contain coefficients which are functions of time because they are all functions of the state vector \( s \), defined as:

\[
\begin{bmatrix}
    y_w \\
    P \\
    T
\end{bmatrix}
\]

(5.4)

It may be assumed that the coefficients remain constant over the time interval, in which case they need be evaluated only at the beginning of each time step. However, such an assumption is in most instances unsatisfactory, and an iterative technique is required. The first step in such a procedure is a step forward in time using coefficients determined by the state vector at the beginning of the time interval. The second step is concerned with the same step forward in time but the coefficients are determined by the mean value of the state vector over the time interval. This procedure is repeated until the change in the future value of the state vector from one repeat step to the next becomes insignificant. When this occurs, we proceed to the next time step, and repeat the iterative process all over again.

The space derivative terms appearing in the model equations present a further difficulty. The general form of these terms is:

\[
C_\alpha(s) \cdot \frac{\partial s_\alpha}{\partial x} + C_\beta(s) \cdot \frac{\partial s_\beta}{\partial x}
\]

(5.5)
where

\[ \text{Co} \] is the coefficient,
\[ s_\alpha, s_\beta \] is a state variable; \( y_w, P \) or \( T \).

Clearly, if we substitute the Crank-Nicholson formulae directly, we end up with cross multiplied terms in two state variables defying easy solution. The algorithm devised reformulates equation (5.5) as:

\[
Co(s) \cdot \frac{\partial s_\alpha}{\partial x} \cdot \frac{\partial s_\beta}{\partial x} = Co_\alpha \frac{\partial s_\alpha}{\partial x} + Co_\beta \frac{\partial s_\beta}{\partial x}
\]

(5.6)

where

\[
Co_\alpha = \frac{1}{2} \frac{\partial s_\beta}{\partial x}
\]

(5.7)

and

\[
Co_\beta = \frac{1}{2} \frac{\partial s_\alpha}{\partial x}
\]

(5.8)

The pseudo coefficients \( Co_\alpha \) and \( Co_\beta \) are treated as time varying coefficients i.e. an iterative procedure to determine their mean value over the time interval is employed.

It is now possible to express the model equations in a more compact form using vector notation:

\[
\begin{bmatrix}
e(s) \end{bmatrix} \frac{\partial s}{\partial t} = \begin{bmatrix} c(s) \end{bmatrix} \frac{\partial^2 s}{\partial x^2} + \begin{bmatrix} d(s) \end{bmatrix} \frac{\partial s}{\partial x}
\]

(5.9)

It is to be noted that the matrix \([e(s)]\) is not an identity matrix, and need not necessarily be reduced to one in order to effect a solution (although it may be convenient to do so).
5.3 SURFACE BOUNDARY CONDITIONS

The derivative boundary conditions for mass and heat transfer are respectively of the form:

\[
\frac{\partial y}{\partial x} \bigg|_{x=0} = \alpha \left( y_{ws} - y_{w\infty} \right) \tag{5.10}
\]

\[
\frac{\partial T}{\partial x} \bigg|_{x=0} = h(T_s - T_\infty) \tag{5.11}
\]

Where subscript \( s \) refers to the surface and subscript \( \infty \) refers to the bulk phase.

The central difference representation of the temperature derivative at the surface is:

\[
\frac{\partial T_s}{\partial x} = \frac{T_3 - T_f}{2\Delta x} \tag{5.12}
\]

which, on the grid becomes:

\[\text{f refers to a fictitious point outside the material.}\]
Combining equations (5.11) and (5.12) and re-arranging, we have:

\[ T_f = T_3 - 2\Delta xh(T_s - T_\infty) \quad (5.13) \]

The same procedure may be followed to derive an expression for \( y_{w_f} \):

\[ y_{w_f} = y_{w_3} - 2\Delta x\alpha \left( y_{w_s} - y_{w_\infty} \right) \quad (5.14) \]

A representation of the pressure conditions at the surface is achieved by taking account of the fact that the pressure derivative at the surface is zero. This results in a simple expression for the fictitious pressure:

\[ P_f = P_3 \quad (5.15) \]

Equations (5.13) to (5.15) apply to all time levels.

It is also the case that the surface pressure follows the bulk air pressure which in this instance is known to remain constant. The second of the three model equations i.e. the air continuity equation, can, therefore, be replaced at the surface by the equation:

\[ \frac{\partial P_s}{\partial t} = 0 \quad (5.16) \]

When the Crank-Nicholson formulae are substituted into the model equations at the surface of the material, equations (5.13 to 5.15) are used to eliminate the fictitious state vector at both time levels. Thus, the three reformulated model equations at the surface contain only six unknowns, the future value of the state vector at the surface and at the first internal point.
5.4 CENTRE SLAB BOUNDARY CONDITIONS

The slab of material is subject to identical boundary conditions at both surfaces. This results in the equation:

\[
\frac{\partial s}{\partial x} \bigg|_{x=L} = 0
\]  

(5.17)

The finite difference grid at the slab centre is:

The expressions for the value of the state vector at the point \( f \) are obvious:

\[
y_{wf} = y_{w_{n-1}}
\]  

(5.18)

\[
p_f = p_{n-1}
\]  

(5.19)

\[
t_f = t_{n-1}
\]  

(5.20)

These three equations at the centre of the slab are utilised in the same manner and with the same objective (of eliminating the 'fictitious' state vector) as were equations 5.13 to 5.15 at the surface.
5.5 STARTING CONDITIONS

The model is applicable to the falling rate period of drying at the onset of which it is known that a significant moisture profile has developed. The initial moisture profile (and the other attendant profiles of e.g. temperature, pressure) is determined by starting the simulation at some hypothetical high constant moisture content and allowing the programme to proceed normally until a specified average moisture content is reached. The model can be said to be valid when the average moisture content has reached an experimentally determined value consistent with the onset of the falling rate period.

The initial values chosen are determined by trial and error, the requirement being that by the time the specified moisture content is reached, the profiles conform to experimentally determined values. The flat moisture content, pressure and temperature profiles are first fixed, the values of the other variables are determined using the equilibrium condition.
LIST OF SYMBOLS USED IN CHAPTER V

\( h \)  
heat transfer coefficient  
\( (\text{erg/cm}^2\cdot\text{sec.k}) \)

\( L \)  
distance from centre of slab to surface  
\( (\text{cm}) \)

\( P \)  
pressure  
\( (\text{dyne/cm}^2) \)

\( s \)  
variable

\( s \)  
state vector

\( T \)  
temperature  
\( (\text{K}) \)

\( x \)  
distance  
\( (\text{cm}) \)

\( y \)  
mole fraction in vapour phase

\( \alpha \)  
mass transfer coefficient  
\( (\text{gm-mole/cm}^2\cdot\text{sec}) \)

\( \Delta x \)  
space interval  
\( (\text{cm}) \)

\( \Delta t \)  
time interval  
\( (\text{sec}) \)

Subscripts

\( f \)  
fictitious

\( i \)  
position (space)

\( j \)  
position (time)

\( s \)  
surface

\( w \)  
water vapour

\( \infty \)  
bulk
CHAPTER VI

RESULTS, DISCUSSION AND CONCLUSIONS
6.1 Introduction

This chapter deals with the limitations of the applicability of the mathematical model. These are considered not only from the theoretical standpoint but also as a result of the necessary strictures in achieving a satisfactory numerical solution. Having qualified the model, the results of some computer simulations are discussed. A number of findings and conclusions are presented. The difficulties encountered and overcome in the progression from the initial mathematical development through to the final programming stage are outlined. Areas for further study and improvement are proposed.

6.2 Theoretical Constraints

The one-dimensional form of the mathematical model has precluded its application to the modelling of batch drying situations where drying is explicitly two-dimensional. Conversion of the existing one-dimensional model to a true two-dimensional model in order to portray variations in the direction of air flow would be prohibitive in terms of programming effort and in cpu time. In order to model two-dimensional drying it would be preferable - at the very minimum - not to increase the amount of cpu time that the current model requires. This could be achieved only by reducing the number of physical parameters which the current model treats as variables i.e. by simplifying the model. However, this would be unsatisfactory, because it would widen the gap between the experimentally observed trajectories and those predicted by the model. Given that the one-dimensional approach is to be retained, the solution to the problem in batch drying could be found by employing log-mean
driving forces calculated longitudinally along the material surface in the direction of air flow. Even this is far from satisfactory in situations where the two-dimensional effect is pronounced due to dryer design, which is largely a consequence of the physical dimensions of the material being dried. A classic example is the kiln seasoning of timber, where complex drying schedules are employed involving several reversals in air flow direction in order to achieve a uniform product. These schedules have evolved through extensive experimentation and experience without recourse to theoretical information.

The dusty gas model forms the basis for the gaseous flux equations in the overall drying model. No account is taken of the migration of moisture by a liquid phase capillary transport mechanism, therefore, the model must necessarily be limited to a time in the process when the capillary transport mechanism has ceased to function. The requirement that water migration must occur only in the vapour phase precludes the application of the model to the entire drying process, and presents a problem in the setting up of initial profiles. The model is limited to the falling rate period which is defined—somewhat arbitrarily—as beginning when the surface first becomes dry.

The dusty gas model depicts the system as a network of stationary obstacles dispersed in the gas on a molecular scale. The consequence of this starting point is that when the model purports to describe a real porous medium, there is no explicit representation of the void fraction. The material is ambiguously defined by the three parameters $c_0$, $c_1$ and $c_2$. Such a description is adequate for isotropic porous media with a narrow range of pore sizes, however, it is no longer satisfactory for a porous medium with, say, a bimodal pore size distribution. Also, anisotropic media and materials containing a large proportion of small
diameter pores (less than $5 \times 10^{-7} \text{cm}$) must necessarily be excluded from the foregoing analysis.\textsuperscript{11} In many publications, it is by no means clear that the equations for the fluxes apply to the entire cross-sectional area or just to the voids. (The latter view has been adopted in this work). In the drying literature, it is also apparent that many authors have no appreciation of the impact of pore size distribution on the flux models they employ. Since Harmathy's published work did not rely on the dusty gas equations for predicting the fluxes, the value of $c_1$ and $c_2$ were not known. $c_1$ and $c_2$ are both geometric factors of the porous medium and are functions of its structure. The view was taken that the presence of liquid water within the porous material will affect the values of these constants because the void geometry - from the point of view of the vapour fluxes - will be affected. Since the model covers only the falling rate period of drying, small quantities of water should not significantly affect the value of these two constants. Only the smaller pores will contain liquid and these usually do not contribute a significant amount to the total flux. There is even a possibility that an improvement of the predictive properties of the dusty gas equations may be achieved: deviations observed between experimental and theoretical fluxes have been attributed to the effects of small radius pores. Alternatively, certain values may be chosen so that good agreement is achieved between experimental observations and the predictions of the model. In the latter instance, the constants determined may be viewed as those modified to suit the range of moisture content covered.

Consideration of common practical configurations of dryers\textsuperscript{84} leads to a mathematical definition of the system based upon identical boundary conditions on either side of the slab. This is not entirely satisfactory since this imposes two limitations on the applicability of
the model. Firstly, that the boundary conditions on either side of the slab are indeed identical, secondly, that the starting profiles are symmetrical about the centre line of the slab. However, this limitation could easily be overcome but only at the expense of doubled computation time.

6.3 Practical Constraints

The requirement for an implicit method for the numerical solution meant that the non-linear terms presented an abstruse problem. No completely satisfactory method of dealing with non-linear terms is immediately available from the sparse literature on the subject. Carnaham et al. suggests that the only really feasible approach is to linearise by taking the coefficient part as being constant over the time interval. It was necessary to advance this concept a stage further because, in addition to the coefficients being functions of the state vector, the majority of the terms in the model equations comprise of the product of two partial derivatives.

Having programmed the numerical solution, a reasonable space interval was chosen and the requirement for a satisfactory level of numerical convergence pursued by altering the magnitude of the time step. (As the time step is reduced, the numerical solution should tend asymptotically to its true value). In this instance, convergence was achieved when the time step had been reduced to an impractically small value. It became necessary to uncouple the equations i.e. to manipulate the three model equations prior to solving them, so that the matrix multiplying the vector of the time derivative of the state variable is transformed into
an identity matrix. When this was carried out, it was discovered that the time constants of the pressure equation were several orders of magnitude smaller than those of the other two equations. Mathematically, the system of equations was 'stiff'. In order to reduce the computational time to a reasonable level, the pressure profile was assumed piecewise constant over the time interval and was subsequently updated at the end. In the solution, the pressure values were stored and the equation replaced with $\frac{\partial P}{\partial t} = 0$. The set of uncoupled equations were then solved, and the pressure profile re-calculated by solving the previously stored pressure equation, using the updated values of $y_w$ and $T$. This approach is consistent with the stiff nature of the set of equations. The necessary compromise between cpu time and numerical convergence was met with $\Delta x = 2.5 \times 10^{-2}$ cm and $\Delta t = 4$ seconds.

The model was evaluated by comparing the theoretical curves with the experimental results of Harmathy\textsuperscript{9,10}. The modified boundary equations employed are shown in Appendix A.

The model was found to be unsuited for use in a classical optimisation study\textsuperscript{85}, where the computer storage requirement for the forward trajectory is too large for a model of such complexity.

In the course of the development of the model, some deficiencies were discovered in Harmathy's work. The numerical procedure he employed, wherein solution of the model equations at the surface is carried out prior to and separate from their solution internally within the solid, is of dubious validity. His equilibrium moisture content model, based on the Kelvin equation and adopted in early work by Litchfield and Warren\textsuperscript{86}, was found to be inaccurate and was subsequently dropped in
The first set of results (figures 4-9) models one of Harmathy's experiments, utilising, wherever justifiable, his original correlations for the surface boundary conditions. (See Appendix A for modifications to Harmathy's original correlations.) Since the first set of results exhibited only moderate pressure gradients, a second set of results (figures 10 and 11) is included in which constant slab pressure is assumed ($\partial P/\partial x = 0$ for all $t$) in order to explore this proposition as a basic assumption for a model. A third set of graphs displays the response of the material to more severe conditions likely to be experienced in a dryer (figures 12-17).
favour of a less sophisticated model based on Henderson's equation. The deficiency of Harmathy's model was due to the gross inaccuracy of the empirical equation employed to describe the dependance of the saturated vapour pressure of water upon temperature.

6.4 Results

The main computer programme is listed in Appendix C. The output from this programme was written to a large data file which contained the profiles of the more important state variables within the material at ten minute intervals. This output file served as an input file to several plotting programmes which employed the various GINO library plotting routines. The graphical results, each the output from a single plotting programme, are to be found in Appendix B and show the profiles at half hourly intervals.

The theoretical results of the model, with simplified boundary equations (see Appendix A) compare favourably with the experimental observations of Harmathy (figures 4 and 5). The predicted average temperature displays two decreases in the rate of temperature rise as does the experimental curve. The theoretical profiles (figures 6 to 9) are as would be expected and agree almost entirely with previous experimental work. The moisture profile curves show excellent agreement with published profiles for similar materials.30-36

The pressure within the slab continues to rise for a significant period after the onset of the falling rate period (figure 8) before falling (figure 9). Significantly, the shallow temperature profiles of figure 7
indicate the process is mass transfer controlled.

The results for a constant slab pressure (figures 10 and 11) provide conclusive evidence that a pressure gradient does contribute significantly to the fluxes. A comparison of figures 4 and 10 indicate that the inclusion of pressure gradients increases the rate of moisture loss.

Figures 12 to 17 are the result of applying much more severe boundary conditions. Though the air is very slightly cooler and the humidity higher, the air velocity is much greater (such conditions are more likely to be found in a typical dryer). The most prominent feature of these graphs is, again, the shallow temperature profile.

In the course of applying increasingly severe boundary conditions, it was discovered that beyond a certain temperature, the moisture content no longer decreased as the temperature increased (in line with general experimental observations). Figure 3 illustrates this. There would thus, appear to be an upper limit on temperature for the moisture content model. It is not clear why the moisture content model shows this deficiency. Although Henderson presents a rigorous thermodynamic basis for the model, the basic equation was first presented as an observed relationship for various materials at near ambient temperatures. Temperature as a variable was incorporated utilising assumptions which have never been completely substantiated. Clearly, the model requires extensive experimental verification for each material in order to establish the limits of its validity.
6.5 CONCLUSIONS

The major difficulty in modelling the phenomenon of the drying-out of a slab of porous material is that different transport mechanisms predominate at different stages of the process. The modelling of the entire process is clearly beyond the capability of a single model.

It is generally accepted that at the onset of drying, when all the voids are completely filled with liquid, migration of moisture to the surface occurs exclusively as a consequence of capillary transport. As drying proceeds, vapour pockets develop in the larger voids. Gradually vapour transport becomes the dominant factor. By the time liquid phase moisture transport has become extinct, evaporation-condensation prevails and the falling rate period can be said to have begun. Weakly adsorbed moisture will begin to be stripped away from the ever increasing portion of internal surface exposed to vapour. The rate of desorption will increase and then decline as the internal conditions approach the boundary conditions. Thus, for a range of average moisture contents, not only may there be more than one active transport mechanism, the existence of a moisture content profile may mean that one mechanism may be predominant near the surface, while another is controlling within the material.

Given that the model purports to represent the latter stages of drying, it accounts rather well for many of the observed phenomena. However, it does not cope with the initial transition from liquid phase to vapour phase transport in an entirely satisfactory manner. Initial falling rate profiles have to be generated.
The shallow temperature profiles observed confirm that the assumption of minimal influence of the Soret effect is likely to be correct. Onsager has shown that the Soret and Dufour effects are linked, it would appear that neglecting the Dufour flux (the flow of energy due to concentration or pressure gradients) is substantiated. Constant temperature may be a reasonable simplifying assumption in future modelling studies.

The most unsatisfactory assumption in the model is that the latent heat of vaporisation is independent of moisture content \( \frac{\partial Q}{\partial \Theta} = 0 \). However, there is, at present, little experimental data available on which to base a correlation.

It is apparent from the work that the number of physical parameters which must be taken into account in order to achieve a satisfactory level of model accuracy is excessive. Not only must there be a fairly sophisticated experimental apparatus to measure the relevant aspects of the drying process, there are also additional experimental requirements for the determination of the various properties of the porous solid. A diffusion cell is necessary in order to determine the transport parameters \( c_0 \), \( c_1 \) and \( c_2 \); a mercury or nitrogen porosimeter is required for the pore size distribution; the physical properties of the porous solid, such as density, thermal conductivity etc., all have to be determined. Moreover, from one material exposed to a specific drying atmosphere to another material under a different set of conditions, the requirements for modelling certain parameters such as diffusivity, thermal conductivity etc., as variables will change altogether. Therefore, not only is it extremely difficult to cope adequately with the ascendance, overlapping, and decline of the various transport mechanisms as the drying process proceeds, it is impossible to propose a
model applicable to more than a very narrow range of porous materials and drying conditions. These crucial points do not seem to have been fully appreciated by van Brackel in his otherwise excellent review of convective drying theories.

There is an outstanding requirement for experimental verification of some of the underlying assumptions of the model. The variation of latent heat of vaporisation with moisture content is an obvious candidate. The rate at which equilibrium is reached between the solid and vapour phases is another conspicuous topic for investigation. A most useful set of experiments is envisaged that would constitute a study of the effect of moisture content on the dusty gas parameters $c_0$, $c_1$ and $c_2$. This would have wider application than to the modelling aspect alone. The blocking out of small diameter pores would undoubtedly lead to a better understanding of the limitations of the dusty gas model and contribute to the resolution of the controversy over the characterisation of the porous medium in terms of the three constants. The main steps in this undertaking would be:

1. the attainment of constant sample mass for a given vapour pressure of adsorbant (water).

2. the sudden freezing of the structure by switching to, say, low temperature nitrogen,

3. the measurement of $c_0$, $c_1$ and $c_2$ using standard procedures at temperatures below $0^\circ C$.

The model proved unsuitable for use in a classical optimisation study
primarily because of the massive computer storage requirements of the state vector and coefficient trajectories. Even in the event of a limiting form of the dusty gas equation being applicable, it is doubtful that the storage requirement could be brought down to manageable levels. The way forward for classical optimisation studies in the area of drying would appear to lie in the modelling of the porous material in terms of a simple set of equations with constant temperature coefficients. Since this approach has been pursued for many years with little success, it is extremely doubtful that progress will be made in this area in the near future.
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APPENDIX A

MODIFIED BOUNDARY EQUATIONS
A vital part of a model concerned with the transfer of moisture and energy between a porous solid and its surroundings are the equations used to describe the mass and heat transfer coefficients at the interface of the two regions. The equations utilised by Harmathy9,10 in his model were found to be of an unnecessarily complicated nature. Consequently, simpler equations were adopted of a more familiar form, however, care was taken to ensure that these equations corresponded closely to the experimental conditions described.

Whereas Harmathy used an expression for the mass transfer coefficient based on an expression given for a heat transfer coefficient89 (!), it was decided that given the lack of evidence suggesting that any experimental verification of the validity of the expression was carried out, a constant value would be appropriate. Accordingly, a value was estimated based on the specified experimental conditions:

\[ \alpha = 4.0 \times 10^{-5} \text{ (gm-mole/cm}^2\cdot\text{sec)} \]

The expression for the heat transfer coefficient used by Harmathy was based upon an expression found in the literature89. The expression used by Harmathy to account for radiative heat transfer was retained, giving a final equation of the form:
\[ h_c = 4481.6(T_{\infty} - T_s)^{0.25} + \sigma e(T_{\infty}^4 - T_s^4) \]

where

\[ T_{\infty} \] bulk phase temperature (K)
\[ T_s \] surface temperature (K)
\[ B \] height of the vertical surface (cm)
\[ \sigma \] Stefan-Boltzmann constant (gm/sec\(^3\).K\(^4\))
\[ e \] a dimensionless constant determined experimentally

The following values were employed:

\[ \sigma = \text{5.67 x 10}^{-5} \text{ gm/sec}^3.\text{K}^4 \]
\[ e = 0.8 \]
APPENDIX B

MODEL PARAMETER VALUES AND GRAPHICAL RESULTS
The parameter values used in the model are based primarily on the experimental work of Harmathy^{9,10}.

### TABLE B.1

Model Parameter Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>(4.97)</td>
<td>18.39 cm</td>
</tr>
<tr>
<td>$c_0$</td>
<td>(4.12)</td>
<td>$2.5 \times 10^{-10}$ cm$^2$</td>
</tr>
<tr>
<td>$c_1$</td>
<td>(4.15), (4.16)</td>
<td>$4.0 \times 10^{-5}$ cm (see note (i))</td>
</tr>
<tr>
<td>$c_2$</td>
<td>(4.12)</td>
<td>0.465 (see note (ii))</td>
</tr>
<tr>
<td>$c_3$</td>
<td>(4.21)</td>
<td>$4.962 \times 10^{-5}$ cm$^2$/sec.K$^{1.5}$ (see note (iii))</td>
</tr>
<tr>
<td>$C_{P_a}$</td>
<td>(4.72)</td>
<td>$1.0063 \times 10^7$ erg/gm.K</td>
</tr>
<tr>
<td>$C_{P_L}$</td>
<td>(4.74)</td>
<td>$4.1793 \times 10^7$ erg/gm.K</td>
</tr>
<tr>
<td>$C_{P_S}$</td>
<td>(4.73)</td>
<td>$0.815 \times 10^7$ erg/gm.K</td>
</tr>
<tr>
<td>$C_{P_W}$</td>
<td>(4.71)</td>
<td>$1.8646 \times 10^7$ erg/gm.K</td>
</tr>
<tr>
<td>$k'$</td>
<td>(4.5)</td>
<td>27.4 (see note (iv))</td>
</tr>
<tr>
<td>$k_g$</td>
<td>(4.67)</td>
<td>$2.613 \times 10^3$ erg/cm.sec.K</td>
</tr>
<tr>
<td>$k_L$</td>
<td>(4.67)</td>
<td>$0.616 \times 10^5$ erg/cm.sec.K</td>
</tr>
<tr>
<td>$k_S$</td>
<td>(4.67)</td>
<td>$2.207 \times 10^5$ erg/cm.sec.K</td>
</tr>
<tr>
<td>$L$</td>
<td>(5.16)</td>
<td>0.5 cm</td>
</tr>
<tr>
<td>$M_a$</td>
<td>(4.16)</td>
<td>28.952 gm/gm-mole</td>
</tr>
</tbody>
</table>
\( M_w \)

(4.15) 18.016 gm/gm-mole

\( n \)

(4.66) 0.25

\( n' \)

(4.5) 1.39 (see note (iv))

\( R \)

(4.12) \( 8.3149 \times 10^7 \) erg/gm-mole-K

\( \Delta t \)

(5.1), (5.2) 4 sec

\( \Delta x \)

(5.3) \( 2.5 \times 10^{-2} \) cm

\( \varepsilon \)

(4.31) \( 0.26 \) cm\(^3\)/cm\(^3\)

\( \lambda \)

(4.70) \( 2.4418 \times 10^{10} \) erg/gm

\( \mu_m \)

(4.12) \( 1.83 \times 10^{-4} \) gm/cm/sec

\( \rho_k \)

(4.75) \( 0.99707 \) gm/cm\(^3\)

\( \rho_s \)

(4.74) \( 2.68 \) gm/cm

Notes

(i) Value determined by visual best fit between experimental and theoretical moisture content trajectories.

(ii) Value deduced directly from the effective diffusion coefficient quoted by Harmathy\(^{10}\).

(iii) Based on a value of \( 0.275 \) cm\(^2\)/sec at 40\(^0\)C.

(iv) Values determined by fitting the equilibrium moisture content model to end of experiment conditions i.e. equilibrium conditions corresponding to the boundary conditions.
GRAPHICAL RESULTS
The equation for the saturated vapour pressure of water given by Prausnitz et al.\textsuperscript{75} and used in all the simulations is:

\[ P_w^0(T) = 1013250 \exp(70.4346943 - 7362.6981 + \frac{6.952085 \times 10^{-3} T - 9.0 \log_e T}{T}) \]  

\textit{T in Kelvin}

Experimental points plotted in figure 1 are from Perry and Chilton\textsuperscript{90}. 

\textbf{FIGURE 1}

Plot of the Empirical Relationship Describing the Saturated Vapour Pressure of Water as a Function of Temperature
SATURATED VAPOUR PRESSURE vs TEMPERATURE

X - experimental point

FIGURE 1
Gilliland shows there is a theoretical basis for an equation of the form...

\[ D_{w,a} = c_3 T^{1.5} \]  \hspace{1cm} (4.21)

The range of interest was estimated to lie between 20°C and 60°C. Based on the experimental results of Bolz and Tuve, we arrive at a value for \( c_3 \)...

\[ c_3 = 4.962 \times 10^{-5} \]

The experimental results of Bolz and Tuve are shown in Figure 2.
DIFFUSIVITY vs TEMPERATURE

x - experimental point

FIGURE 2
Equilibrium Moisture Content Isotherms as a Function of Percent Humidity

The equilibrium moisture content is determined from a modified form of Henderson's model\textsuperscript{22}:

$$m = k' \frac{(1-\varepsilon)\rho_s}{\rho_x} \left( \frac{\log_e \left( \frac{1 - y_w \rho_p}{\rho_w(T)} \right) \left( \frac{y_w \rho_p}{\rho_w(T)} \right)^{n'} \right)$$

Percent humidity is given by the expression:

$$H_{pc} = \frac{100y_w(P-P_w(T))}{(1-y_w)P_w(T)}$$

The model is deficient in that the inequality $\frac{\partial m}{\partial T} < 0$ is not always observed. For example, at 30 percent humidity the equilibrium moisture content decreases until at some point between 40°C and 50°C it starts to rise again. This is in conflict with general experimental evidence and represents a serious drawback to the versatility of the model.
FIGURE 3  

$X_{10^{-3}}$ MOISTURE ISOTHERMS

Equilibrium moisture content (cc/cc) vs. Percent humidity

- 60°C
- 20°C
- 30°C
- 10°C
- 50°C
- 40°C

FIGURE 3
FIGURES 4 - 9

Modelling of Specific Experimental Conditions: I

Figure 4  Average Moisture Content versus Time.

Figure 5  Average Temperature versus Time.

Figure 6  Slab moisture Content as a Function of
          Distance from the Surface at Half-Hour Intervals.

Figure 7  Slab Temperature as a Function of
          Distance from the Surface at Half-Hour Intervals.

Figure 8  Slab Pressure (Rising) as a Function of
          Distance from the Surface at Half-Hour Intervals.

Figure 9  Slab Pressure (Falling) as a Function of
          Distance from the Surface at Half-Hour Intervals.

(i)  Boundary Conditions

\[ Y_w = 0.010539 \]
\[ P = 1013250 \text{ dynes/cm}^2 \]
\[ T = 318.9 \text{ K} \]
(ii) Boundary Equations
As per Appendix A.

(iii) Starting Conditions \((t = -0)\)
- \(m = 0.095 \text{ cm}^3/\text{cm}^3\)
- \(P = 1013250 \text{ dynes/cm}^2\)
- \(T = 306.2 \text{ K}\)

(iv) Simulation starts \((t = 0)\) when \(m_{av} = 0.06 \text{ cm}^3/\text{cm}^3\)
AVERAGE MOISTURE CONTENT vs TIME

+ - experimental trajectory

x - model trajectory

FIGURE 4
AVERAGE TEMPERATURE vs TIME

+ - experimental trajectory

× - model trajectory

FIGURE 5
Figure 6: Moisture Profile vs Time

- Distance (cm) vs Moisture Content (cc/cc)
- The graph shows the moisture profile over time, with time in hours labeled on the curves.
- The x-axis represents distance in centimeters, ranging from 0 to 0.5 cm.
- The y-axis represents moisture content in (cc/cc), ranging from 0 to 9.
- Curves indicate the moisture content at different times: 0, 1/2, 1, 1 1/2, 2, 2 1/2, 3, 3 1/2, 4, 4 1/2, 5, and 5 1/2 hours.
TEMPERATURE PROFILE vs TIME

Distance (cm) vs Time (hours)

Distance (cm) X 10^-1

0 1 2 3 4 5

Temperature (K)

319
318
317
316
315
314
313
312
311
310
309
308

0 (time in hours)

FIGURE 7
PRESSURE PROFILE vs TIME

Distance (cm)

P-Palm. (dyne/cm.cm)

0 (time in hours)

FIGURE 8
PRESSURE PROFILE vs TIME

FIGURE 9
FIGURES 10 - 11

Modelling of Specific Experimental Conditions: II

Figure 10 Average Moisture Content versus Time.

Figure 11 Average Temperature versus Time.

(i) Boundary Conditions

\[ y_w = 0.010539 \]

\[ P = 1013250 \text{ dynes/cm}^2 \]

\[ T = 318.9 \text{ K} \]

(ii) Boundary Equations

As per Appendix A.

(iii) Starting Conditions (\( t = -0 \))

\[ m = 0.095 \text{ cm}^3/\text{cm}^3 \]

\[ P = 1013250 \text{ dynes/cm}^2 \]

\[ T = 306.2 \text{ K} \]
(iv) Simulation starts \((t = 0)\) when \(m_{av} = 0.06 \text{ cm}^3/\text{cm}^3\)

(v) Constant slab pressure.
AVERAGE MOISTURE CONTENT vs TIME

Moisture Content (cc/cc)

Time (minutes)

+ - experimental trajectory

x - model trajectory

FIGURE 10
AVERAGE TEMPERATURE vs TIME

+ - experimental trajectory

x - model trajectory

FIGURE 11
FIGURES 12 - 17

Modelling of Dryer Conditions

Figure 12 Average Moisture Content versus Time.

Figure 13 Average Temperature versus Time.

Figure 14 Slab Moisture Content as a Function of Distance from the Surface at Half-Hour Intervals.

Figure 15 Slab Temperature as a Function of Distance from the Surface at Half-Hour Intervals.

Figure 16 Slab Pressure (Rising) as a Function of Distance from the Surface at Half-Hour Intervals.

Figure 17 Slab Pressure (Falling) as a Function of Distance from the Surface at Half-Hour Intervals.

( i ) Boundary Conditions

Air at 45°C, 30% humidity.

\[ y_w = 0.0382 \]

\[ P = 1013250 \text{ dynes/cm}^3 \]
T = 318.15 K

(ii) Boundary Equations
As per section 4.3
Parallel air velocity = 508 cm/s (1000 ft/min)

(iii) Starting Conditions (t = -0)
m = 0.095 cm³/cm³
P = 1013250 dynes/cm²
T = 306.2 K

(iv) Simulation starts (t = 0) when mᵥ = 0.06 cm³/cm³
AVERAGE MOISTURE CONTENT vs TIME

FIGURE 12
AVERAGE TEMPERATURE vs TIME

FIGURE 13
MOISTURE PROFILE vs TIME

(time in hours) 0

Distance (cm)

Moisture Content (cc/cc)

FIGURE 14
FIGURE 15
FIGURE 17

P-P\textsubscript{Atm}, (dyne/cm.\textsubscript{cm})

(time in hours) 1 1\frac{1}{2} 2 2\frac{1}{2} 3 3\frac{1}{2} 4 4\frac{1}{2} 5 5\frac{1}{2} 6 6\frac{1}{2} 7

Distance (cm) \times 10^{-1}
APPENDIX C

COMPUTER PROGRAM LISTING
APPENDIX C

C.1 COMPUTER PROGRAM

The program listed on the following pages is the version responsible for figures 12 - 17.

The formatted output from the program becomes the input file for several separate programs, which, by employing standard GINO library plotting routines, then plot a single graph each. These plotting programs are of a simple nature and are not listed.

C.2 PROGRAM VARIABLES AND OVERALL STRUCTURE

The integer N is the number of space points in the space matrix including the surface and centre-slab points. Conditions within the slab are completely defined by the array $S(i,j)$. Dimension $i$ of this array denotes a specific property listed below, while dimension $j$ denotes the position; $j = 1$ denotes the bulk air, $j = 2$ denotes the surface, $j = 3$ denotes the first internal point, $j = 4$ denotes the second internal point, etc.

\[ S(1,j) = y_w \text{ at position } j \]
\[ S(2,j) = \text{P at position } j \]
$S(3,j) = T$ at position $j$
$S(4,j) = \frac{\partial y_w}{\partial P_w}$ at position $j$
$S(5,j) = m$ at position $j$
$S(6,j) = m$ at position $j$
$S(7,j) = k$ at position $j$
$S(8,j) = \frac{\partial k}{\partial \theta}$ at position $j$
$S(9,j) = \frac{\partial \theta}{\partial y_w}$ at position $j$
$S(10,j) = \frac{\partial \theta}{\partial P}$ at position $j$
$S(11,j) = \frac{\partial \theta}{\partial T}$ at position $j$
$S(12,j) = \frac{\partial \theta}{\partial m}$ at position $j$
$S(13,j) = \frac{\partial y_w}{\partial x}$ at position $j$
$S(14,j) = \frac{\partial P}{\partial x}$ at position $j$
$S(15,j) = \frac{\partial T}{\partial x}$ at position $j$

The main program has an overall executive function. The boundary conditions are set up and the state vector initialised according to the specified starting conditions ($t = -0$). The program begins to generate the changing profiles until the model becomes valid ($t = 0$), thereafter printing the profiles at 10 minute intervals. The program ceases
execution when there are no more experimental points for comparison.

C.3 SUB-PROGRAM FUNCTIONS

(i) Sub-routine CHKFIT.
Redundant (was used to assess the proximity of the theoretical average moisture trajectory with the experimental curve).

(ii) Function PSAT.
Calculates the saturated vapour pressure of water as a function of temperature.

(iii) Function DPSAT.
Calculates the differential of the saturated vapour pressure of water with respect to temperature.

(iv) Sub-routine STATVE.
Calculates various combinations of the state vector array depending upon the value of a computational switch integer (K) in the parameter list.

(v) Sub-routine GETOBJ.
Redundant.

(vi) Sub-routine HCOEFS.
Calculates the coefficients of the three main equations (equation (4.36)) for each point in the
space matrix. The values of the coefficients are stored in the array \( HC(i,j,k) \). Dimension \( i \) refers to the number of the equation \((k=1,2 \text{ or } 3 \text{ in equation } (4.36))\); dimension \( j \) refers to the coefficient i.e. \( j = 1 \) refers to \( A_k \) (equations \((4.38), (4.52) \text{ and } (4.79))\), \( j = 2 \) refers to \( B_k \) (equations \((4.39), (4.53) \text{ and } (4.80))\), \( j = 3 \) refers to \( C_k \) etc., dimension \( k \) refers to a point in the space matrix \((k = 2 \text{ denotes the surface point, } k = 3 \text{ denotes the first internal point, } k = 4 \text{ denotes the second internal point, etc.})\).

(vii) Sub-routine THCEFS.
This sub-routine uncouples the three main equations. Uncoupling entails the manipulation of the equations until there is one equation for \( \partial y_w/\partial t \), another for \( \partial P/\partial t \) and a third for \( \partial T/\partial t \). For example, in the equation for \( \partial y_w/\partial t \), the coefficients of \( \partial P/\partial t \) and \( \partial T/\partial t \) in the general equation will be zero. The pressure equation is stored in a special location and replaced for all \( x \) with \( \partial P/\partial t = 0 \). The uncoupled equations leave the sub-routine in the array \( THC(i,j,k) \) (the stored pressure equation is in location \( i = 4 \)).

(viii) Sub-routine MCOEFS.
The coefficients of the cross multiplied terms are dealt with in the manner specified by equations \((5.6), (5.7) \text{ and } (5.8))\). Note that the coefficients of the cross multiplied terms lose their individual identity because they are reformulated in terms of the
coefficients of $\partial y_w/\partial x$, $\partial P/\partial x$ and $\partial T/\partial x$. The manipulated coefficients leave the sub-routine in the array $HC(i,j,k)$.

(ix) Sub-routine COEMTX.
The complex manipulation of the reformulated coefficients is carried out in this sub-routine. Array $X(i,j)$ contains the coefficients of the unknown state vector $s$ while the array $Y(i)$ contains the constants. Since there are three unknowns at each point, there are $3N$ equations.

(x) Sub-routine REPEAT.
Repeats the recalculation of the state vector $s$ at the next time level with a better estimate of the average value of the coefficients.

(xi) Sub-routine UPDATP.
Calculates the new pressure profile given the new values of $y_w$ and $T$ across the slab.

(xii) Sub-routine TRCOEF.
Calculates the coefficients for heat and mass transfer at the surface.

(xiii) Sub-routines, SCALE, LU and SOLVLU.
These sub-routines are to be found in the literature and have not been listed here. They are of general application and used in the solution of a set of simultaneous equations.
COMPUTER PROGRAM LISTING
**MAIN PROGRAM**

**DATE:** TUE, MAY 04 1982

```
C PVAR.FBC
C ==
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER RUN,ORDER(153)
INTEGER *4 ITENO,ITER,I4,ITP1
DOUBLE PRECISION KG,KL,KS,L,LMDA,MA,MUM,MW,NN,MC(3,9,52),MER(100)
DOUBLE PRECISION KO,ND,MI,K1,K2,K3,K4,K5
LOGICAL VALID,FITIN
DIMENSION S(15,52),BCS(3,60000),X(153,153),Y(153),ANS(153)
DIMENSION H(3,12,52),THC(4,12,52),S0(15,52),SM(15),GA(3,52)
DIMENSION SMT(15,100),TER(100),SF(15,52)
COMMON/CONS/A,APHA,B,BB,BETA,CO,Cl,C2,C3,C4,C5,C6,CPA,CPL,CPS,KO,
+ CPW,E,EP,GAWO,KG,KL,KS,L,LMDA,MA,MUM,MW,NN,ND,RHOL,RHOS,SGMA,ND
COMMON/CONA/K1,K2,K3,K4,K5
COMMON/COM1/BCS,X
COMMON/COM2/HC,THC,MC
C--
C DEFINE THE CONSTANTS
C
A = 1.209658D-12
B = 5080.00+00
BB = 100.00D+00
BETA = 0.1670+00
C0 = 2.5D-10
READ(5,1100)CO
READ(5,1100)C1
READ(5,1100)C2
C3 = 6.4962D-5
CPA = 1.00630D+07
CPL = 4.17930D+07
CPS = 4.8150D+07
CPW = 1.86460D+07
E = 0.80+00
EP = 0.26D+00
GAWO = 121.2D+00
KD = 27.4D0
KG = 2.613D+03
KL = 9.616D+05
KS = 2.207D+05
L = 0.5D+00
LMDA = 2.4418D+10
MA = 28.952D+00
```
MAIN PROGRAM

MUM = 1.83D-04
MW = 18.016D+00
ND = 1.39D0
NN = 0.25D+00
Q = MW * LMDA
R = 6.3149D+07
RHOL = 0.99707D+00
RHOS = 2.68D+00
SGMA = 5.67D-05
U = 508.0D0
WRITE(6,1000) C1, C2

NOW THE DERIVED CONSTANTS
C4 = DSQRT(R*MW)/C1
C5 = DSQRT(MW/MA)
C6 = C5 - 1.00D+00

NOW THE HYDROTHERMAL CONSTANTS
K1 = MW/MA
K2 = R/(MA*1013250.0D0)
K3 = R/(MW*1013250.0D0)
K4 = CPA
K5 = CPW

C NOW THE PROGRAM PARAMETERS
C
READ(5,1101)
N
NO. OF POINTS (MAXIMUM OF 51)
NM1 = N-1
NP1 = N+1
NT3 = N*3
DX = L/NM1
C
READ(5,1100)
DT
SPACE INTERVAL (CM)
C
WRITE(6,1001) DX, DT
ETIME = 1000.0D+00
END TIME (MINS)
C
VALID = .FALSE.
C
READ IN THE INITIAL CONDITIONS, GENERATE THE BOUNDARY CONDITIONS
C
FIRST GET THE INITIAL CONDITIONS ON THE STATE VARIABLES
ITENO = ETIME*60.0D0/DT + 0.5D0
RUN = 0
WRITE(7) RUN
READ(5,1100)
TI
READ(5,1100)
MI

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DO 10 I=2,NP1
SO(2,I) = 1.01325D6
SO(3,I) = TI
SO(6,I) = MI
10 CONTINUE
WRITE(6,1013)TI
WRITE(6,1002)MI
CALL STATEVE(SO,DX,NP1,1)
READ(5,1100)YW
READ(5,1100)TI
ITP1 = ITEND + 1
DO 20 I4=1,ITP1
BCS(1,I4) = YW
BCS(2,I4) = 1.01325D6
BCS(3,I4) = TI
20 CONTINUE
WRITE(6,1014)YW, TI
C SET UP THE CONSTANTS IN SUBROUTINE TRCOEF
CALL TRCOEF(DU1,DU1,YW,TI,U,DU1,DU1,1)
C
TIME = 0.000
DO 30 J=1,3
SO(J,1) = BCS(J,1)
30 CONTINUE
SO(4,1) = SO(1,1)*SO(2,1)/PSAT(SO(3,1))
SO(2,2) = SO(2,1)
DO 40 I=1,NP1
DO 40 J=1,15
S(J,I) = SO(J,I)
40 CONTINUE
WRITE(6,1003)TIME,((I,(S(J,I),1,J=1,6)),I=1,NP1)
C READ IN THE EXPERIMENTAL RESULTS
READ(5,1101)J
IF (J .NE. 0) GOTO 50
FITIN = .FALSE.
GOTO 70
50 FITIN = .TRUE.
DO 60 I=1,J
READ(5,1100)MER(I)
60 CONTINUE
READ(5,1101)J
IF (J .EQ. 0) GOTO 70
DO 70 I=1,J
70
**MAIN PROGRAM**

```
READ(S,1100)TER(I)
CONTINUE
C  DO 690 ITER=1,ITEND
C
C++*************** CALL COMO$$(000010,0,0,0,IFIXIT) 
WRITE(1,9999)
9999 FORMAT(' Program running.... PLEASE LEAVE !')
CALL COMO$$(000020,0,0,0,IFIXIT)
C++***************
DO 100 J=1,3
S(J,1) = BCS(J,ITER)
100 CONTINUE
S(4,1) = S(1,1)*S(2,1)/PSAT(S(3,1))
S(2,2) = S(2,1)
C ESTIMATE THE S VECTOR DT/2 IN THE FUTURE
DO 110 J=1,3
SF(J,1) = (S(J,1)+BCS(J,ITER+1))/2.OD0
110 CONTINUE
SF(4,1) = SF(1,1)*SF(2,1)/PSAT(SF(3,1))
DO 120 I=2,NP1
DO 120 J=I,15
SF(J,1) = S(J,I) + (S(J,I) - SO(J,I))/2.OD0
120 CONTINUE
SF(2,2) = SF(2,1)
C CALL HECEFS(SF,NP1)
CALL THCEFS(NP1)
CALL MCEFS(S,SF,DY,DT,NP1)
CALL COEMTX(S,SF,X,Y,DX,NP1,NT3,U)
CALL SCALE(X,Y,NT3,153,IFAIL)
IF (IFAIL .EQ. 1) GOTO 999
CALL LU(X,NT3,153,ORDER,IFAIL)
IF (IFAIL .EQ. 1) GOTO 999
CALL SOLVLU(X,Y,ANS,NT3,153,ORDER)
CALL UPDATP(S,SF,ANS,DX,NT3,NP1)
CALL REPEAT(2,S,SF,ANS,DX,DT,N,NP1,NT3,IFAIL,U)
IF (IFAIL .EQ. 1) GOTO 999
C UPDATE ALL SYSTEM AND STATE VARIABLES
TIME = TIME + DT/60.0D+00
```

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DO 190 J=1,15
DO 190 I=1,NP1
SQ(J,I) = S(J,I)
190 CONTINUE
DO 200 I=1,N
S(1,I+1) = ANS(I)
S(2,I+1) = ANS(N+I)
S(3,I+1) = ANS(2*N+I)
200 CONTINUE

CALL STATVE(S,DX,NP1,3)

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C DETERMINE AVERAGES FOR T AND m ACROSS THE SLAB
SUMT = 0.0D+00
SUMM = 0.0D+00
DO 210 I=2,N
SUMT = SUMT + (S(3,I) + S(3,I+1))/2.0D+00
SUMM = SUMM + (S(6,I) + S(6,I+1))/2.0D+00
210 CONTINUE
SM(3) = SUMT/NM1
SM(6) = SUMM/NM1

IF (SM(6) .GT. MER(1)) GOTO 310
IF (VALID) GOTO 300

C MODEL IS NOW VALID
VALID = .TRUE.
IFIT = 0
IOUT = -1
FITO = 0.0DO
FITN = 0.0DO
WRITE(6,1012)TIME
WRITE(6,1003)TIME,((I,(S(J,I),J=1,6)),I=1,NP1)
WRITE(6,1006)SM(3)
WRITE(6,1007)SM(6)
300 CONTINUE
IOUT = IOUT + 1
IF (IOUT .LT. IDINT(600.0DO/DT + 0.5DO)) GOTO 310
IOUT = 0
WRITE(6,1003)TIME,((I,(S(J,I),J=1,6)),I=1,NP1)
MAIN PROGRAM

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WRITE(6,1006)SM(3)
WRITE(6,1007)SM(6)
IFIT = IFIT + 1
SMT(3,IFIT+1) = SM(3)
SMT(6,IFIT+1) = SM(6)
IF (MER(IFIT), GT, 1.000) GOTO 700
CALL CHKFIT(MER(IFIT),SM(6),FITO,FITN,IFIT)

CONTINUE

IF (MER(IFIT) .GT. 1_0) DO 700
CALL CHKFITCMERCIFIT),SMC6),FITO,FITN,IFIT)
CONTINUE

C-----------------------------------------------------------------------
C
RETURN ITER
690 CONTINUE
C-----------------------------------------------------------------------
700 CONTINUE
WRITE(6,1003)TIME,((I,(S(J,I),J=1,6)),I=1,NP1)
WRITE(6,1006)SM(3)
WRITE(6,1007)SM(6)
CALL GETOBJ(S,GA,OBJ,DX,EP,NP1,1)
WRITE(6,1009)OBJ
WRITE(6,1011)FITO,FITN
IFIT = IFIT - 1
WRITE(6,1015)MER(I),SMT(6,1),TERC1),SMT(3,1)
DO 720 I=2,IFIT
IF (TER(I) .LT. 1.000) GOTO 710
WRITE(6,1016)MER(I),SMTC6,I),TER(I),SMT(3,I)
GOTO 720
710 CONTINUE
WRITE(6,1017)MER(I),SMT(6,1),SMTC3,I)
720 CONTINUE
CALL STATVECS,DX,NP1,2)
CALL GETOBJ(S,GA,OBJ,DX,EP,NP1,2)
WRITE(6,1010)((I,(GA(J,I),J=1,3)),I=2,NP1)
730 CONTINUE
C=======================================================================
999 CONTINUE
C
1000 FORMAT(//5X,'C1 = ',1PD13.6,//5X,'C2 = ',1PD13.6)
1001 FORMAT(//5X,'DX = ',1PD13.6,' cm //5X,'DT = ',1PD13.6,' Seconds')
1002 FORMAT(//5X,'INITIAL SLAB MOISTURE CONTENT = ',1PD13.6,cc/cc')
1003 FORMAT(//5X,'TIME = ',1PD13.6,' Minutes //5X,'POINT',5X,'YW',
+ 14X,'P',14X,'T',11X,'Pw/Psat',10X,'TH',14X,'m//' + (5X,I3,2X,1PD13.6,2X),3PD13.6,2X,3(1PD13.6,2X)))
1004 FORMAT(//5X,'TIME = ',1PD13.6,' MINS //5X,'POINT',5X,'k',
+ 11X,'dk/dTH',9X,'dTH/dyw',9X,'dTH/dP',9X,'dTH/dT',9X,'dTH/drh //
+ (5X,I3,2X,6(1PD13.6,2X)))
MAIN PROGRAM       DATE: TUE, MAY 04 1982

1005 FORMAT(///5X,'TIME = ',1PD13.6,' MINS'//5X,'POINT',5X,'dYw/dx', + 9X,'dP/dx',9X,'dT/dx'/(5X,13.2X,3(1PD13.6,2X)))
1006 FORMAT(///5X,'AVERAGE TEMPERATURE = ',3PD13.6,' K')
1007 FORMAT(///5X,'AVERAGE MOISTURE CONTENT = ',1PD13.6,' gm/cc')
1008 FORMAT(///5X,'THE GAIN INTRINSIC IN THE NEW BOUNDARY ', + 'CONDITIONS IS ',1PD13.6)
1009 FORMAT(///5X,'THE OBJECTIVE IS ',1PD13.6,' gm.cm/cc')
1010 FORMAT(///5X,'POINT',4X,'Ga(1)',10X,'Ga(2)',10X,'Ga(3)'// + (5X,13.2X,3(1PD13.6,2X)))
1011 FORMAT(///5X,'FITO = ',1PD13.6,' (gm/cc)**2'//5X,'FITN = ', + 1PD13.6,' gm.min/cc')
1012 FORMAT(///5X,'MODEL NOW VALID, TIME = ',2PD13.6,' Minutes ')'
1013 FORMAT(///5X,'INITIAL SLAB TEMPERATURE = ',3PD13.6,' K')
1014 FORMAT(///5X,'BOUNDARY Yw = ',1PD13.6//'5X,'BOUNDARY TEMPERATURE = ',3PD13.6,' K')
1015 FORMAT(///5X,'DRYING EXPERIMENT; EXPERIMENTAL AND THEORETICAL PROFI +LES'//5X,'(AVERAGE VALUES)'//8X,'m (exp)',11X,'m',11X,'T (exp)',9X,'T' + //(5X,2(1PD13.6,2X),2(3PD13.6,2X)))
1016 FORMAT(5X,2(3PD13.6,2X),2(3PD13.6,2X))
1017 FORMAT(5X,2(1PD13.6,2X),15X,3PD13.6)

C
1100 FORMAT(5X,D11.4)
1101 FORMAT(5X,I3)
C=======================================================================
STOP
END
SUBROUTINE CHKFIT(AE,AT,FITO,FITN,I)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
IF (I .EQ. 1) GOTO 20
ITAB = -1
IF (AT .GT. AE) ITAB = 1
IF ((ITAB + ITABO).EQ. 0) GOTO 10
FITN = FITN + (DABS(AT-AE) + DABS(AT0-AEO))*10.0D0/2.0D0
GOTO 30
10 CONTINUE
C CURVES HAVE CROSSED OVER
X = 10.0D0*(AEO-AT0)/(AT-AT0-AE+AEO)
A1 = DABS(AEO-AT0)*0.5D0*X
A2 = DABS(AE-AT)*0.5D0*(10.0D0-X)
FITN = FITN + A1 + A2
GOTO 30
20 CONTINUE
ITAB = -1
IF (AT .GT. AE) ITAB = 1
30 CONTINUE
FITO = FITO + (AT - AE)**2
ATO = AT
AE0 = AE
ITABO = ITAB
RETURN
END

DOUBLE PRECISION FUNCTION PSAT(T)
DOUBLE PRECISION PSAT,T
PSAT = 101325000 * DEXP( 70.4346943D0 - 7362.6981D0/T +
+ 6.952085D-3*T - 9.0D0*DLOG(T) )
RETURN
END

DOUBLE PRECISION FUNCTION DPSAT(T)
DOUBLE PRECISION DPSAT,PSAT,T
DPSAT = PSAT(T) * (7362.6981D0/(T*T) + 6.952085D-3 - 9.0D0/T)
RETURN
END

SUBROUTINE STATVECS(DX,NP1,K)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION KG,KL,KS,L,LMDA,MA,MUM,MW,NN,KD,ND
DIMENSION S(15,NP1)
COMMON/CONS/A,APHA,B,BB,BETA,C0,C1,C2,C3,C4,C5,C6,CPA,CPL,CPS,KD, 
N = NP1-1 
DOTO (10,30,70,90),K 
RETURN 
10 CONTINUE 
C P T AND m DEFINED, GIVE TH Yw AND Pw/Psat 
DO 20 I=2,NP1 
S(5,I) = S(6,I)/EP 
S(1,I) = (1.0D0-DEXP(-S(3,I)*RHOL/((1.0D0-EP)*RHOS*KD)) 
+ ***(1.0D0/ND)) / (S(2,I)/PSAT(S(3,I))) 
S(4,I) = S(1,I)*S(2,I)/PSAT(S(3,I)) 
20 CONTINUE 
RETURN 
30 CONTINUE 
C S(1,I) TO S(6,I) DEFINED, GIVE ALL REMAINING STATE VARIABLES 
CII = (1.0D0-EP)*RHOS*KD/ND / RHOL 
DO 40 I=2,NP1 
S(7,I) = (KG**NN*EP*(1.0D+00-S(5,I)) 
+ KL**NN*EP*S(5,I) 
+ KS**NN*(1.0D+00-EP)**(1.0D+00/NN) 
S(8,I) = EP*(KL**NN - KG**NN)/NN * (S(7,I)**NN)** 
+ (1.0D+00/NN-1.0D+00) 
S(12,I) = 1.0D0/EP 
CII = 1.0D0 - S(4,I) 
S(9,I) = S(12,I)*CII/S(3,I) * (-DLOG(CII)/S(3,I))**(ND-1.0D0) * 
S(2,I) / (PSAT(S(3,I))-S(1,I)*S(2,I)) 
S(10,I) = S(9,I)*S(1,I)/S(2,I) 
S(11,I) = S(12,I)*CII*(-DLOG(CII)/S(3,I))**(ND-1.0D0) * 
+ (-DPSAT(S(3,I))*S(1,I)*S(2,I)/S(3,I)*PSAT(S(3,I)) 
+ (PSAT(S(3,I))-S(1,I)*S(2,I)**) + DLOG(CII)/S(3,I)**2) 
40 CONTINUE 
DO 60 J=13,15 
DO 50 I=2,N 
S(J,I) = (S(J-12,I+1)-S(J-12,I-1)) / (2.0D+00*DX) 
50 CONTINUE 
S(J,NP1) = 0.0D+00 
60 CONTINUE 
RETURN 
70 CONTINUE 
C Yw P AND T DEFINED, GIVE Pw/Psat m AND TH 
DO 80 I=2,NP1 
S(4,I) = S(1,I)*S(2,I)/PSAT(S(3,I)) 
CII = 1.0D0 - S(4,I)
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S(6,I) = (1.0D0-EP)*RHOS*KD/RHOL * (-DLOG(CI2)/S(3,I))**ND
S(5,I) = S(6,I)/EP

CONTINUE
RETURN
CONTINUE
RETURN
END

SUBROUTINE GETOBJ(S,GA,OBJ,DX,EP,NP1,M)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION S(15,NP1),GA(3,NP1)
N = NP1-1
GOTO (10,30,50),M
RETURN

10 CONTINUE
C EVALUATE THE OBJECTIVE
OBJ = 0.D+00
DO 20 I=2,N
OBJ = OBJ + 0.5D+00*(S(6,I) + S(6,I+1))*DX
20 CONTINUE
RETURN

30 CONTINUE
C EVALUATE THE LAGRANGIANS
DO 40 I=2,NP1
DO 40 K=1,3
GA(K,I) = EP*S(K,I)
40 CONTINUE
RETURN

50 CONTINUE
RETURN
END

SUBROUTINE HCOEFS(S,NP1)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION KG,KL,KS,L,LMDA,MA,MUM,MW,NN,MC(3,9,52),KD,ND
DIMENSION S(15,NP1),HC(3,12,52),THC(4,12,52)
COMMON/CONS/A,APHA,B,BB,BETA,C0,C1,C2,C3,C4,C5,C6,CPA,CPL,CPS,KD, + CPW,E,EP,GAWO,KG,KL,KS,L,LMDA,MA,MUM,MW,NN,O,R,RHOL,RHOS,SGMA,ND
COMMON/COM2/HC,THC,MC
DO 10 I=2,NPl
C7 = C4*S(3,1)**0.5D0 + R*S(3,1)**(-0.5D0)*(C6*S(1,1)+1.0D0) /
+ (C2*C3)
C8 = C0*S(1,1)*S(2,1) / (R*MUM*S(3,1))
C9 = C2*C3*C4*S(3,1)**2.0D0 + R*S(3,1)*(C6*S(1,1)+1.0D0)
C10 = C2*C3*S(3,1)**1.5D0 + C1*(R*S(3,1)/MA)**0.5D0
C11 = C2*C3*S(3,1)**1.5D0 + C1*(R*S(3,1)/MW)**0.5D0
D6 = 0.0D0
C12 = -EP*RHOL*(Q/MW+S(5,1))*D6

D5 = S(8,1)
D2 = S(9,1)
D3 = S(10,1)
D4 = S(11,1)
D1 = S(12,1)

HC(1,1,1) = EP*(1.0D0-S(5,1))*S(2,1)/C7
HC(1,2,1) = EP*(1.0D0-S(5,1))*(C10*S(1,1)/C9+C8)
HC(1,3,1) = 0.0D0
HC(1,4,1) = -EP*S(2,1)/C7 *( D2 + C6*R*(1.0D0-S(5,1))/
+ (C2*C3*C7*D5/S(3,1)) )
HC(1,5,1) = EP*C8*(1.0D0-S(5,1))/S(2,1) - EP*D3*(C10*S(1,1)/C9+C8)
HC(1,6,1) = 0.0D0
HC(1,7,1) = EP*(1.0D0-S(5,1))/C7 - EP*S(2,1)*D3/C7 +
+ EP*C8*(1.0D0-S(5,1))/S(1,1) - EP.*(1.0D0-S(5,1))/C9+C8)*D2 +
+ EP*C10*(1.0D0-S(5,1))/C9*(1.0D0-C6*R*S(3,1))/S(3,1)/C9
HC(1,8,1) = - EP*S(2,1)*D4/C7 -
+ EP*C4*(1.0D0-S(5,1))*S(2,1)/(2.0D0*C7*D5/S(3,1))
+ (1.0D0-R*(C6*S(1,1)+1.0D0)/(C2*C3*C4*S(3,1)))
HC(1,9,1) = - EP*(1.0D0-S(5,1))/D4 + EP*(1.0D0-S(5,1))/
+ (2.0D0*C9)*(3.0D0-C2*C3*D5/S(3,1)) + C1*D5/S(3,1)/(R*(MA*S(3,1))))
+ - EP*C8*(1.0D0-S(5,1))/S(3,1) - EP*C10*(1.0D0-S(5,1))/C9*C9) *
+ (2.0D0*C2*C3*C4*S(3,1) + R*(C6*S(1,1)+1.0D0))
HC(1,10,1) = RHOL*EP*D2/MW + EP*S(2,1)/(R*S(3,1)) *
+ (1.0D0-S(5,1)-D3*S(2,1))
HC(1,11,1) = RHOL*EP*D3/MW + EP*S(1,1)/(R*S(3,1)) *
+ (1.0D0-S(5,1)-D3*S(2,1))
HC(1,12,1) = RHOL*EP*D4/MW - EP*S(2,1)*S(1,1)/(R*S(3,1))**2) *
+ (1.0D0-S(5,1)+D4*S(3,1))
MAIN PROGRAM

HC(2,1,I) = -C5*HC(1,1,I)
HC(2,2,I) = EP*(1.0DO-S(5,I))*(1.0DO-S(1,I))*(C5*C11/C9+C8/S(1,I))
HC(2,3,I) = 0.0DO
HC(2,4,I) = -C5*HC(1,4,I)
HC(2,5,I) = EP*C8*(1.0DO-S(5,I))*(1.0DO-S(1,I))/(S(1,I)*S(2,I)) +
            + EP*(1.0DO-S(1,I))*(D3*(C5*C11/C9 + C8/S(1,I))
HC(2,6,I) = 0.0DO
HC(2,7,I) = -EP*C5/C7*(1.0DO-S(5,I)-S(2,I)*D3) -
            + EP*(1.0DO-S(1,I))*D2*(C5*C11/C9+C8/S(1,I)) -
            + EP*C5*C11*(1.0DO-S(5,I)/C9*(1.0DO+C6*R*S(3,I))*(1.0DO-S(1,I))/C9)
HC(2,8,I) = -C5*HC(1,8,I)
HC(2,9,I) = EP*C5*(1.0DO-S(5,I))/(2.0DO*C9) *
            + (3.0DO*C2*C3*DSQRT(S(3,I)))+C1*DSQRT(R/(MW*S(3,I)))) -
            + EP*C5*C11*(1.0DO-S(5,I))*(1.0DO-S(1,I))/(C9*C9) *
            + (C2*C3*C4*S(3,I) + R*(C6*S(1,I)+1.0DO)) -
            + EP*C8*(1.0DO-S(5,I))*(1.0DO-S(1,I))/(S(1,I)*S(3,I)) -
            + EP*(1.0DO-S(1,I))*D4*(C5*C11/C9+C8/S(1,I))
HC(2,10,I) = -EP*S(2,I)/(R*S(3,I))*(1.0DO-S(5,I)+D2*(1.0DO-
            + S(1,I)))
HC(2,11,I) = EP*(1.0DO-S(1,I))/(R*S(3,I))*(1.0DO-S(5,I) -
            + D3*S(2,I))
HC(2,12,I) = -EP*S(2,I)*(1.0DO-S(1,I))/(R*S(3,I)**2)*
            + (1.0DO-S(5,I)+D4*S(3,I))

HC(3,1,I) = 0.0DO
HC(3,2,I) = 0.0DO
HC(3,3,I) = S(7,I)
HC(3,4,I) = 0.0DO
HC(3,5,I) = 0.0DO
HC(3,6,I) = D4*D5
HC(3,7,I) = 0.0DO
HC(3,8,I) = D2*D5 + HC(1,1,I)*(MW*CPW-C5*MA*CPA)
HC(3,9,I) = D3*D5 + (MW*CPW*HC(1,2,I)+MA*CPA*HC(2,2,I))
HC(3,10,I) = C12*D2
HC(3,11,I) = C12*D4 - EP*(1.0DO-S(5,I))
HC(3,12,I) = C12*D4 + EP*(1.0DO-S(5,I))*S(2,I)/(R*S(3,I))*
            + (MW*CPW*S(1,I) + MA*CPA*(1.0DO-S(1,I)) + EP*RHO*CPL*S(5,I))
            + + RHOS*(1.0DO-EP)*CP
SUBROUTINE THCEFS(NP1)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER ORDER(3)
DOUBLE PRECISION MC(3,9,52)
DIMENSION HC(3,12,52),THC(4,12,52),C(3,3)
COMMON/COM2/HC,THC,MC

C------------------------------------------------------------------------
C REPLACE AIR CONTINUITY EQUATION BY PRESSURE BOUNDARY CONDITION
C AT THE SURFACE ONLY

DO 2 J=1,12
HC(2,J,2) = 0.0D0
2 CONTINUE
HC(2,11,2) = 1.0D0

C------------------·-----------------------------------------------------
C GENERATE THE UPPER TRIANGULAR MATRIX OF THE TIME DERIVATIVE
C COEFFICIENTS REFORMULATING THE ROWS CONCURRENTLY

DO 120 I=2,NP1
DO 8 K=1,3
BIG = DABS(HC(K,10,I))
DO 6 J=11,12
IF (BIG .GE. DABS(HC(K,J,I))) GOTO 6
BIG = DABS(HC(K,J,I))
6 CONTINUE

DO 8 J=1,12
HC(K,J,I) = HC(K,J,I)/BIG
8 CONTINUE

DO 20 K=1,3
ORDER(K) = K
DO 10 J=1,3
C(K,J) = HC(K,9+J,I)
10 CONTINUE

DO 20 J=1,12
THC(K,J,I) = HC(K,J,I)
20 CONTINUE

DO 80 JCOL=1,2
CALL PIVOT(C,3,3,ORDER,JCOL)
DO 40 K=JCOL,3
KO = ORDER(K)
IF (KO .EQ. K) GOTO 40
40 CONTINUE
DO 30 J=1,12

MAIN PROGRAM

X = THC(K, J, I)
THC(K, J, I) = THC(K0, J, I)
THC(K0, J, I) = X
30 CONTINUE
GOTO 50
40 CONTINUE
50 CONTINUE
JCOLP1 = JCOL + 1
DO 70 KROW = JCOLP1, 3
ORDER(KROW) = KROW
IF (DABS(C(KROW, JCOL)) .LT. 1.0D-20) GOTO 70
F = C(KROW, JCOL) / C(JCOL, JCOL)
DO 60 J = 1, 3
C(KROW, J) = C(KROW, J) - F * C(JCOL, J)
60 CONTINUE
DO 70 J = 1, 12
THC(KROW, J, I) = THC(KROW, J, I) - F * THC(JCOL, J, I)
70 CONTINUE
80 CONTINUE
C UPPER-TRIANGULARISATION COMPLETED
C NOW BACK-SUBSTITUTE TO ELIMINATE OFF-DIAGONAL ELEMENTS
DO 100 KROW = 1, 2
K = 3 - KROW
KPI1 = K + 1
DO 90 JCOL = KPI1, 3
IF (DABS(THC(K, J + JCOL, I)) .LT. 1.0D-20) GOTO 90
F = THC(K, J + JCOL, I) / THC(JCOL, J + JCOL, I)
DO 90 J = 1, 12
THC(K, J, I) = THC(K, J, I) - F * THC(JCOL, J, I)
90 CONTINUE
100 CONTINUE
C STORE THE PRESSURE EQUATION, REPLACE IT WITH dP/dT = 0
DO 110 J = 1, 12
THC(4, J, I) = THC(2, J, I)
THC(2, J, I) = 0.000
110 CONTINUE
THC(2, 11, I) = 1.000
120 CONTINUE
RETURN
END
SUBROUTINE MCOEFS(S,SF,DX,DT,NP1)
IMPLIED DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION MC(3,9,52)
DIMENSION S(15,NP1),HC(3,12,52),THC(4,12,52),SF(15,NP1)
COMMON/COM2/HC,THC,MC
DO 50 I=2,NP1
DO 50 K=1,3
DO 10 J=1,6
MC(K,J,I) = THC(K,J,I)
10   CONTINUE
DO 20 J=7,9
MC(K,J,I) = THC(K,J+3,I)
20 CONTINUE
C NOW DEAL WITH THE MIXED TERMS
MC(K,4,I) = MC(K,4,I) * SF(13,I)
+   + THC(K,7,I) * SF(14,I)/2.0D0
+   + THC(K,8,I) * SF(15,I)/2.0D0
MC(K,5,I) = MC(K,5,I) * SF(14,I)
+   + THC(K,7,I) * SF(13,I)/2.0D0
+   + THC(K,9,I) * SF(15,I)/2.0D0
MC(K,6,I) = MC(K,6,I) * SF(15,I)
+   + THC(K,8,I) * SF(13,I)/2.0D0
+   + THC(K,9,I) * SF(14,I)/2.0D0
DO 30 J=1,3
MC(K,J,I) = MC(K,J,I) * DT / (2.0D0*DX*DX)
30 CONTINUE
DO 40 J=4,6
MC(K,J,I) = MC(K,J,I) * DT / (4.0D0*DX)
40 CONTINUE
50 CONTINUE
RETURN
END

SUBROUTINE COEMTX(S,SF,X,Y,DX,NP1,NT3,U)
IMPLIED DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION KG,KL,KS,L,LMDA,MA,MUM,MW,NN,KD,ND
DIMENSION S(15,NP1),HC(3,12,52),THC(4,12,52),SF(15,NP1)
DIMENSION HC(3,12,52),THC(4,12,52),C(3,9,52)
COMMON/CONS/A,APHA,B,BB,BETA,C0,C1,C2,C3,C4,C5,C6,CPA,CPL,CPS,KD,
MAIN PROGRAM

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+ CPW, E, EP, GAWO, KG, KL, KS, L, LMDA, MA, MUM, MW, NN, Q, R, RHOL, RHOS, SGMA, ND
COMMON/COM2/HC, THC, C
N = NP1 - 1
DO 20 I = 1, NT3
DO 10 J = 1, NT3
X(I, J) = 0.0D+00
10 CONTINUE
Y(I) = 0.0D+00
20 CONTINUE

SET UP THE 'CONSTANTS' FOR THE BOUNDARY EQUATIONS
CALL TRCOEF(ALPHA, HTC, SF(1, 1), SF(3, 1), U, SF(1, 2), SF(2, 1), 2)
C13 = 2.0D+00*DX*ALPHA*R*SF(3, 2)**(-0.5DO)*(1.0D+00-SF(1, 2)) / 
       (C3*SF(2, 2))
H = HTC + SGMA*E*(SF(3, 1)**4-SF(3, 2)**4)/(SF(3, 1)-SF(3, 2))
C14 = 2.0D+00*DX*H/SF(7, 2)

DO 90 K = 1, 3
DO 80 I = 2, NP1
J = N*(K-1)+I+1
IF (I .NE. 2) GOTO 60
FIRST POINT
X(J, 1) = -2.0D+00*C(K, 1, I) - C(K, 7, I) - C13*E(C(K, 1, I) - C(K, 4, I))
X(J, 2) = 2.0D+00*C(K, 1, I)

X(J, N+1) = -2.0D+00*C(K, 2, I) - C(K, 8, I)
X(J, N+2) = 2.0D+00*C(K, 2, I)

X(J, 2*N+1) = -2.0D+00*C(K, 3, I) - C(K, 9, I) - C14*E(C(K, 3, I) - C(K, 6, I))
X(J, 2*N+2) = 2.0D+00*C(K, 3, I)

Y(J) = (2.0D+00*C(K, 1, I) - C(K, 7, I) - C13*(-C(K, 1, I) + C(K, 4, I)))*S(1, 2)
      + (2.0D+00*C(K, 2, I) - C(K, 8, I)))*S(2, 2)
      + (2.0D+00*C(K, 3, I) - C(K, 9, I) - C14*(-C(K, 3, I) + C(K, 6, I)))*S(3, 2)
      + (-2.0D+00*C(K, 3, I)))*S(3, 3)
      + (-2.0D+00*C13*(C(K, 1, I) - C(K, 4, I)))*S(1, 3)
      + (-2.0D+00*C(K, 2, I)))*S(2, 3)
      + (-2.0D+00*C(K, 3, I)))*S(3, 3)
      + (2.0D+00*C13*(C(K, 1, I) - C(K, 4, I)))*S(1, 1)
      + (2.0D+00*C14*(C(K, 3, I) - C(K, 6, I)))*S(3, 1)

GOTO 80
60 CONTINUE
MAIN PROGRAM

IF (I.EQ. NP1) GOTO 70

C GENERAL INTERNAL POINT

X(J,I-2) = C(K,1,I) - C(K,4,I)
X(J,I-1) = -2.0D+00*C(K,1,I) - C(K,7,I)
X(J,I) = C(K,1,I) + C(K,4,I)

C

X(J,N+I-2) = C(K,2,I) - C(K,5,I)
X(J,N+I-1) = -2.0D+00*C(K,2,I) - C(K,8,I)
X(J,N+I) = C(K,2,I) + C(K,5,I)

C

X(J,2*N+I-2) = C(K,3,I) - C(K,6,I)
X(J,2*N+I-1) = -2.0D+00*C(K,3,I) - C(K,9,I)
X(J,2*N+I) = C(K,3,I) + C(K,6,I)

C

Y(J) = (-C(K,1,I) + C(K,4,I))*S(I-1)
+ (2.0D+00*C(K,1,I) - C(K,7,I))*S(I)
+ (-C(K,1,I) - C(K,4,I))*S(I+1)

+ (-C(K,2,I) + C(K,5,I))*S(2-I)
+ (2.0D+00*C(K,2,I) - C(K,8,I))*S(2)
+ (-C(K,2,I) - C(K,5,I))*S(2+1)
+ (-C(K,3,I) + C(K,6,I))*S(3-I)
+ (2.0D+00*C(K,3,I) - C(K,9,I))*S(3)
+ (-C(K,3,I) - C(K,6,I))*S(3+1)

GOTO 80

C LAST POINT

70 CONTINUE

X(J,N-1) = 2.0D+00*C(K,1,I)
X(J,N) = -2.0D+00*C(K,1,I) - C(K,7,I)

C

X(J,2*N-1) = 2.0D+00*C(K,2,I)
X(J,2*N) = -2.0D+00*C(K,2,I) - C(K,8,I)

C

X(J,3*N-1) = 2.0D+00*C(K,3,I)
X(J,3*N) = -2.0D+00*C(K,3,I) - C(K,9,I)

C

Y(J) = -2.0D+00*C(K,1,I)*S(I-1)
+ (2.0D+00*C(K,1,I) - C(K,7,I))*S(I)
+ -2.0D+00*C(K,2,I)*S(2-1)
+ (2.0D+00*C(K,2,I) - C(K,8,I))*S(2)
+ -2.0D+00*C(K,3,I)*S(3-1)
+ (2.0D+00*C(K,3,I) - C(K,9,I))*S(3)
SUBROUTINE REPEAT(NR, S, SF, ANS, DX, DT, N, NP1, NT3, IFAIL, U)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
INTEGER ORDERCI53) DOUBLE PRECISION
MC(3,9,52)
DIMENSION S(15,NP1), ANS(NT3), SF(15,NP1)
DIMENSION X(153,153), Y(153), HC(3,12,52), THC(4,12,52)
COMMON/COM2/HC, THC, MC
COMMON/RPT/X
C-----------------------------------------------------------------------
IF (NR .EQ. 0) RETURN
SF22 = SF(2,2)
DO 60 IREP=1,NR
DO 5 I=2,NP1
SF(1,I) = (S(1,I) + ANS(I-1))/2.0DO
SF(2,I) = (S(2,I) + ANS(N+I-1))/2.0DO
SF(3,I) = (S(3,I) + ANS(2*N+I-1))/2.0DO
C
CONTINUE
SF(2,2) = SF22
C
CALL STATVE(SF,DX,NP1,3)
CALL HCOEFS(SF,NP1)
CALL THCEFS(NP1)
CALL MCOEFS(S,SF,DX,DT,NP1)
CALL COEMTX(S,SF,X,Y,DX,NPI,NT3,U)
C
CALL SCALE(X,Y,NT3,153,IFAIL)
IF (IFAIL .EQ. 1) RETURN
CALL LU(X,NT3,153,ORDER,IFAIL)
IF (IFAIL .EQ. 1) RETURN
CALL SOLVLU(X,Y,ANS,NT3,153,ORDER)
CALL UPDATP(S,SF,ANS,DX,NT3,NP1)
C
60 CONTINUE
SUBROUTINE UPDATP(S, SF, ANS, DX, NT3, NP1)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
INTEGER ORDER(51)
DIMENSION HC(3,12,52), THC(4,12,52), C(3,9,52), ANS(NT3), ANP(51)
DIMENSION S(15,NP1), SF(15,NP1), X(51,51), Y(S1)
COMMON/COM2/HC, THC, C

C-----------------------------------------------------------------------
N = NP1 - 1
DO 20 I=1,N
   X(I,J) = 0.0D0
10 CONTINUE
Y(I) = 0.0D0
20 CONTINUE
C SET UP THE COEFFICIENT MATRIX
DO 30 I=3,N
   X(I-1,I-2) = THC(4,2,I) - 
   + THC(4,5,I)*(S(14,I)+2.0D0*(SF(14,I)-S(14,I)))*DX/2.0D0 - 
   + THC(4,7,I)*(ANS(I)-ANS(I-2))/4.0D0 - 
   + THC(4,9,I)*(ANS(2*N+I)-ANS(2*N+I-2))/4.0D0
   X(I-I-1) = -2.0D0*THC(4,2,I)
   X(I-I-1) = - X(I-I-1,I-2) + 2.0D0*THC(4,2,I)

C
   Y(I-I) = - THC(4,1,I)* (ANS(I-2,0D0*ANS(I-1)+ANS(I-2)) - 
   + THC(4,3,I)*(ANS(2*N+I-2,0D0*ANS(2*N+I-1)+ANS(2*N+I-2)) - 
   + THC(4,4,I)*(ANS(I-AN-1-2))**2/4.0D0 - 
   + THC(4,6,I)*(ANS(2*N+I)-ANS(2*N+I-2))**2/4.0D0 - 
   + THC(4,8,I)*(ANS(I-1)-ANS(I-2))*(ANS(2*N+I-2))/4.0D0

30 CONTINUE
C NOW DEAL WITH THE SURFACE PRESSURE BOUNDARY EQUATION
C
   X(1,1) = 1.0D0
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Y(1) = S(2,2)

C
NOW THE INTERNAL BOUNDARY EQUATION

C X(N,N-1) = 2.0DO*THC(4,2,NP1)
C X(N,N) = - 2.0DO*THC(4,2,NP1)
C
C Y(N) = - THC(4,1,NP1)*2.0DO*(ANS(N-1)-ANS(N)) -
         THC(4,3,NP1)*2.0DO*(ANS(3*N-1)-ANS(3*N))

C-----------------------------------------------------------------------

C SOLVE FOR THE NEW PRESSURE PROFILE
C CALL SCALE(X,Y,N,51,IFAIL)
C IF (IFAIL .EQ. 1) RETURN
C CALL LU(X,N,51,ORDER,IFAIL)
C IF (IFAIL .EQ. 1) RETURN
C CALL SOLVLU(X,Y,ANP,N,51,ORDER)
C IF (IFAIL .EQ. 1) RETURN
C
C UPDATE THE ANS MATRIX
D0 40 I=1,N
   ANS(N+I) = ANP(I)
40 CONTINUE
RETURN
END

SUBROUTINE TRCOEF(MTC,HTC,YWC,TC,U,YWS,PC,IS)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DOUBLE PRECISION KG,KL,KS,L,LMDA,MA,MUM,MW,NN,MTC,JD,MTCD,KD,ND
DOUBLE PRECISION K1,K2,K3,K4,K5
COMMON/CONS/A,APHA,B,BB,BETA,C0,C1,C2,C3,C4,C5,C6,CPA,CPL,CPS,KD,
COMMON/CONA/K1,K2,K3,K4,K5
GOTO (10,40,10,50),18
RETURN

10 CONTINUE
HC = K1*YWC/(1.0DO-YWC)
RHOG = (1.0DO+HC)/(TC*(K2+K3*HC))
RE = BB*U*RHOG/MUM
IF (RE .GE. 15000.000) GOTO 20
MAIN PROGRAM

JD = 0.664D0/RE**0.5D0
GOTO 30
20 CONTINUE
JD = 0.036D0/RE**0.2D0
30 CONTINUE
DAB = C3*TC**1.5D0
SC = MUM/(RHOG*DAB)
MTCD = U*JD/SC**0.66667D0
YAC = 1.0D0 - YWC
CP = (K4+K5*HC)
IF (IS .EQ. 3) GOTO 40
RETURN
40 CONTINUE
VAS = 1.0D0 - YWS
YALM = (YAC-YAS)/DLOG(YAC/YAS)
MTC = MTCD*PC/(R*TC*YALM)
PR = CP*MUM/KG
HTC = JD*CP*RHOG*U/PR**0.66667D0
RETURN
50 CONTINUE
RETURN
END