

1.6. WATER DIFFUSION IN MEAT

1.6.1. Mass transfer by diffusion in meat

Mass transfer occurs in a number of meat processing operations such as dehydration, pickling, curing, cooking and packaging. During drying of meat, water leaves the meat and migrates into the surrounding air. Similarly, during the initial stages of pickling, salt moves from surface into the meat. When dry-cured products are processed, water migrates to the environment while salt and other compounds are being distributed into the product. The above examples, among others, make evident that mass transfer is a common, important phenomenon in meat processing. By definition, mass transfer is the migration of matter from one location to another due to concentration or partial pressure gradient.

A distinction between microscopic (diffusion) and macroscopic (convection) transport mechanism should be made, where diffusion would be defined as microscopic motion, no matter what the driving force is (Gekas, 1992).

For general purposes, mass transfer can be subdivided into molecular mass transfer and convective mass transfer (Floros, 1992). For the former, the term diffusion is often used. Convective mass transfer involves the migration of matter from a surface into a moving fluid or a stream of gas while diffusion deals with the random molecular migration of matter through a medium. Diffusion may be further subdivided into molecular diffusion, capillary diffusion, Knudsen diffusion, etc. Among these, molecular diffusion is the most important phenomenon that, has a major influence when other kinds of diffusion are also present.

Molecular diffusion of matter is analogous to the conductive transfer of heat. In heat conduction, energy is transferred from a region of high temperature to a region of low temperature due to the random motion of gas or liquid molecules or the vibration of solid molecules. Similarly, in molecular diffusion, matter is transferred from a region of high

concentration to a region of low concentration due to the random motion of the molecules of that substance. Therefore, molecular diffusion can be defined as the net transport of matter on a molecular scale due to a concentration or partial pressure gradient through a medium, which is either stagnant or flows in a laminar flow with a direction perpendicular to that of the concentration gradient. For example, water will evaporate from an open surface into still surrounding air, by diffusion in gaseous boundary layer.

Diffusion of a substance may occur in gases, liquids, or solids. Within the range of validity of the ideal gas law, the rate of diffusion in gases is mainly affected by temperature and pressure. When considering diffusion in liquids, however, the effect of pressure is usually negligible because liquids are incompressible. Diffusion in solids is far more complex than diffusion in gases or liquids, because: (1) the substance diffusing through a solid may actually be diffusing through a liquid or gas contained within the pores of the solid, (2) many solids are anisotropic, in which case the molecules have a preferential direction of movement, (3) and solid may interact with the substance which diffuses.

Diffusion of gases and liquids in solids are phenomena occurring in many processes. The two classifications of diffusion in solids could be an independent structure or a dependent one. In the former, the Fick's law can be directly applied. In the latter, pores, capillaries, and other interconnected voids in the solid allow some flow of the diffusing substance. Because this porous solid is anisotropic, the diffusion path of molecules will be different than the one described by Fick's law and an overall, apparent, or effective diffusivity coefficient will result.

The diffusion of macromolecules such as enzymes and other proteins in aqueous solutions is complex and difficult to describe by theoretical models. Interactions may occur between them and smaller molecules. As a result, the mobility of the diffusing molecule changes unpredictably, even in dilute solutions. Diffusion in those systems will be expressed as a function of concentration, temperature, viscosity of solutions, and the properties of the medium.

Fick's law is a phenomenological law resulting from experimental evidence. Irreversible thermodynamics, offer a theoretical approach represented by the Generalised Stefan

Maxwell equation which states that if there is a relative motion of molecules with respect to each other there will be a thermodynamic potential gradient set up due to the frictional drag of one type of molecules versus the other. Therefore, as it is known that all systems strive to reach equilibrium and the equilibrium state is characterised by the equality in the chemical potential. A gradient in the chemical potential will cause a molecular movement from the higher chemical potential towards the lower. Such concept may be applied in chemically defined systems where all the types of molecules are known, but in complex systems like meat is very difficult to apply the Generalised Stefan Maxwell equation due to the lack of information about the molecules and its properties (Pakowski, 1999).

Meat is considered to be a capillary, porous and colloidal solid, and water transfer in meat can be governed by different mechanisms. Each of this mechanisms is difficult to study independently, therefore, the whole process is considered as molecular diffusion and will be described further by a phenomenological law which only describes the experimental observations (Fick's law).

Apart from theory, meat is a non homogeneous body that may change depending on the amount of water and solutes, and may yield to structural changes during the drying process. Therefore, diffusivity must be defined as an effective coefficient (D_e) which considers all those different effects and explains the weight loss during the process.

1.6.1.1. Fick's Laws

The first Fick's law for diffusion states that under steady-state conditions the amount of water which is transported per unit of time and area is proportional to the concentration gradient. The proportionality coefficient is called diffusion coefficient (D).

Fick in 1855 was the first to formulate the constitutive equation for mass transfer from the analogy of heat conduction by following Fourier's equation. Fick quantitatively expressed the rate of a substance diffusion, through an isotropic medium with a unit surface area, as being proportional to the concentration gradient measured as a vector normal to the surface (Crank, 1975):

$$j = -D \frac{\partial C}{\partial x} \quad 1.6.1$$

Where units are $\text{kg/m}^2\text{s}$ for moisture flux (j) and kg/m^3 for local moisture concentration (C). x is the coordinate space (m) and D is the moisture diffusivity (m^2/s).

It can be expressed also as,

$$j = -D \frac{\partial X}{\partial x} \rho_v \quad 1.6.2$$

Where X is the water content (kg/kg d.m.) and ρ_v is the density of dry matter considering all volume of meat (kg d.m./m^3). The negative sign in Fick's law indicates that the flow of matter is in the direction of decreasing concentration.

For non-stationary conditions, a mass balance has to be made, and the input must be equal to the output plus the accumulation of the system. In one dimensional case we have the following Figure 1.6.1.

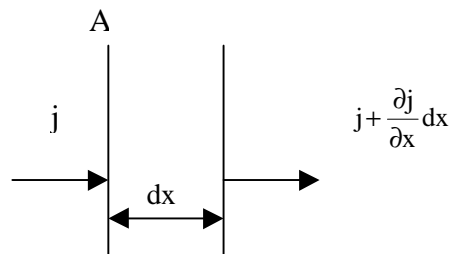


Figure 1.6.1 Difusion in an infinite plate

The mass balance equation for a diffusing component is:

$$j \cdot A - \left(j + \frac{\partial j}{\partial x} dx \right) A = A \cdot dx \cdot \frac{\partial C}{\partial \tau} \quad 1.6.3$$

where A is area (m^2).

This equations can be converted to:

$$\frac{\partial C}{\partial \tau} = D \frac{\partial^2 C}{\partial x^2} \quad 1.6.4$$

which is the so called second Fick's Law.

Things become more complicated when diffusion occurs in a multicomponent solution in a multiphase system.

In such case, the diffusional flux of a given component will be dependent on the fluxes of all other components, and the constitutive equation will take the following form,

$$j_1 = -D_{11} \frac{\partial C_1}{\partial x} - D_{12} \frac{\partial C_2}{\partial x} \quad 1.6.5$$

$$j_2 = -D_{21} \frac{\partial C_1}{\partial x} - D_{22} \frac{\partial C_2}{\partial x} \quad 1.6.6$$

In this case, the flux of component 1 will be dependent on the concentration gradient of component 1, plus the cross effect that considers the diffusion of component 1 being due to the concentration gradient of component 2. The same applies to the flux of component 2. On the ground of the molecular theory of diffusion also one can say that not only collisions between component 1 and the solid, but also collisions with component 2 will influence the flux of component 1. In terms of irreversible thermodynamics, the flux of given component will influence the fluxes of all other components. This approach will now be applied to simultaneous diffusion of salt and water in meat, in which the following derivation is developed (Pakowski, 1998).

For our purposes, the cross effects will be neglected because of the difficulty in measuring the cross coefficients and the involved difficulty in mathematical modelling.

Therefore, the resulting equation of the mass balance established for non-stationary conditions is the result of the following derivation,

Constitutive law for salt transfer

$$j_s = -D_s \frac{dw}{dx} X \rho_v \quad 1.6.7$$

where w is concentration of salt in water (kg NaCl/kg H₂O).

The schematic of the salt diffusion is shown below.

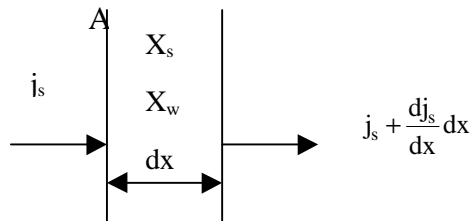


Figure 1.6.2 Salt diffusion in an infinite plate

Considering that salt content expressed by dry basis of meat is

$$X_s = w \cdot X \quad 1.6.8$$

and

$$dX_s = w \cdot dX + Xdw \quad 1.6.9$$

the mass balance becomes

$$j_s \cdot A - \left(j_s + \frac{\partial j_s}{\partial x} dx \right) A = A \cdot dx \cdot \frac{\partial X_s}{\partial \tau} \rho_v \quad 1.6.10$$

By differentiating equation (1.6.7) we obtain,

$$\frac{dj_s}{dx} = - \left(X \rho_v D_s \frac{\partial^2 w}{\partial x^2} dx + \rho_v D_s \frac{\partial w}{\partial x} \frac{\partial X}{\partial x} \right) \quad 1.6.11$$

Finally, the result is

$$X D_s \frac{\partial^2 w}{\partial x^2} dx + D_s \frac{\partial w}{\partial x} \frac{\partial X}{\partial x} = w \frac{\partial X}{\partial \tau} + X \frac{\partial w}{\partial \tau} \quad 1.6.12$$

Salt content is denoted by w (kg NaCl/kg H₂O) and X_s (kg NaCl/kg d.m.). Water content is expressed by X (kg H₂O/kg dm). Density is dry matter content per total volume of meat (kg d.m./m³) and salt diffusivity is D_s (m²/s).

1.6.1.2. Drying kinetics

In order to model the drying, it is necessary not only to have the knowledge of the diffusion inside the material, but also the mass transfer from the surface of the material to the surrounding air. This external mass transfer depends on the air flow conditions (air velocity, temperature, humidity, pressure) and the geometry of the material. It is characterised by the mass transfer coefficient k_y , defined by the following mass balance,

$$\rho V \frac{dX}{d\tau} = -k_y A (Y - Y^*)$$

1.6.13

where ρ is density (kg d.m./m³), V is volume (m³), X is water content (kg/kg dm), τ is time (s), k_y is the mass transfer coefficient (kg/m² s), A is area (m²), Y is the water content of the air (kg H₂O/kg dry air) and Y^* is the water content of the air in equilibrium with the surface of the product (kg H₂O/kg dry air). This value is given by the isotherms of sorption of the product.

The drying process can be classified in the following way:

- Externally controlled drying
- Internally and externally controlled drying
- Internally controlled drying

The criterion that decides into which class a given problem will fall is the diffusional Biot number. The Biot number for mass transfer is defined as,

$$Bi = \frac{k_y R}{\rho D} \left(\frac{Y - Y^*}{X - X^*} \right)$$

1.6.14

Another dimensionless number used for time is the Fourier number,

$$F_o = \frac{D\tau}{R^2}$$

1.6.15

The Biot number considers the relationship between the external mass transfer and the diffusion of mass in the interior of the product. The process of drying solids in conditions when $Bi < 1$ or better 0.1 can be classified as externally controlled, when $1 < Bi < 100$ the process is both internally and externally controlled and when $Bi > 100$ the drying process is purely internally controlled.

In externally controlled drying processes, the mass transfer inside the solid phase is neglected, and it is assumed that the water content profiles inside the solid are flat (Figure 1.6.3) and the average water content of the solid equals to that of the gas-solid interface.

In the case which the drying process is partly or fully internally controlled the profiles of water content develop in the solid phase (Figure 1.6.3). The respective gradients are deeper when Bi is larger or the evaporation rate greater. In the case ii) of Figure 1.6.3), water content on the interface varies with time from the initial to the equilibrium value X^* , while in the case iii) of Figure 1.6.3) this surface water content instantly reaches and remains there until the end of the process.

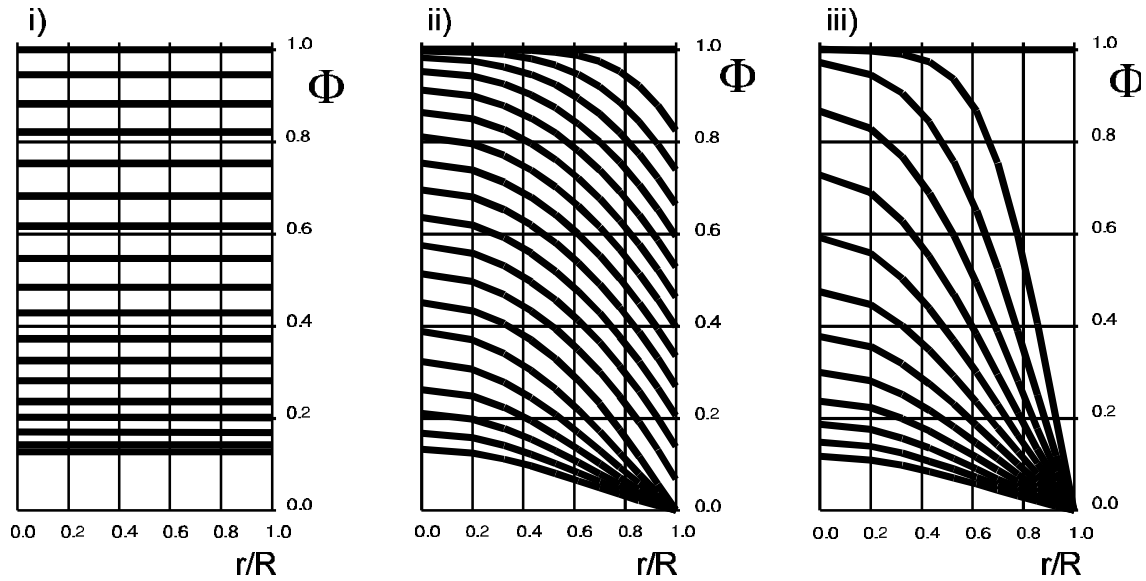


Figure 1.6.3 Dimensionless moisture content (ϕ). Profiles inside solid in i) externally, ii) externally and internally, iii) internally controlled drying processes.

Internally controlled drying can be described by the second Fick's law with the following boundary conditions:

- Type I considers that the surface of the product reaches instantaneously the equilibrium with the environment, and no mass transfer coefficient is needed to model the drying.
- Type II considers that the surface of the product does not reach instantaneously the equilibrium with the environment. In such a case, the knowledge of the mass transfer coefficient is very important.

The problem of calculating drying kinetics in the case of internally controlled process becomes very difficult due to multitude of complex mechanisms of moisture transfer in solid. The following difficulties may appear independently or jointly with the drying process:

- drying gas temperature and humidity may vary in the process,
- solid structure may be non homogeneous showing areas of different permeability to the diffusing moisture e.g. skin.
- solids may have intricate structure or shape, which are difficult to describe mathematically and do not correspond to one of three one-dimensional cases e.g. infinite plate, infinite cylinder and sphere.

- moisture diffusivity may depend strongly on moisture content,
- solids may shrink in the process.

Because of this, it is generally very hard to describe the process with a single and simple model. In spite of the extensive work on the subject resulting in many mathematical models published up to date (Okos, 1992), a universal, practically solvable mathematical model of a real solid drying remains unknown.

The lack of such model results in alternative methods for describing drying kinetics of an internally controlled drying. First of all, experimentally measured drying kinetics data can be curve fitted and such a curve is used for process calculations. Second, a simplified model can be used, using coefficients obtained from experiment or literature (Pakowski, 1999).

1.6.1.2.1. Drying curve

The drying kinetics experiment are performed in controlled conditions. The relationship of the mean water content versus time is known as the drying kinetic curve. It is divided into a constant-drying-rate period (or period I) and falling-drying-rate period (or period II) with the critical moisture content X_c separating the two periods as shown in Figure 1.6.4. In period I water evaporates as if there is no solid present, and its rate of evaporation is not dependent on the solid. It is usually assumed that in this period, drying is externally controlled. Period II is divided in two sections. In section IIa, the wet areas on the surface become completely dry. When the surface is dry (point τ_B), the evaporation will continue moving toward the center of the solid (section IIb). Drying in the period II is assumed to be internally controlled.

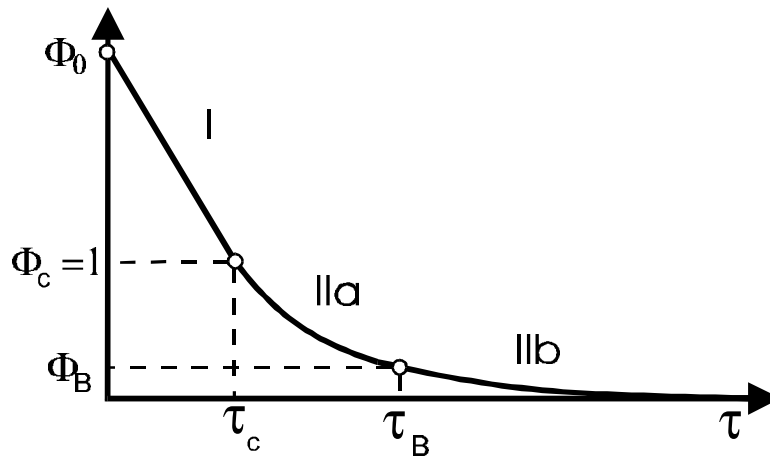


Figure 1.6.4 Idealized drying kinetic curve

The second Fick's law is used to describe the drying kinetic curve. The analytical solution of equation (1.6.4) has a form of Fourier series, and the convergence of the series for a given Bi is dependent on drying time (in the form of Fourier number Fo). With onset of the process, the series is slowly converging but for long periods of time its convergence becomes so fast that all terms can be neglected except the first one. By defining the relative error committed by neglecting terms for $i \geq 2$ as

$$E = \frac{\sum_{i=2}^{\infty} U_i}{U_1} \quad 1.6.16$$

where A_1 is the first term of the series and U_i is the i^{th} term of the series, it is possible to solve the analytical equation for minimum Fo which ensures that E will not be larger than a given value (Figure 1.6.5).

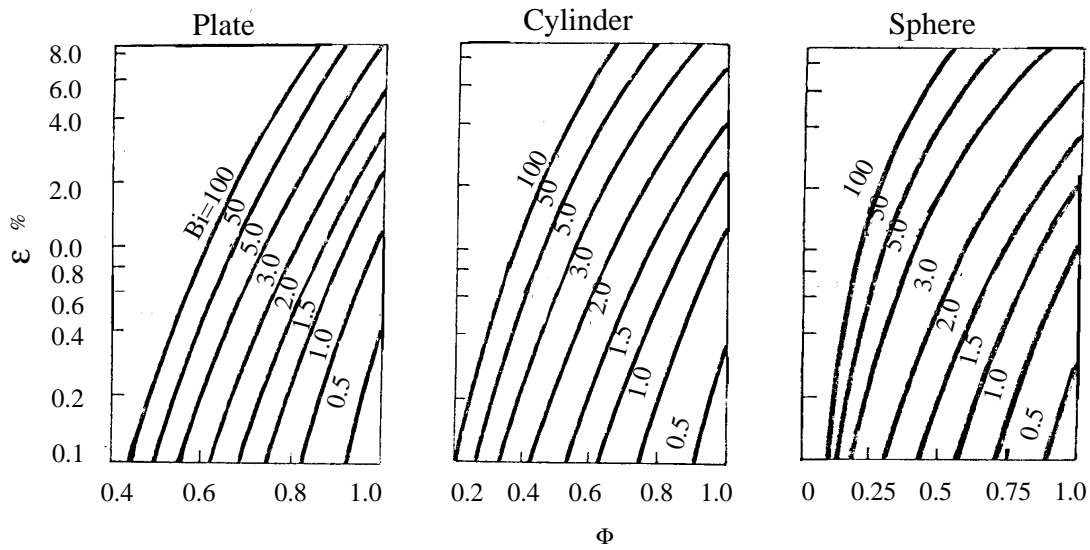


Figure 1.6.5 Relative error committed by neglecting terms of Fourier series depending on dimensionless averaged moisture content at different Bi number (Pakowski, 1999).

Another method that was developed to enable calculations concerning the drying process for materials with a diffusivity that is highly dependent on moisture content is the regular regime model (Schoeber, 1976). In this model, the moisture profile inside the material to be dried determines the different drying periods. The drying process is divided into three periods: (1) the constant-rate period, where the water transport depends only on external transfer resistance; (2) the penetration period, where the moisture profile starts to develop in the product (it occurs at the critical moisture content) and (3) the regular regime period, where a stable moisture profile is developed and it moves toward the center of the product.

1.6.2. Effective diffusivity determination

1.6.2.1. Methods

There is no standard method for the experimental determination of water diffusivity in solids. The methods used can be summarised as follows (Marinos-Kouris and Maroulis, 1995):

- Sorption kinetics.
- Permeation methods.
- Concentration-distance curves.
- Drying techniques.

A review of various methods has been done by Zogzas *et al.* (1994).

1.6.2.1.1. Sorption kinetics

The sorption (adsorption or desorption) rate is measured with a sorption balance while the solid sample is kept in a controlled environment.

The method is based on the amount of diffusant sorbed by a sample which is placed in a constant concentration source. This source may be a suitable buffer solution (or a constant pressure gas supply) of the diffusant at constant temperature. The source must be well mixed to provide boundary conditions of type I. The weight of the sample is recorded at specified time intervals until final equilibrium is attained. For a slab material geometry of thickness L and constant diffusivity, Crank (1975), has proved that

$$\frac{W_t}{W_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \frac{\pi^2 D \tau}{L^2}\right]$$

1.6.17

where, W_τ (kg) is the amount of diffusant absorbed in time τ (s), and W_∞ , is the amount of diffusant absorbed after infinite time, e.g. after the equilibrium state is reached.

This equation assumes that the slab, initially free of diffusant, is placed immediately at the constant concentration source, and if each surface attains a steady state equilibrium with the surroundings during the process, in the desorption process the ratio W_t/W_∞ can be calculated as,

$$\frac{W_\tau}{W_\infty} = \frac{\bar{X} - X_o}{X_e - X_o} \quad 1.6.18$$

Crank (1975) has shown that the diffusivity of a slab material can be easily evaluated by the following relation with an estimation error of less than 0.001 per cent.

$$D = \frac{0.049}{\left(\frac{\tau}{R^2}\right)_{\frac{1}{2}}} \quad 1.6.19$$

where the term $(\tau/R^2)_{1/2}$ is used here as the value of (τ/R^2) for which $W_\tau/W_\infty=1/2$. This value can be determined from the sorption data by numerical or graphical interpolation of the ratio curve (W_τ/W_∞) versus time.

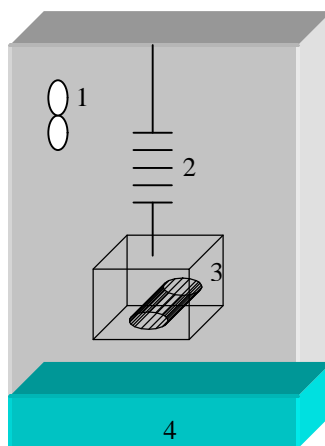


Figure 1.6.6 Experimental apparatus: Method of sorption kinetics. 1. Air circulator fan. 2. Weighing device. 3. Sample. 4. Buffer solution.

The moisture diffusivity can be estimated in an absorption process or in a desorption process, taking the mean as the representative value.

A significant problem is encountered by the formation of the concentration boundary layer on the gas side, offering a considerable external resistance. This problem is faced by stirring the surrounding fluid if the internal resistance to mass diffusion is not small (e.g. small slab thickness and/or high diffusivity and surface area values). In these situations the overall mass transport is not controlled by diffusion, and the main controlling mechanism becomes that of mass transfer at the interfaces.

Partial pressure of the diffusant may be measured instead of weighed, by means of a sensitive pressure gauge if the diffusant absorbed is in very small amounts and the method of weighing may prove useless.

1.6.2.1.2. Permeation method

Another method can be employed to measure the diffusion coefficient, it consists of using the material as a membrane and let the moisture diffuse through the material under a concentration gradient and steady-state conditions.

Steady state: A thin sheet of material is placed between two constant concentrations of the diffusant. After a time period, the surfaces of the sheet come into equilibrium with the diffusant sources, developing a constant gradient of surface concentration, leading to steady state conditions of diffusion (Marinos-Kouris and Maroulis, 1995; Zogzas *et al.* 1994). This state can be expressed, in a plane sheet, by the following equation,

$$j = D \frac{(C_{RA} - C_{RB})}{R} \quad 1.6.20$$

where, j is the constant flux of the diffusant ($\text{kg/m}^2\text{s}$). D is the diffusivity which, in this equation, does not depend on concentration (m^2/s). C_{RA} , C_{RB} are the constant surface concentrations of the sheet (kg/m^3). And R is the thickness of the sheet (m).

It is clear from the above equation that diffusivity can be estimated by measuring the flux of the diffusant, knowing surface concentrations and the thickness of the material sheet. The flux can be determined by the flow rate or the diffusant passing through the membrane sheet (Figure 1.6.7). This can be done experimentally by successive weighing of the diffusion cells at predetermined time intervals. Surface concentrations can be evaluated by using the equilibrium sorption isotherms of the material.

When C_{RA} and C_{RB} are variables, the flux will be pseudo-steady state, rather than a true steady state. With the aid of a material balance between the compartments and some rearranging, the following working equation can be obtained,

$$\ln\left(\frac{C_{RA} - C_{RB}}{C_{RA1} - C_{RA2}}\right) = -\frac{D A}{R} \left(\frac{1}{V_A} + \frac{1}{V_B}\right) (\tau - \tau_1) \quad 1.6.21$$

where A is area (m^2). V is volume (m^3) and τ is time (s). The subscript 1 denotes the time in which the first concentration measurement is made.

Plotting the experimental value of the left-hand side of equation (1.6.21) as a function of time, the effective diffusion coefficient D_e is obtained from the slope of the straight line. This can be carried out as soon as pseudo-steady state is attained. It must not be confused with time zero at which the experimental device is assembled and the process starts. In the traditional liquid diffusion application, the pseudo-steady states can be arranged at zero time. Alternatively, the errors introduced by including the initial non-steady-state period can be assumed to be negligible. The ratios between the diaphragm volume and the compartment volumes should be less than 0.1 (Westrin, 1991).

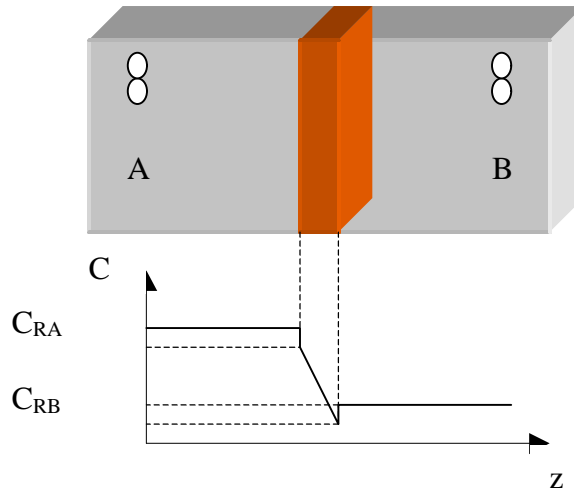


Figure 1.6.7 Above: schematic representation of the pseudo-steady-state diaphragm cell. Below: concentration profile.

In case the diffusion is concentration dependent, the assumption of a constant D_e is invalid. The obtained value of D_e will only be an integral value, corresponding to a finite concentration interval, rather than to one single concentration. It can be proved that this integral value is equal to the true differential value corresponding to the concentration of $C_R = (C_{RA1} + C_{RB1})/2$, at least, if the concentration dependence of D_e is linear, or near linear, in the interval between C_{RB1} and C_{RA1} .

The time-lag method is based on the time period prior to the establishment of the steady state diffusion of the permeation device. If by some convenient means, one of the sheet surfaces is maintained at concentration C_{RA} , while the other at zero concentration, after a theoretically infinite time period a steady state condition of diffusion will be achieved. Assuming that, the diffusion coefficient is constant, the sheet is initially completely free of diffusant, and that the diffusant is continually removed from the low concentration side, the amount of diffusant which will permeate the sheet (when time tends to infinity), is given as a linear function of time by the following equation,

$$W_\tau = -\frac{A D C_{RA}}{R} \left(\tau - \frac{R^2}{6D} \right) \quad 1.6.22$$

where W_τ is the amount of diffusant (kg).

Thus, if the amount of diffusant as a function of time is measured, it is possible to plot a curve (Figure 1.6.8). After a relatively large time interval, it will reduce to a straight line intercepting the t -axis at the quantity $(R^2/6D)$. From the intercept, D will be obtained. Similarly, the method can be applied in the case of variable diffusivity and cylindrical or spherical geometries.

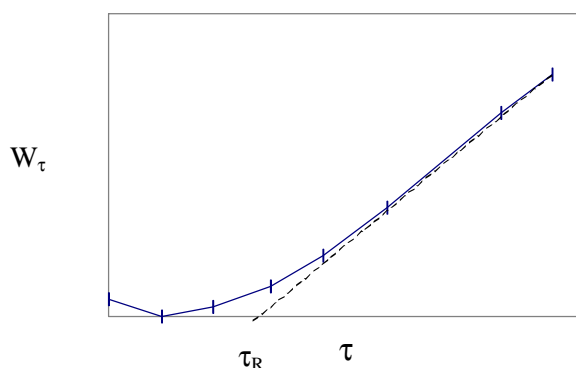


Figure 1.6.8 Evaluation of results obtained with the time-lag permeation method.

Although these permeation methods seem to be simple in application, there are problems from the experimental point of view. One of them is the manufacturing of a thin material sheet of constant thickness and homogenous structure. A second, is the sealing of the membrane edges, so as to ensure the diffusant to permeate only through the membrane area. A third, is the erroneous measurement of the flow rate of the diffusant, which results from the formation of stagnant mass boundary layers. This problem can not be adequately solved and is partially faced by stirring. Other problems arise from the swelling of the membrane material under the experimental conditions, the maintenance of constant concentration sources of the diffusant, as well as, from the use of the equilibrium data necessary to evaluate the surface concentrations of the sheet (Westrin, 1991; Zozgas *et al.*, 1994). The application of this permeation methods to materials which may swell or shrink, such as foodstuffs, is difficult (Motarjemi, 1988). Such method have been used for the determination of diffusivity coefficient of salt into meat (Gonzalez-Mendez *et al.*, 1983; Djelveh and Gros, 1988).

1.6.2.1.3. Concentration-distance curves

The method is based on the measurement of the diffusant concentration distribution as a function of time. Light interference methods, as well as radiation adsorption or simply gravimetric methods, can be used as concentration measurements. The analysis is also based on Fick's diffusion equation (Zozgas *et al.*, 1994)

The local concentration of the diffusant within the sample as a function of distance is determined in case of unidimensional diffusion.

One of the ways to determine the concentration-distance curve, is by using a long cylindrical sample undergoing unidimensional diffusion along its axis, in a sorption process (Figure 1.6.9). After a specified time interval, the cylinder is sliced in many equal parts and the content of each part is determined as soon as possible.

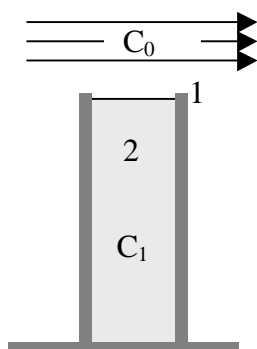


Figure 1.6.9 Concentration-distance curve method: Axial diffusion in a cylindrical sample. 1. Impermeable case. 2. Sample.

Another technique is by using two cylindrical samples of the same length and radius (Figure 1.6.10). One of the samples is equilibrated in excess of diffusant at a specified constant temperature, while the other is kept at a zero (or a low) concentration at this same temperature. At time $t=0$, the two cylinders are joined together to form a cylinder of double length. The diffusion takes place along the axis of the joined cylinders. After a specified time interval, the diffusant concentration profile along the axis can be determined by slicing and weighing the samples slices. According to Crank (1975), for the above case of

interdiffusion, the diffusivity at a specified concentration, C_1 , can be evaluated by the equation that follows:

$$D(C_1) = -\frac{1}{2\tau} \frac{dx}{dC} \int_0^{C_1} x dC \quad 1.6.23$$

where x is the distance from the interface of the two cylinders (m), and τ is the time at which the concentration profile is determined (s). The integral and the gradient of x at the specified concentration, C_1 , can be determined by numerical or graphical integration of the concentration-distance curve. The diffusivity may be evaluated as a concentration function by the repetitive use of equation (1.6.23).

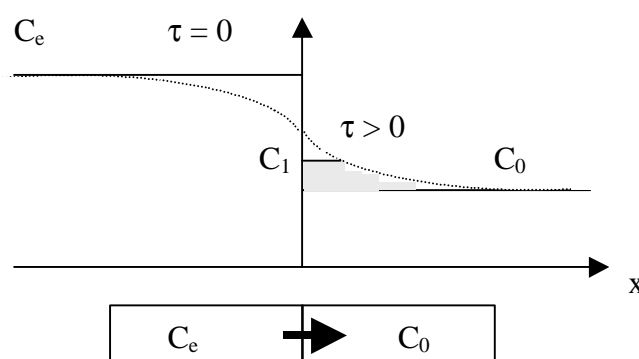


Figure 1.6.10 Concentration-distance curve method. Schematic presentation in the case of two cylinders interdiffusion.

Some specialised experimental techniques may be used for the determination of the concentration profiles, e.g. measuring the change of the refractive index of the sample; also the use of radioactive tracers, which may be mixed with the diffusant, the intensity of radioactivity can then be measured as an indication of the concentration; Nuclear Magnetic Resonance (NMR) and Electron Spin Resonance (ESR) techniques may be used. Chemical analysis may also be used in cases where the diffusant can be easily analyzed. Holographic laser interferometry has been used in solids like gels (Westrin, 1991).

Concentration-distance curves has been used for evaluation of diffusivity coefficient of sodium chloride in cheese. Motarjemi (1988) used this method for the determination of the

effective diffusivity coefficient of water in meat beef. Daudin *et al.* (1992) used the same technique to estimate the profiles of water and NaCl content in dry sausages.

Nuclear magnetic resonance (NMR): Since a nucleus is a charged, spinning particle, it has a magnetic moment and will orientate parallel to an external magnetic field. This property allows to obtain a tracer-diffusion coefficient, which is a measure of the mean distance travelled by the spin-carrying molecules. As advantages, the method is non destructive, and does not need assumptions about diffusional mechanism. The D value is obtained from the following equation:

$$\ln \left[\frac{A(2\tau)}{A(0)} \right] = -2\tau/T_2 - (\gamma G \delta)^2 D * (\Delta - \delta/3)$$

1.6.24

where the quantity within brackets represents the ratio between the signal intensities, T_2 is the spin-spin relaxation time, γ is the magnetogric factor, G is the amplitude and δ the duration of the gradient magnetic field pulses, and Δ is the time between these pulses.

As a disadvantage, the method can impose some restrictions on some systems (Westrin, 1991). It is very sensible to the non homogeneous samples and to the right value of dry matter, and needs a complex filtration of data for its mathematical analysis.

1.6.2.1.4. Drying methods

The samples are placed in a dryer and, moisture diffusivity is estimated from drying data. All the drying methods are based on Fick's equation of diffusion, and they differ with respect to the solution methodology.

Simplified methods

Fick's equation is solved analytically for certain sample geometries considering that the surface mass transfer coefficient is high enough, so that the material moisture content at the surface is in equilibrium with the air conditions. The air drying conditions must be constant, and the moisture diffusivity is also considered constant (independent of material moisture content) for each temperature. The analytical solution for slab, spherical, or cylindrical samples is used in the analysis. Several alternatives exist concerning the methodology of diffusivity estimation, which differ essentially on the variable, on which a regression analysis is applied. (Marinos-Kouris and Maroulis, 1995).

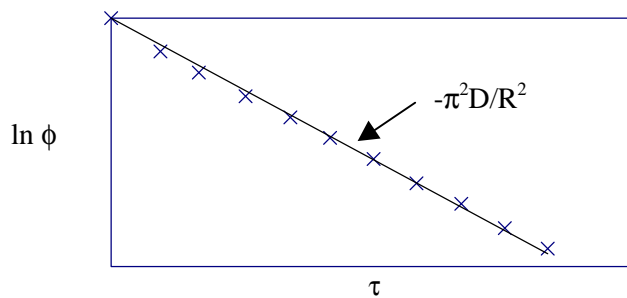


Figure 1.6.11 Simplified method. Obtention of D from the slope

Moisture diffusivity determination results from plotting the dimensionless moisture ratio Φ , which is calculated from the experimental data, against time on a semilogarithmic diagram (Figure 1.6.11). This plot is a straight line over the first falling period, but it may deviate at the late drying stages. The slope of this straight line is considered equal to the quantity $(\pi^2 D/R^2)$ from which diffusivity is determined by considering times large enough. (equation 1.6.25):

$$\ln \left(\frac{\bar{X} - X_e}{X_0 - X_e} \right) = \frac{-\pi^2 D_e}{4r^2} \cdot \tau \quad 1.6.25$$

Examples of using this simplified technique can be found in the literature for a large variety of food materials (Zozgas *et al.* 1994)

The method can not be used in cases where diffusivity depends strongly on moisture content. However, an alternative procedure is described in order to compensate for the case of moisture dependent diffusivity (Figure 10). In this procedure, the theoretical moisture ratio Φ , is evaluated numerically for a range of Fourier numbers ($F_o = D\tau/L^2$). Then, the same ratio Φ , is evaluated using experimental data. Both curves of experimental and theoretical moisture ratio Φ , are plotted versus time and Fourier number, respectively, on a semilogarithmic diagram (Figure 1.6.12).

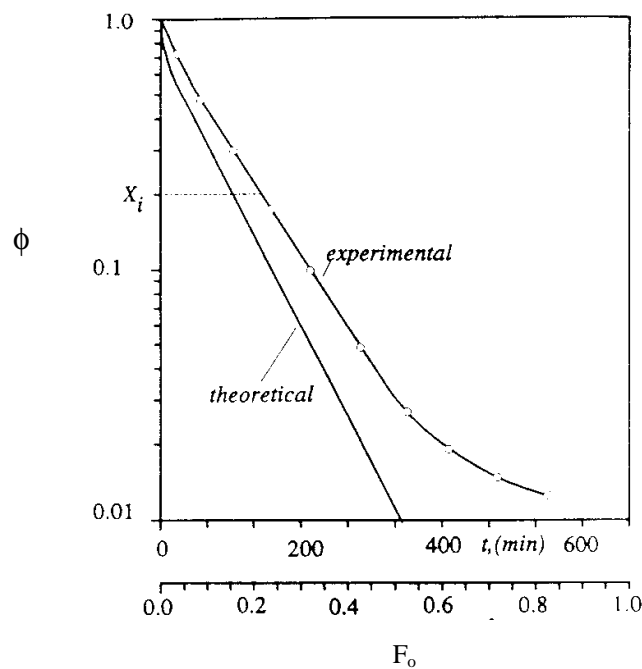


Figure 1.6.12 Simplified method. Example for the evaluation of variable moisture diffusivity (Zozgas *et al.*, 1994)

By comparing the slopes of the two curves at a specified moisture ratio, Φ_i , diffusivity is evaluated from the following equation:

$$D_i = \left[\frac{\left(\frac{d\Phi}{d\tau} \right)_{\text{exp}}}{\left(\frac{d\Phi}{d\tau} \right)_{\text{the}}} \right] R^2 \quad 1.6.26$$

The slopes of experimental and theoretical curves can be determined by numerical differentiation. Since there is a moisture content, X_i , which corresponds to the specified ratio, Φ_i , D can be found as a function of moisture content, by repeatedly applying equation (1.6.26) over the range of Φ . Examples of using the method of slopes for variable moisture diffusivity, can be found for starch gels (Karathanos *et al.*, 1990).

This method is simple and easy to use for routine engineering calculations, although it must bear in mind that the analytical solution applied considers moisture diffusivity and thickness of the slab to be constant. The diffusivity as a function of moisture content can be best approximated by numerical methods. This solution may also incorporate shrinkage effects.

This method is also very much dependent on the length of the sample.

Regular Regime Method

The regular regime method is based on the experimental measurement of the regular regime curve, which is the drying curve when it becomes independent of the initial concentration profile. Using this method, the concentration- dependent diffusivity can be calculated from one experiment. (Marinos-Kouris and Maroulis, 1995)

There is the existence of a time period in which the influence of the initial moisture distribution, within a specimen undergoing unsteady state diffusion, can be neglected. The diffusion equation is solved numerically for the regular regime period of an isothermal diffusion process. Various geometries are used at various types of diffusivity moisture dependence. The shrinkage is also considered.

Regular regime method is rather complicated and needs successive interpolations and differentiations of the experimental drying data. The relative error is less than 5%. The method can be applied for relatively low moisture contents (1.5 kg/kg d.b. or less).

Examples of using this method for foodstuff are reported by Luyben *et al.* (1980) and Tong and Lund (1990).

Numerical solution-regression analysis method

The regression analysis method can be considered as a generalization of the other two types of methods. It can estimate simultaneously some additional transport properties (Marinos-Kouris and Maroulis, 1995).

Numerical solutions can predict figures with amazing accuracy and speed, but they will never predict the appropriate models. These must be guessed, and statistically justified by the researcher. A numerical approach may need a deeper understanding of the drying phenomena than an analytical one would demand. The suggested procedure of this method could be summarised as follows.

First a set of the governing partial differential equations is created. The geometry and particular boundary conditions must be taken into account. Diffusivity may be introduced into the model as a parametric model of local moisture content, temperature, or any other desirable property (e.g. porosity)

After making a first guess for the values of the parameters introduced by the model, the set of equations is evaluated numerically. The computed values are compared to the experimental ones by non-linear regression analysis. If the criterion of the least sum of squares is not satisfied, a new guess of the model parameters is fed back to the numerical calculation. Procedure is iterative and continues until a final convergence to the desired statistical criterion is accepted. Finally, a statistical analysis of calculated and experimental data must be performed.

The method of numerical evaluation used is the finite difference method with fully explicit or implicit Crank-Nikolson schemes, or finite elements, or control volumes. Several studies have been done using numerical methods (Mulet *et al.*, 1989). Zogzas *et al.* (1994) reviewed a list of references that use these methods.

Most of the diffusivity estimation methods are based on Fick's law of diffusion, but there are significant differences in the way of applying these laws on experimental data as well as in the kind of experiments used. Some researchers use the analytical solution of second Fick's law, while others prefer the numerical solutions pertinent to the particular conditions of their experiments. Several statistical data evaluation methods are used as well.

Therefore, it exists no standard method of evaluating the moisture diffusivity.

In the studies carried out in meat products, different methods have been used: sorption kinetics, concentration-distance curves (c/d curves), drying technique, and NMR methods (Table 1.6.1).

Table 1.6.1 Studies on diffusivity in meat products

| Meat product | Temp. (°C) | Water Content (kg/kg dm) | $D_e \times 10^{-11}$ (m ² /s) | Method | Reference |
|--|---------------|-----------------------------|--|-----------|--------------------------------------|
| Beef | 30 | - | 1.0 | Sorption | Saravacos and Stinchfield, 1965 |
| Pepperoni | 12 | - | 4.7-5.7 | Drying | Palumbo <i>et al.</i> , 1977 |
| Freeze dried Beef | 25 | 0.13 | 3.1 | Sorption | Lomauro <i>et al.</i> , 1985 |
| Minced Beef | 30-120 | 0.3-1.8 | 5.0-53.0 | Drying | Motarjemi, 1988 |
| Minced Beef | 5-30 | 2.85 | 0.9-7.2 | d/c curve | Motarjemi, 1988 |
| Sobrasada | 10-16 | - | 2.9-5.4 | Drying | Mulet <i>et al.</i> , 1992 |
| Pork lean | 10-30 | 0.4-1.0 | 1.1-2.0 | Drying | Palmia <i>et al.</i> , 1993 |
| Pork ham | 13 | | | NMR | Ruiz-Cabrera <i>et al.</i> , 1998 |
| Salami | 10-20 | 0.40-0.45 | 0.03-0.37 | Drying | Diaferia <i>et al.</i> , 1998 |
| Dry cured ham (<i>Semimembranosus muscle</i>) | 19 | 0.5 | 3.43 | Drying | Malet, 1999 |

The D_e results of the different studies obtained in meat products (Table 1.6.1) show a wide range of estimated D_e values, which are supposedly due to the different determination methods, products, initial and boundary conditions (mass transfer coefficient, shrinkage), considering or not the water content dependence among others.

Radford (1976) reported an equation of D_e (m^2/s) in sheep meat that considered the effect of temperature:

$$D_e = 1.1 \cdot 10^{-6} \exp\left(\frac{-2300}{T}\right) \quad 1.6.27$$

1.6.3. Factors affecting water diffusivity

1.6.3.1. Temperature

The dependence of the diffusivity on temperature is generally described by the Arrhenius equation as follows:

$$D_e = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad 1.6.28$$

where D_e is the effective diffusivity (m^2/s), E_a is the activation energy (J/mol), D_0 is a pre-exponential factor (m^2/s), R is the gas constant (8.31441 J/mol K) and T is the absolute temperature (K). One trend that should be noted is that activation energy is inversely related to moisture content (Okos *et al.*, 1992). This can be explained by the increase of the binding strength between the water and the meat at decreasing moisture content. Palmia *et al.* (1993) in pork lean shows that the activation energy decreases from 28 to 22 kJ/mol when water content increases from 0.4 to 0.8 kg/kg (dm).

Temperature is also included in Stokes-Einstein relation (equation 1.6.29) for diffusion of low concentration solutes in liquids. The equation also considers the effect of viscosity. Any factor altering the viscosity of the fluid will affect the diffusion of the solute in the liquid.

$$D = \frac{kT}{6\pi\eta r}$$

1.6.29

where r is the radius of the diffusing particle (m), η is the viscosity (Pa s) and k is the Boltzmann constant ($13.8062 \cdot 10^{-24}$ J/K).

1.6.3.2. Heat of sorption and activation energy

Some comments should be made to the terms called heat of sorption and activation energy, which are used in modeling of sorption isotherms and in modeling of drying kinetics respectively.

On the one hand, heat of sorption (Q_s) of water, called also isosteric heat and binding energy in some occasions, is used in Clausius-Clapeyron equation. This equation describes the effect of temperature on vapour pressure ratio or water activity. Q_s can be determined by differential scanning calorimetry (Paeaeckkoenen and Plit, 1991). Q_s is defined as the difference between the total heat of sorption (ΔH) of water and its latent heat of condensation (ΔH_v): $\Delta H = Q_s + \Delta H_v$. For most food material Q_s is positive since water readily adsorbs onto the food. For hydrophobic materials (e.g. peanut oil), heat of sorption can be negative. Q_s is higher at lower moisture content as well as at lower temperatures. Also the heat of sorption tends to zero at high moisture contents since water eventually behaves as free water. Therefore at high moisture levels D_e is independent of moisture content. Q_s is related to the equilibrium state.

In the other hand, the activation energy (E_a) is used to describe the dependence of the diffusivity on temperature. According to the energy levels involved in a reaction and to the collision theory of reactive molecules, enough energy must be generated to provide the necessary activation energy to be able to develop the reaction (Figure 1.6.13).

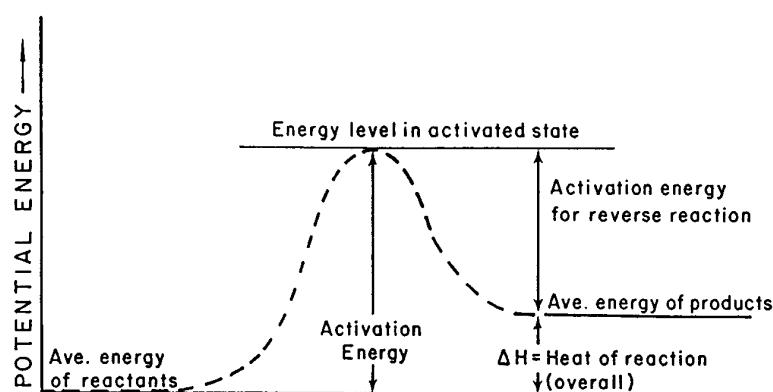


Figure 1.6.13 Representation of potential energy levels during the process of a given endothermic reaction (Villota and Hawkes, 1992).

E_a will not itself provide any idea of the reactivity of a given system, only information on temperature dependence of the reaction. E_a is also inversely related to moisture content. It may also depend on the type and the amount of solutes in water. The dependence between the E_a and the moisture content of various agricultural products has been expressed in some occasions as exponential relationship (Ben Mabrouk and Belghith, 1995). For meat, Motarjemi (1988) found E_a values of 34 to 54 kJ/mol, depending on the type of meat.

D_0 depends only on the pore structure of the food material (Okos *et al.*, 1992) and therefore can be considered as a structure parameter. In kinetics reaction, it is considered a frequency or collision factor.

1.6.3.3. Composition of meat

The composition of meat and meat products may affect their water diffusivity properties.

1.6.3.3.1. Water Content

D_e is found to be smaller at lower moisture contents, increasing with moisture, and eventually becoming constant at sufficiently high moistures (Okos *et al.*, 1992), although for less hydrophilic materials (e.g. polymers) the moisture diffusivity decreases by increasing water content, and in other occasions D_e can appear to be independent of the concentration (e.g. hydrophobic polyolefins) (Marinos-Kouris and Maroulis, 1994). Several relationships

that describe simultaneous dependence of the diffusivity upon temperature and moisture have been reported (Table 1.6.2).

Table 1.6.2 Effect on water content and temperature on diffusivity (Marinos-Kouris and Maroulis, 1994)

| Materials of application | Equation | No. of parameters |
|--|--|-------------------|
| Apple, carrot, starch | $D(X, T) = a_0 \exp(a_1 X) \exp(-a_2/T)$ | 3 |
| Bread, biscuit, muffin | $D(X, T) = a_0 \exp\left(\sum_{i=1}^3 a_i X^i\right) \exp(-a_2/T)$ | 5 |
| Polyvinylalcohol | $D(X, T) = a_0 \exp\left(\sum_{i=1}^{10} a_i X^i\right) \exp(-a_2/T)$ | 12 |
| Vegetables | $D(X, T) = a_0 \exp(-a_1/X) \exp(-a_2/T)$ | 3 |
| Glucose, coffee extract, skim milk, apple, potato, animal feed | $D(X, T) = a_0 \exp[-a_1(1/T - 1/a_2)]$ $a_1 = a_{10} + a_{11} \exp(-a_{12} X)$ | 5 |
| Silica gel | $D(X, T) = a_0 \exp(-a_1/T)$ $a_1 = a_{10} + a_{11} X$ | 3 |
| Clay brick, burned clay, pumice concrete | $D(X, T) = a_0 X^{a_1} T^{a_2}$ | 3 |
| Corn | $D(X, T) = a_0 \exp(a_1 X) \exp(-a_2/T)$ $a_1 = a_{11} T + a_{10}$ | 4 |
| Rough rice | $D(X, T) = a_1 \exp(a_2 X)$ $a_1 = a_{10} \exp(a_{11} T),$ $a_2 = a_{20} \exp(a_{21} T + a_{22} T^2)$ | 5 |
| Wheat | $D(X, T) = a_0 + a_1 X + a_2 X^2$ $a_0 = a_{01} \exp(a_{02} T),$ $a_1 = a_{11} \exp(a_{12} T),$ $a_2 = a_{21} \exp(a_{22} T)$ | 6 |
| Semolina, extruded | $D(X, T) = a_0 \exp(-a_1/T) \frac{a_2 \exp(-a_3/T)}{1 + a_2 \exp(-a_3/T)}$ $a_3 = F(a_{3i}, X)$ | >4 |
| Porous starch | $D(X, T) = (a_0 + a_1 X^{a_2}) \exp(-a_3/T)$ $a_0 = F(\epsilon),$ | >5 |

D, moisture; X, material moisture content; T, temperature; a_i , constants; ϵ = porosity

Some of these equations consider the pre-exponential factor of the Arrhenius equation as a function of material moisture content or considering the activation energy for diffusion as a function of material moisture content. Other equations are not based on the Arrhenius form,

they are empirical. Equation for extruded semolina is more sophisticated as it considers different diffusivities of bound and free water and introduces the functional dependence of material moisture content on the heat of sorption of desorption. These equations resulted from fitting experimental data, and the equations description by three parameters only in some occasion makes simple the dependence of diffusivity upon the material moisture content and temperature. Other authors like Okos *et al.* (1992), Zogzas *et al.* (1996) and Pakowski (1998) have also reviewed equations that consider the effect of temperature and water content on D_e .

Ruiz-Cabrera *et al.* (1998) found that the water content of meat or meat product affects the D_e . In his study D_e increases from $3.0 \cdot 10^{-11}$ to $70 \cdot 10^{-11}$ when water content increases from 1.3 to 2.8 kg/kg (d.b.). Besides, Motarjemi (1988) and Palmia *et al.* (1993) did not observe a clear effect on the water content in the range from 0.3 to 1.8 kg/kg d.m.

1.6.3.3.2. Salt content

Although meat has a small amount of salt, the importance of this solute is due to the fact that many of the dried meat products are salted and cured. Some studies shows that NaCl content modifies the water diffusivity in pork meat, for instance, Palmia *et al.* (1993) observed that D_e decreased when NaCl content increased, mostly at high temperatures and at low water content.

Other types of solutes and additives may be added to meat, like the curing salts (nitrate and nitrite, potassium chloride, etc) but no studies have come out relating those solutes and the effective water diffusivity in meat.

Diffusion of salt in meat

Several studies have been developed to obtain the diffusion coefficient of NaCl into meat (Wood, 1966; Andújar and Tarrazo, 1981; Fox, 1980; Mittal *et al.*, 1982; González-Méndez *et al.*, 1983; Djelveh and Gros, 1988; Froystein *et al.*, 1989; Palmia and Bolla, 1991).

For a given tissue the rate of diffusion is largely governed by the concentration gradient and the temperature.

The effect of temperature is not explained by the Arrhenius-type relationship in the study developed by Wood (1966), confirming that E_a is not the sole factor governing the temperature dependence of diffusion. It may include effects due to osmosis and protein denaturation and possibly diffusion of other components of the meat caused by the salt concentration gradient. On the contrary, Djelveh and Gros (1988) could explain the temperature effect by the arrhenius-type law. They obtained an E_a of 19 to 26 kJ/mol. They also state that the diffusion coefficient increase may be due to the decrease of water viscosity with temperature. Fox (1980), Gonzalez-Mendez (1983) and Gros *et al.* (1984) relate the effect of temperature on diffusion through the viscosity of the medium by the Stokes-Einstein relationship (equation 1.6.30).

$$D_{T1} = D_{T2} \frac{T_1}{T_2} \frac{\eta_{T2}}{\eta_{T1}} \quad 1.6.30$$

where D is the coefficient of diffusion (m^2/s), T is temperature ($^{\circ}\text{C}$) and η is the diffusion medium viscosity (Pa s).

Brine concentration effect is not clear in the study of Djelveh and Gros (1988). Wood (1966) indicates that the diffusion coefficient does not depend on the brine concentration and therefore it means that the rate of salt uptake by cork immersed in brine is predominantly a concentration rather than an activity controlled process. He reported from other authors that immediately after death, the electrical resistance is greater across the muscle fibres than along them. Later, however, when the pH has dropped to 5.7 the muscles become more conducting and the relative difference to the direction of the muscle fibres almost disappears. Although Gonzalez-Mendez *et al.* (1983) did not find significative differences of salt diffusivity versus pH. Initially, the meat has a close microstructure, where fluid is contained within the muscle fibres. The production of lactic acid causes the fibres become filled with fluid.

Wood (1966) and Djelveh and Gros (1988) conclude in their experiences that the tissues studied were isotropic to salt diffusion. Fox (1980) finds no differences between the muscle types.

González-Méndez (1983) and Gros *et al.* (1984) find that diffusion is faster in frozen and thawed meat than in fresh meat, and what is more, it is influenced by the rate of the freezing and/or the thawing steps. On the contrary, Wood (1966) did not find significantly differences between frozen and non frozen meat. The same author studied the diffusion of salt into subcutaneous back fat, which value obtained was $7.7 \cdot 10^{-12} \text{ m}^2/\text{s}$, concluding that the different fat content into the meat may affect to the salt diffusion into meat. This is confirmed by Froystein *et al.* (1989) which study of cured hams X-ray tomography, reflects that the subcutaneous fat layer represents an effective barrier to salt uptake.

Table 1.6.3 Effective diffusion coefficients of different ions in pork tissues.

| Type of tissue | $D_{e,\text{NaCl}} (\times 10^{-10})$ m^2/s | Temp. (°C) | Solute | Salting process | Reference |
|----------------|--|---------------|---------------|-----------------|--------------------------------------|
| Raw pork meat | 1.20 | -2 | Cl^- | Brine solution | Wood (1966) |
| | 330.0 | 2 to 4 | Cl^- | Solid salt | Andujar and Tarrazo (1981) |
| | 2.25 | 1 to 4 | Cl^- | Solid salt | Palmia and Bolla (1991) |
| | 2.10 | 2 | Cl^- | Solid salt | Gonzalez-Mendez <i>et al.</i> (1983) |
| | 1.80 | 3.2 | Cl^- | Brine solution | Djekveh and Gros (1988) |
| | 2.20 | 5 | Cl^- | Brine solution | Fox (1980) |
| Pork sausage | 8.5 to 13.6 | 55 | Cl^- | | Mittal <i>et al.</i> (1982) |
| Pork sausage | 8.8 to 13.8 | 55 | Na^+ | | Mittal <i>et al.</i> (1982) |
| Pork back fat | 0.077 | -2 | Cl^- | | Wood (1966) |
| | 0.28 | 5 | Cl^- | Brine solution | Fox (1980) |

Most of the studies done in meat NaCl diffusion were made by evaluating the chloride ion (Cl^-) content. Mittal *et al.* (1982) studied the mobility of sodium and chloride ions during thermal processing of meat emulsion. They concluded that the diffusion coefficient of Cl^- is greater by 0.8 to 19.5% than the diffusion coefficient of Na^+ , with values between 5.8 to

$13.8 \cdot 10^{-10} \text{ m}^2/\text{s}$. They also found that these diffusion coefficients are 40 to 60% lower in meat than the diffusion coefficients of NaCl in bulk water for the same concentrations and temperatures. The diffusion coefficients of Na^+ and Cl^- are not the same for similar processing conditions and formulations. The values of activation energy were 13.3 and 14.8 kJ/mol Na^+ and Cl^- respectively.

They also stated that Na^+ and Cl^- are never constant at the beginning of his thermal process until the concentrations equilibrates during product ageing. The nonuniform distribution of these ions may effect the water-holding capacity of the meat.

In dilute bulk solution, the size of the ion, its degree of hydration, and the normal fluidity of water determine its diffusivity. Additional factors tending to reduce its apparent diffusivity in meat are the reduction of the cross sectional area available for the flow. The modified water fluidity presumably decreases in association with the components and in clusters, and the tortuosity of the flow path and electrostatic restrictions. The anions and cations must move with the same velocity (in a binary electrolyte), to maintain electrical neutrality so that the faster moving ion is slowed down and the slower moving ion is speeded up, however, in this system there are other ions moving, and the biochemical changes in proteins may also change their movements. Therefore, the other ions will influence the net effective diffusion rate to maintain electrical neutrality. The cations may participate in the diffusive movement by surface diffusion while they are absorbed on solid mass. Anions are either not absorbed or, when they are, the absorption forces are usually so strong and the absorption sites are so far apart that practically no exchange takes place between anion absorption sites without the anions going through the energy level characteristic in the equilibrium solution. Cation exchange sites are often sufficiently close together that the weakly held cations can trade positions without attaining the high energies characteristic in the equilibrium solution (Mittal *et al.*, 1982).

The moisture gradient is believed to be cause up to 40% of the Na^+ mobility (Mittal *et al.*, 1982).

1.6.3.3.3. Fat and protein

Only studies in minced meat considering the effect of fat content have been found. Palumbo *et al.* (1977) observed in pepperoni an increase of D_e from $4.7 \cdot 10^{-11} \text{ m}^2/\text{s}$ to $5.6 \cdot 10^{-11}$ when fat content was reduced from 25.1% to 17.4%, although when fat content was reduced to 13.3%, D_e did not change significantly. Mulet *et al.* (1992) in sobrassada also showed that protein content (considered complementary to fat content) affected D_e , which increased from $2.86 \cdot 10^{-11}$ to $5.19 \cdot 10^{-11} \text{ m}^2/\text{s}$ when protein content increased from 14.8 to 33.6% (dry basis). There have been found no studies of meat at lower fat content and in whole pieces of meat with intramuscular lipids.

1.6.3.4. pH

Many studies show that the water holding capacity of meat depends on its pH (section 1.3.3.2.2.), although no references have been found studying the effect of pH on D_e .

1.6.3.5. Structure

Literature on the structural influences on D_e are rare. Godsálve *et al.* (1977) and Thorvaldsson and Skjöldbrand (1996) studied the influence of meat fibre direction on the heat transfer and water loss rate of meat. Both concluded that water and heat transport are faster in parallel to the meat fibres than perpendicularly to them. They attributed this difference to the path length, where the water molecules that move perpendicular to the fibre direction, probably have to move around the fibres, which involves a longer path. Godsálve *et al.* (1977) in their study found that perpendicular fiber orientation with respect to airflow direction, gave a higher rate of water loss in the early stages of cooking. They also reported from other studies that fiber structure is an important influence on heat and mass transfer in frozen dried beef.

1.6.3.5.1. Shrinkage

Most of the shrinkage occurs in the early drying stages, where 40 to 50% shrinkage may occur (Okos *et al.*, 1992).

Luyben *et al.* (1980) observed different types of shrinking behaviour (Figure 1.6.14). He measured the shrinkage for various foods. Among them, shrinking of animal food could be described by type I or type II behaviour (Figure 1.6.14). Glucose showed a type II behaviour. Apple tissue exhibited type IV behaviour and potato tissue type V. No reference has been found for shrinkage of meat, although we are aware if different meat products may show different types of shrinking behaviour, for instance, dry sausages could be considered as type IV.

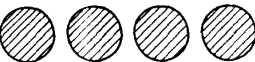
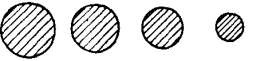
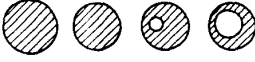
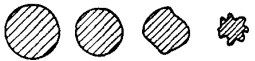
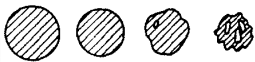
| TYPE | SHRINKING BEHAVIOUR | DESCRIPTION |
|------|---|---|
| I |  | no-shrink |
| II |  | perfect homoge- neous shrink |
| III |  | perf. hom. shrink - first external - later internal |
| IV |  | hom. shrink - first perfect - later rimpling (const. surf. area) |
| V |  | combination of III & IV |

Figure 1.6.14 Schematic representation of the various types of shrinking behaviour observed (Luyben *et al.*, 1980).

The perfect homogeneous shrinkage is the most common assumption when the effect of shrinking is considered into the models of D_e . This assumption however is not correct.

Gekas *et al.* (1987) differentiated between isotropic and anisotropic shrinkage. Isotropic shrinkage is when the dimensions of the product change proportionally equal in all directions, therefore an isotropic three-dimensional volume changes. That gives the following relationship:

$$\frac{1}{l'} = \left(\frac{V}{V'} \right)^{\frac{1}{n}}$$

1.6.31

where l' , V' are the dimensions after shrinkage and n represents the dimension of the shrinkage. $n=1$ for monodimensional shrinkage and $n=3$ for isotropic three-dimensional shrinkage.

Crank (1975), considering the diffusion of a substance A through a medium B, proposed to use a unit of length ζ_B so that the unit ζ_B contains the unit basic volume per unit area. By basic volume is meant the volume of the product in the absence of moisture. The co-ordinate system is changing in the direction of the moisture transfer. The diffusion coefficient obtained, with this frame of reference, is denoted by D_A^B where A is the diffusing substance and B the medium. Therefore, if the thickness of dry matter is used for the obtention of diffusivity in the analytical solution of second Fick's law, D_e is converted to D_A^B . This diffusion coefficient can be converted to the volume fixed diffusion coefficient D^V (equation 1.6.32).

$$D_A^B = D^V \left(\frac{\text{volume of dry matter}}{\text{total actual volume}} \right)^{\frac{2}{3}}$$

1.6.32

Fish (1958) used the mass of the dry matter as the unit of volume. The unit of the length is accordingly $(\text{mass})^{1/3}$. Another approach also used in the literature is, to calculate first a reference diffusion coefficient, D_{ref} , by using the initial thickness of the product in the analytical solution of 2nd Fick's law. The diffusion coefficient obtained can thereafter be corrected for the shrinkage by applying:

$$D_e = D_{\text{ref}} \left(\frac{\text{actual thickness}}{\text{initial thickness}} \right)^2$$

1.6.33

This approach is similar to the one used by Crank, except for the calculation of the reference diffusion coefficient where the initial thickness is used instead of the final thickness.

Several studies have found a linear relationship between the size and the moisture content. Sjöholm and Gekas (1995) reported a linear relationship between volume and water content in the drying of apple. Also Raghavan *et al.* (1995) during convective drying of grapes showed a linear volume change with water content. Motarjemi (1988) also found that thickness of meat decreased linearly with moisture content. Ben Mabrouk and Belghith (1995) also described a linear evolution of carrot pieces thickness versus the moisture content. This author, among others, by using the lagrangean coordinates (ζ , t) writes the 2nd Fick's law to semi-infinite media or slabs considering the shrinkage effect in the following manner,

$$\frac{\partial X}{\partial \tau} = \frac{\partial}{\partial \zeta} \left(\left[\frac{D(X,T)}{(1 + \epsilon X)^2} \right] \frac{\partial X}{\partial \zeta} \right) \quad 1.6.34$$

where X is the water content (kg H₂O/kg d.m.) and ϵ is the shrinking coefficient.

1.6.3.6. Air Relative Humidity

The air relative humidity and the water content at equilibrium on the surface of the product gives the driving force for the drying process. It is a parameter included in all drying equations.

D_e should not be dependent on the air relative humidity, because it is a parameter included in the drying models, unless it has an effect on the surface of the product allowing some structural or microbiological changes that may affect to the water content at equilibrium on the surface as well as the mass transfer.

No references have been found considering such effect.

1.6.3.7. Air Pressure and Air Components

Air pressure should not affect D_e in meat since solid and liquid phase that form meat are considered not to be much compressible and their properties do not depend on pressure.

Besides pressure will affect diffusivity of water vapour in the gas phase according to the following equation,

$$D = 21.6 \cdot 10^{-6} \left(\frac{T}{T_0} \right)^{1.75} \left(\frac{P_0}{P} \right) \quad 1.6.35$$

where T is the actual temperature (K), T_0 is the reference temperature (273.15 K), P is the actual pressure P_0 is the reference pressure (101.325 Pa) and D is the diffusion of water vapour in the air.

It will also change viscosity and density of the air, therefore the external mass transfer (k_y) will be affected. From calculation, simulating the meat as a cylinder of 0.2 m in diameter, at 20 °C, relative humidity of 60% and an air velocity of 0.1 m/s, it is possible to see the changes in k_y (Table 1.6.4). Data for gases other than air are also included.

Table 1.6.4 Mass transfer depending on pressure and gas components (Pakowski, 1998).

| Pressure Pa | Absolute air humidity kg H ₂ O/kg d.a. | k_y Air kg/m ² s | k_y 100 % N ₂ kg/m ² s | k_y 100 % CO ₂ kg/m ² s |
|----------------|---|-------------------------------------|--|---|
| 50000 | 0.00179 | 0.00171 | 0.00166 | 0.00243 |
| 101325 | 0.00876 | 0.00241 | 0.00234 | 0.00343 |
| 151000 | 0.00586 | 0.00292 | 0.00283 | 0.00416 |
| 202000 | 0.00437 | 0.00335 | 0.00325 | 0.00489 |

One has to remember that the change of pressure will also affect the driving force due to the change of air relative humidity.

Removal of oxygen of the air may have small effects on k_y depending of the gas component (Table 1.6.4) because the differences on molar masses.

1.6.3.8. Other factors

Other factors that may affect the D_e may be the enzymatic and microbiological changes in the meat, as well as the crust formation. Enzymatic reactions may change the internal properties of the meat, while the micro-organisms may influence also the surface of the meat, changing the equilibrium moisture content of the meat at the surface.

Crust formation may be due to the fact that the external part of the meat dries quicker than the internal, and therefore the external part of the meat changes becoming harder. The crust formation may also be due to the growing of micro-organisms on the surface of the meat, which may lead the same effect as explained in the previous paragraph.

The importance of these factors have been reported in other studies (Poma, 1987; Daudin *et al.*, 1992).