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Predictive Models of Migration for Legislative Purposes

by

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Description of work: To analyse by means of mathematical and physical models the migration of additives and residual small chemical species from plastics into foods with which they are in contact. It is hoped that a limited number of models will cover the behaviour of most cases of practical interest leading to a basis for legislation.

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MAFF PROJECT 584
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P.C. Chatwin and L.L. Katan

TECHNICAL SUMMARY

The principal aims of the report written on termination of this project are (i) to summarize the most important mathematical models of migration that have so far been used, (ii) to provide a critical commentary on these models, and (iii) to assess what further work is necessary before mathematical models can be used to their full potential in framing, and monitoring, legislation on migration that is both scientifically sensible and practical.

Chapter One of the report summarizes the principal classes of migration behaviour, and the classification adopted is close, in physical terms, to that adopted by Katan in 1971; however the precise definition of the classes is given in terms of mathematical models.

The next Chapter deals first with the units and notation used throughout the report. Then some relatively simple models are presented and used to highlight several features that recur throughout the report and which have crucial influences on the success, in both practical and scientific terms, of any mathematical model of migration. The first of these is that systematic use of non-dimensional quantities in data analysis and presentation, and in mathematical predictions of migration, should be routine procedure; unfortunately it is not. The second feature is that the geometry of the food/package system is among its most important properties in the sense that changes in the shape or size of the system can cause large changes in the amount of migration; this point has largely been ignored in the past. All workers are agreed on the final feature which is the importance of correctly modelling the boundary and initial conditions that apply to the migrant concentration. The description of mathematical models, and commentary on them, are the subjects of Chapter Three. This begins with a discussion of well-known formulae that give the maximum possible concentration of the migrant in the food. The rest of this Chapter deals with models that predict how the mass of migrant in the food varies with time.

Most of the models in the literature apply to Class II systems which, roughly speaking, are those where the food may influence migration but does not have a controlling influence. All the models assume that migration is a diffusion process, and there is a substantial account in this Chapter of the governing equations for such a process (and of useful approximations to them). In view of the importance of geometry, this account gives the equations in forms which apply in allgeometries and it also emphasizes the need for further experiments, particularly on conditions during migration at the interface between the food and the plastic. There then follows a critical summary of the solutions of these equations that have been used in migration work. All these solutions apply only in one-dimensional geometry and may be reasonably accurate predictors of what occurs in most migration test cells; however it is unlikely that they are quantitatively applicable to most real-life food/package systems although they do enhance understanding of the relative importance of the various physical processes

that influence the quantity of migration, and this is valuable. This section of the report also presents a new solution which includes all the earlier ones as special cases.

Class III systems are considered next; in such systems migration is controlled by the food (often as a result of the food penetrating the plastic). Although such systems are believed to form the majority there has been less effort on their mathematical modelling than on that of Class II systems. All known models are reviewed; the prime conclusion of this is that much more work needs to be done, not least on comparison with data. The Chapter concludes with a discussion of some complications, including chemical change and inherent variability. One conclusion of this discussion is that there should be more consideration than hitherto of modelling migration as a stochastic process.

The first three Chapters emphasize (but not exclusively) the use of mathematical models in scientific research. Their use in drafting legislation and in designing food/package systems that meet legal standards is the major concern of Chapter Four, the final Chapter of the report. It is noted that legislative standards that are expressed in terms of total transfer per unit area of the package surface, but with no reference to the package geometry, should not be accepted since they do not control the concentration of migrant which can be made arbitrarily high. The report endorses standards expressed in terms of the concentration itself (expressed as a mass-ratio) and supports the use of decision-trees. However it is concluded that there is inadequate knowledge at present for all branches in such a tree to be specified reliably.

We believe that it is very likely that work satisfying the requirements established in the report will lead to a small group of mathematical models covering most real situations, giving results reliable to at least an order of magnitude. This should be perfectly adequate, when combined with toxicity data of similar, or greater variability, to utilise as a basis for legislation.

CHAPTER ONE: BACKGROUND

§1.1 Introduction

Plastics used in food packaging comprise a range of molecular species from very high to very low molecular weights. It is generally accepted that the higher molecular weight species (macromolecules) are so immobile and insoluble that their migration into the food is so low that it can be ignored, i.e. the migration of such molecules is, in practical terms, zero. The remaining species can, potentially at least, migrate. Examples of such substances are residual monomers or processing reagents, additives such as antioxidants or plasticisers, colouring materials and decomposition or reaction products formed in processing or work-up. Potential migrants may or may not have any vapour pressure; in this regard it is important to recognise the wide range of temperatures that packaged food can be exposed to from the time at which containment occurs until the package is finally removed or the food within it has been totally consumed. Throughout this report, the term contaminant* will be used to denote a single potential migrant.

Some contaminants have undesirable effects on the consumer if they are present in sufficient quantity in food. Such effects range from unpleasant (but harmless) taste and smell to the ingestion of dangerous materials like heavy metals or VCM. Inevitably therefore legislators wish to lay down standards which control both the manufactured plastic packaging and its migration properties when it is in contact with food. Considerable legislation is already in force and widespread consultation is taking place on new draft proposals which, if adopted, are intended to finalise the legislation. However it is obviously desirable that such legislation, designed to protect the consumer, should be as soundly based, scientifically speaking, as possible.

There are several, more or less distinct, themes to this scientific research, and this report is a contribution to one of these, namely the use of mathematical and physical models to describe and predict migration.

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*Use of this term should not cause confusion even though, perhaps, ordinary English usage would require it to be used only after migration has occurred.

§1.2 Classification of migration behaviour

The use of mathematical models is potentially attractive because it may be that a single model* can describe, to acceptable practical accuracy, what occurs in many apparently different situations. If so, the need for costly and time-consuming chemical analyses of innumerable special cases will be significantly reduced; however the need for such analyses can never disappear since we are concerned with science and the real world. Mathematical models must be validated and tested against data, and physical properties such as diffusion and partition coefficients will have to be determined for new materials.

An additional advantage of mathematical models is that they will permit the rigorous classification and quantification of migration behaviour. It is fortunate that, in qualitative terms, there appear to be only a moderate number of types of such behaviour; the summary below is based on the treatment in Katan (1971) - see also Briston and Katan (1974) - and further relevant discussion has been given by many authors, including Figge (1980), Crosby (1981) and Shepherd (1982). Class I systems are those in which essentially no migration takes place, and possible examples include cases where the contaminant combines chemically with the polymer that forms the basic plastic, and those involving some hard and/or dry foods like salt and sugar. In considering this class, however, it must be remembered that the surface of the packaging may contain some residual toxic material from the manufacturing process and abrasion may occur. Systems in Class II were defined to be those where the migration of contaminants occurs from the plastic whether or not it is in contact with food. Although the food may accelerate migration, it does not have a controlling influence. Katan (1971) - see Briston and Katan (1974, pps. 145-149) - further subdivides this class; for the present it is sufficient to note that it includes most monomers, water in all plastics

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*The concept of a mathematical model is difficult to define concisely or precisely. Roughly speaking, a model of a migration process involves a set of hypotheses about the underlying physics and chemistry which, when expressed in mathematical terms, enable quantitative deductions to be made about quantities like the concentration of a contaminant in a food and its dependence on time. These ideas should become clearer from later work in this report, especially in Chapter Three.

and some additives (such as antistatic agents and colourants). For the purposes of the present report, the above definition will be slightly modified to include all cases where any penetration of the plastic by the food has an insignificant effect on migration. Finally Class III, often referred to as leaching, includes all cases where migration is controlled by the food with the implication that it is negligible in the absence of food. An important group in this class is that in which the food penetrates the plastic, perhaps with a change in volume, and thereby enables substantial migration to occur. This class includes, for example, most additives in most plastics in contact with oily or fatty foods, or in hydrophilic plastics such as nylons in contact with aqueous foods. Useful as it is, the above classification is not rigid; for example, improvements in analytical techniques may result in a system previously in Class I being transferred to Class II. Furthermore, the classification is for a specific trio of food, polymer and contaminant. Since polymers normally contain many different contaminants when they are used to form plastic packaging, it is often true that a food/packaging system exhibits behaviour in all three classes.

§1.3 References

Briston, J.H. and Katan, L.L. 1974 "Plastics in Contact with Food", Food Trade Press Ltd., London. 466pp.

Crosby, N.T, 1981 "Food Packaging Materials. Aspects of Analysis and Migration of Contaminants", Applied Science Publishers Ltd., London. 190pp.

Figge, K. 1980 Migration of components from plastics-packaging materials into packed goods - test methods and diffusion models. Prog. Polym. Sci. **6**, 187-252.

Katan, L.L. 1971 Migration from packaging materials to foodstuffs: a new approach. Paper presented at a conference arranged by The Institute of Packaging, Eastbourne, 5/6 October 1971, 2.1 - 2.35.

Shepherd, M.J. 1982 Trace contamination of foods by migration from plastics packaging - a review. Food Chem. **8**, 129-145.

CHAPTER TWO: MATHEMATICAL AND PHYSICAL PRELIMINARIES

§2.1 Introduction

It has already been noted in Chapter One that legislation should be based on the results of scientific research. The main purpose of this report is to describe the role of the specific disciplines of physics and (especially) mathematics in this regard: thus the Description of Work in the project agreement includes the phrase: "To analyse by means of mathematical and physical models the migration of additives and residual small chemical species from plastics into foods with which they are in contact". At the outset it has to be said that hitherto, and with some notable exceptions, rather too much emphasis has been placed on research into the physical chemistry of migration processes. Many authors have not considered mathematical models and many others have quoted results from e.g. Crank (1979) but have either not subsequently used these results or have not used them efficiently. It is hoped that the outcomes of this report will include

(a) convincing readers that good mathematical models can be much more useful in studying migration than has been generally recognised;

(b) persuading those embarking on future research that success in this field requires full inter-disciplinary collaboration.

Although this chapter has the word "Preliminaries" in its title it is, nevertheless, very important since it exposes certain principles which not only underpin the remainder of the report but also, it is believed, are central to any sound future application of mathematical models to migration.

As far as possible, technical mathematics has been kept to a minimum so that the report will be as accessible to as wide a readership as possible. In any event, understanding the details of the formal mathematics *per se* is less important than sympathising with the underlying philosophy which is to unify, and to quantify, in a scientifically sensible way.

§2.2 Units and notation

The field of migration research has used many different units, as well as many different materials! Concentrations, for example, are expressed in p.p.m. (parts per million), percentages, mg/kg and mg/litre to name but a few; worse still, mongrel units like ing/square inch have been used to describe transfer. In accordance with the desirability for unity (as emphasized by Katan 1979) and with worldwide standard practice in physics, engineering and mathematics, the SI (Systeme International) system of units will be the primary one used throughout this report. This system is based on the fundamental units of metre (m), kilogram (kg) and second (s). Thus one milligram will normally be expressed as 10^{-6}kg, and an overall migration limit of 10mg/dm^2 as 10^{-3}kg/m^2 or - more commonly - as 10^{-3}kg m^{-2} . The standard unit of concentration used in this report will be kg m^{-3} (kilograms per cubic metre) since this can be unambiguously applied in all cases, unlike, for example, percentages, where it is unclear whether the percentage is by mass or by volume. Some states have, and the EEC proposes, a migration limit of 60mg/kg. For food with a density of 10^3kg m^{-3} (the density of water) this is a concentration of 6×10^{-2} kg m^{-3}, i.e. 0.06kg m^{-3}, and similar conversions can be made, if necessary, for foods with other densities. Note that in a later section - §2.4 - of this chapter, the consistent and widespread use of non-dimensional quantities will be strongly advocated. This means that many of the quantities will be pure numbers, i.e. units become irrelevant.

Table 1 summarizes the principal notation that will be used throughout this report. From time to time other notation will have to be introduced for specific purposes; on such occasions full definitions will be given. In addition to the entries in this table, standard mathematical notation will be used for common constants (e.g. π,e) and functions. One function that will often appear is the error function, abbreviated to erf, and defined by the equation

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\, du. \qquad (2.1)$$

The right-hand side of (2.1) involves an ordinary integral, and the factor $(2/\sqrt{\pi})$ is included for arithmetical convenience since, with the definition (2.1), $\operatorname{erf}\infty = 1$. Tables of the error function are readily available and its graph is sketched in Figure 1, together with that of the complementary

QUANTITY or PROPERTY	SYMBOLS	UNITS
Concentration of contaminant	C	Kg m^{-3}
Average concentration of contaminant	$\bar{c}$	Kg m^{-3}
Time	t	s
Cartesian coordinates	x,y,z	m
Radial coordinate	$r = (x^2 + y^2 + z^2)^{\frac{1}{2}}$	m
Mass	m or M	kg
Length	l or h or a	m
Volume	V	m^3
Area	A	m^2
Density	ρ	kg m^{-3}
Temperature	T	K
Diffusion coefficient	D	$m^2 s^{-1}$
Partition coefficient	γ	NONE
Non-dimensional quantities (as illustrated by the partition coefficient in the line above	Greek letters (e.g. α or г)	NONE

TABLE 1: List of the most common notation in the report.

error function erfc, defined by the equation

$$\operatorname{erfc} x = 1 - \operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du. \qquad (2.2)$$

A convenient reference for the properties of these functions is Abramowitz and Stegun (1965, Chapter 7) and a shorter account is given in Crank (1979, Table 2.1 on p.375, and elsewhere). It will be noted from Figure 1 that, like many functions relevant to migration, the curve with equation y = erf x

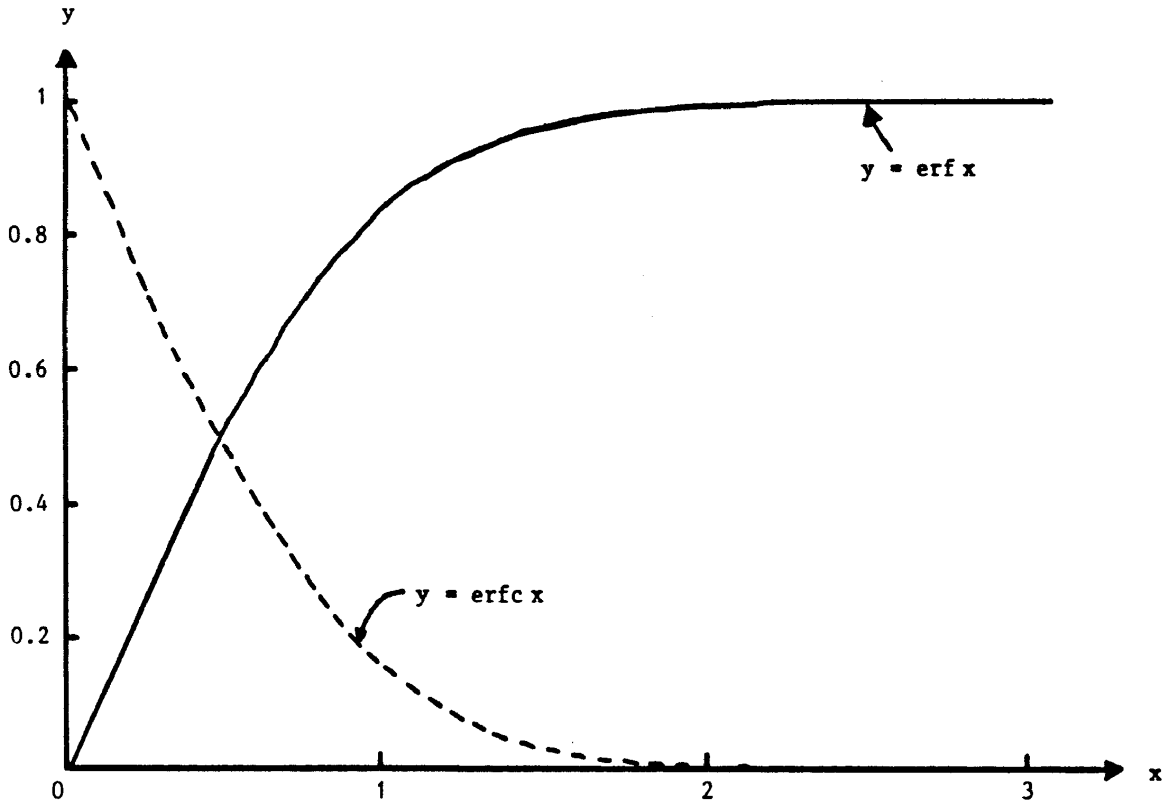

FIGURE 1 Graphs of y = erf x (equation 2.1) and y = erfc x (equation 2.2)

has an asymptote as x approaches infinity, in this case the line y = 1*.

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*Quite deliberately, the variable x has been used in (2.1) and (2.2) to denote the number at which erf and erfc are being evaluated, and it has a quite different meaning from that in Table 1 (where x denotes a Cartesian coordinate). This double use of one symbol to denote two unrelated quantities is unfortunately sometimes inevitable because of the limited number of symbols available; in this case of course both uses are entirely in accord with standard conventions but, in general, the use has to be deduced from context. Exactly the same situation occurs in ordinary English, e.g. "The band played well" and "I put an elastic band round the packet".

§2.3 A class of simple migration problems

Many of the general points to be made in the remainder of this chapter can be illustrated by considering the mathematical structure of a class of migration problems without, at this stage, enquiring about their relevance to real applications. This will be considered later. Figure 2 illustrates the geometry for the first problem. Plastic occupies the region $x > 0$ and food the region $-a < x < 0$. It will be supposed that the thickness of the plastic is irrelevant, i.e. it can be regarded for migration purposes as being of infinite thickness. Initially, at $t = 0$, a contaminant is present in the plastic at uniform concentration C_0. (Throughout this report the term "uniform" means "independent of position"; in this case - therefore - the initial concentration of contaminant in the plastic is the same, viz. C_0, everywhere in the plastic.) For $t > 0$ migration of contaminant takes place across the interface $x = 0$. Within the plastic, assume that transfer of contaminant takes place according to the standard constant-coefficient diffusion equation (Crank 1979)

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{2.3}$$

where D is the diffusion coefficient of the contaminant in the plastic and C is the concentration of contaminant. For $t > 0$, C is no longer uniform and, indeed, depends on both x and t; when this dependence requires emphasis, the notation $C(x,t)$ is used instead of C. For the present exercise, it will be assumed* that the diffusion coefficient of the contaminant in the food is so large (compared with D) that, for $t > 0$, the concentration of contaminant in the food is uniform. Its value will be denoted by C_*, where C_* depends on t (i.e. the notation $C_* = C_*(t)$ may be adopted if required.)

The first general point is now relevant, namely that (2.3) is, in itself, an insufficient piece of information for the problem to be solved completely. Initial conditions and boundary conditions, specific to the problem, are needed in addition. Here the initial conditions have, in fact, already been given in words; in mathematical terms they are:

$$C(x,0) = C_0 \quad \text{for } x > 0 \; ; \quad C_*(0) = 0 \; . \tag{2.4}$$

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*It is worth emphasizing again that the validity, in practice, of the assumptions made in this section will be discussed later.

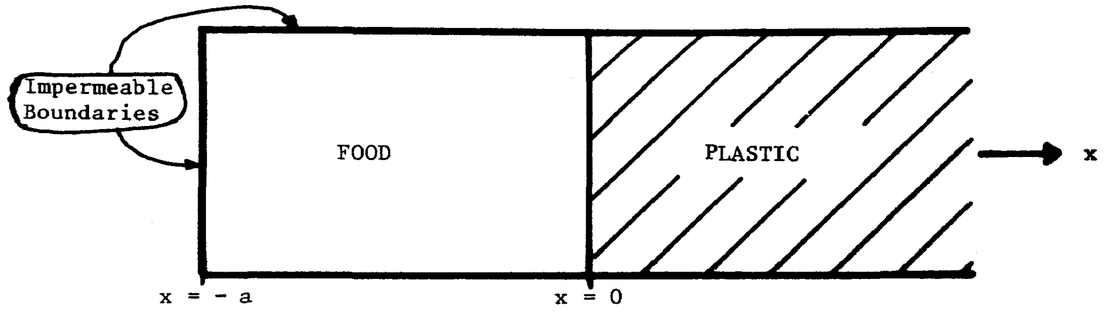

FIGURE 2. Sketch of geometry for first problem in §2.3

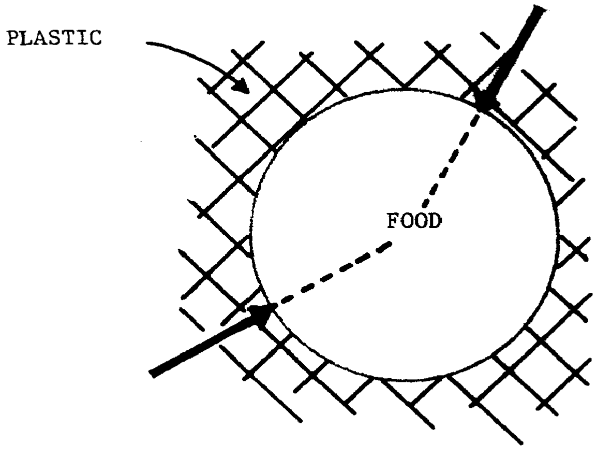

FIGURE 3. Sketch of geometry for second problem of §2.3. Diffusion takes place at <u>each</u> place in the plastic in the direction passing through the centre of the sphere (as indicated by the arrowed lines).

The boundary conditions have not yet been discussed. It will be supposed in this example that the interface at x = - a is impermeable to contaminant and that, for large positive x, C(x,t) is close to its initial value C_0, i.e.

$$C(x,t) \to C_0 \quad \text{as } x \to \infty . \tag{2.5}$$

(Note that the notation C(x,t) in (2.5) emphasizes that (2.5) holds for all t > 0.) Conditions at the food-plastic interface x = 0 are of crucial importance. First of all, since no contaminant is lost from the food to the environment outside, the rate of increase of the mass of contaminant in the food must equal the rate at which contaminant is crossing the interface from the plastic. Let A be the area of the food-plastic interface so that the total mass of contaminant in the food is Aa C_*, and its rate of increase with time is Aa (dC_*/dt) since A and a are constant. Consistent with (2.3), the rate at which contaminant is crossing from the plastic to the food per unit area is $D(\partial C/\partial x)$ evaluated x = 0. Hence

$$Aa\frac{dc_*}{dt} = AD\frac{\partial c}{\partial x}\bigg|_{x=0} \Rightarrow a\frac{dc_*}{dt} = D\frac{\partial c}{\partial x}\bigg|_{x=0}, \tag{2.6}$$

where the conventional notation $\bullet\big|_{x=0}$ denotes evaluation at (in this case) x = 0[*]. Finally, it will be assumed that the concentrations of contaminant on either side of the interface satisfy the following condition:

$$C_* = \gamma C\big|_{x=0}, \tag{2.7}$$

where γ is constant. More will be said later about the initial and boundary conditions, particularly (2.7); for the moment it is sufficient to note that the information that they contain is additional to (2.3) and that some such conditions are essential before the solution can be determined.

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[*] More formally (and more precisely) the phrase "evaluation at x = 0" means "the limit as x → 0 through positive values". The point is that (2.3) cannot hold at x = 0, since - according to the model - this is the interface. However the model assumes (implicitly) that a good approximation to reality can be obtained by assuming that the interface has zero thickness, and this assumption, which can be tested in any real case only by reference to experimental data, justifies the limit process implicit in (2.6).

It is important to note also that it has been assumed that there is no variation of C in the directions perpendicular to the x axis. This can be true only if diffusion occurs as if the plastic is homogeneous and if the lateral boundaries, as well as x = -a, are impermeable to plastic and this is indicated schematically in Figure 2. The interfaces at x = 0 and x = -a must also be plane but their precise shape is irrelevant; they could be square or rectangular or circular etc.

It can then be shown that

$$C* = \gamma C_0 \left\{ 1 - \exp\left(\frac{Dt}{\gamma^2 a^2} \right) erfc\left(\frac{\sqrt{Dt}}{\gamma a} \right) \right\}. \qquad (2.8)$$

This solution is given, for example, in Reid, Sidman, Schwope and Till (1980) where further discussion can be found.

Consider now another problem which has different geometry, but identical physics, to the one that has just been discussed. As illustrated in Figure 3, the food is in the shape of a sphere of radius a completely surrounded by plastic. However, and this illustrates the second general point to be discussed later, the change in geometry is important. For example, diffusion of contaminant in the plastic takes place (because of spherical symmetry) along the radii, i.e. along the lines emanating from the centre of the sphere. Therefore, as shown by the two arrows in Figure 3, the direction of diffusion changes from place to place in the sphere. This is in contrast to the first problem where the direction of diffusion is always a direction fixed in space, viz. the x axis. This basic geometrical difference causes changes in some of the equations. In particular it is now appropriate to use r, distance from the centre of the sphere, instead of x, and (2.3) is replaced by (see e.g. Crank 1979)*

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*It is possible and correct, but mathematically inefficient, to use Cartesian coordinates x,y,z instead of r (where - see Table $1 - r = (x^2 + y^2 + z^2)^{\frac{1}{2}}$) . In this case the governing equation is

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right)$$

and this is, physically speaking, identical with (2.9) although the proof of the truth of this statement requires some technical - but routine - mathematics.

$$\frac{\partial C}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right). \tag{2.9}$$

There are corresponding changes in the mathematical formulation of some of the initial and boundary conditions. Note first that now $C = C(r,t)$; thus (2.4) becomes

$$C(r,0) = C_0 \quad \text{for} \quad r > a\ , \ C_*(0) = 0\ , \tag{2.10}$$

and (2.5) becomes

$$C(r,t) \to C_0 \quad \text{as} \quad r \to \infty. \tag{2.11}$$

As with (2.5), equation (2.11) holds for all $t > 0$. A more substantial change is required in (2.6). The volume of the sphere is $\frac{4}{3}\pi a^3$ and its surface area is $4\pi a^2$. Thus, using the same physical principles that led to (2.6),

$$\frac{4}{3}\pi a^3 \frac{dC_*}{dt} = 4\pi a^2 D \left.\frac{\partial C}{\partial r}\right|_{r=a} \Rightarrow a\frac{dC_*}{dt} = 3D\left.\frac{\partial C}{\partial r}\right|_{r=a}, \tag{2.12}$$

and it is clear that the factor 3 arises entirely from the change in geometry between Figures 2 and 3. Finally (2.7) is replaced by

$$C_* = \gamma C\big|_{r=a}. \tag{2.13}$$

The solution to this second problem turns out to be more complicated than the first, and to have a mathematical structure that depends on the value of γ explained below in §2.4 and as illustrated in Figure 4. For present purposes, it is sufficient to quote two special cases: for small values of γ,

$$C_* = \gamma C_0\left\{1 - \exp\left(\frac{9Dt}{\gamma^2 a^2}\right)\operatorname{erfc}\left(\frac{3\sqrt{Dt}}{\gamma a}\right)\right\}, \tag{2.14a}$$

and for $\gamma = \frac{3}{4}$,

$$C_* = \gamma C_0\left\{\frac{3}{\gamma a}\sqrt{\frac{Dt}{\pi}} + 1 - \left(1 + \frac{9Dt}{2\gamma^2 a^2}\right)\exp\left(\frac{9Dt}{4\gamma^2 a^2}\right)\operatorname{erfc}\left(\frac{3\sqrt{Dt}}{2\gamma a}\right)\right\}. \tag{2.14b}$$

(Whilst (2.14b) holds only if the constant γ has the value $\frac{3}{4}$, it is useful for present purposes not to make the numerical substitution.)

§2.4 Discussion I: The importance of non-dimensional numbers

Suppose we wish to test whether the models above agree, for all t, with experimental data. Thus, in line with normal scientific procedure, we first hypothesize that the results of the mathematical model calculations apply to a given dataset, and then we look for discrepancies. If the discrepancies are judged to be too great, the hypothesis is rejected. (Note that, in line with the principle of falsification, scientific hypotheses can never be proved, but only rejected.) In line with this method, let us suppose that we have data from an experiment in which the geometry is essentially that of Figure 2, and let us hypothesize that equation (2.8) applies to the results. The values of a and C_0 can be measured before the experiment begins. On the other hand, the values of γ and D may or may not be known; suppose they are unknown. By hypothesis, we are entitled to use the data to determine them. Now γ be determined, at least in principle, from the data by measuring the value that C_*, the concentration of contaminant in the food, approaches after a long time; according to (2.8) this is γC_0. It may also be shown from (2.8) that, for sufficiently small values of t, a good approximation to C_* is given by (e.g. Reid, Sidman, Schwope and Till 1980)

$$C_* \approx C_0\sqrt{\frac{4Dt}{\pi a^2}}. \qquad (2.15)$$

(It is noteworthy that (2.15) is independent of the value of γ.) From (2.15) it follows that a graph of C_* against $\sqrt{t}$ has a slope of $C_0\sqrt{(4D)/(\pi a^2)}$ at the origin and, as noted by many authors, this provides a method of determining D.

Thus all the quantities appearing in (2.8) are known, or (in the case of γ and D) can be calculated as indicated above, or (in the case of C_* and t) can be measured as they vary. The results of the experiment can be plotted in many ways; for example C_* can be plotted against t. However, and this is the key point of present concern, the resulting plots would change if any of γ, C_0, D or a changed. This is undesirable and inefficient; fortunately a far more satisfactory alternative is available. Define new variables r and τ by the equations

$$\Gamma = \frac{C_*}{\gamma C_0},\ \tau = \frac{Dt}{\gamma^2 a^2}. \qquad (2.16)$$

Then Γ and τ are non-dimensional quantities, i.e. they have no units and are pure numbers whose values are independent of the particular system of units chosen. We can refer to Γ and τ as non-dimensional concentration and non-dimensional time respectively. In terms of Γ and τ, equation (2.8) can be written in the form

$$\Gamma = \{1 - e^{\tau} \operatorname{erfc}(\sqrt{\tau})\}\,. \qquad (2.17)$$

The graph of Γ against τ given by (2.17) is the solid curve in Figure 4. It represents the behaviour of all systems with the geometry of Figure 2 subject to the hypothesis that (2.8) holds. The single equation (2.17) (or the single solid curve in Figure 4) describes all such systems irrespective of the values (in any particular case) that γ, C_0, D or a may have. It is then easy to test whether the data agree with the hypothesis that (2.8) holds by rescaling the measured values of C_* and t so that they are in their non-dimensional forms Γ and τ.

Use of non-dimensional quantities, as illustrated by the example just discussed, therefore significantly reduces the labour involved in testing experimental data using mathematical models. One important conclusion of this project is that all data and all models should be expressed in appropriate non-dimensional terms.

§2.5 Discussion II: The importance of geometry

In line with the conclusion of §2.4, it is natural to express the results (2.14a) and (2.14b) for the spherical geometry shown in Figure 3 in terms of the non-dimensional concentration Γ and the non-dimensional time τ defined in (2.16). The results are:

(2.14a): $$\Gamma = \{1 - e^{9\tau} \operatorname{erfc}(3\sqrt{\tau})\}\,; \qquad (2.18a)$$

(2.14b): $$\Gamma = \left\{3\sqrt{\frac{\tau}{\pi}} + 1 - \left(1 + \frac{9\tau}{2}\right) e^{\frac{9\tau}{4}} \operatorname{erfc}\left(\frac{3\sqrt{\tau}}{2}\right)\right\}. \qquad (2.18b)$$

The dashed curves labelled (A) and (B) in Figure 4 show the result of plotting Γ against τ for (2.18a) and (2.18b) respectively.

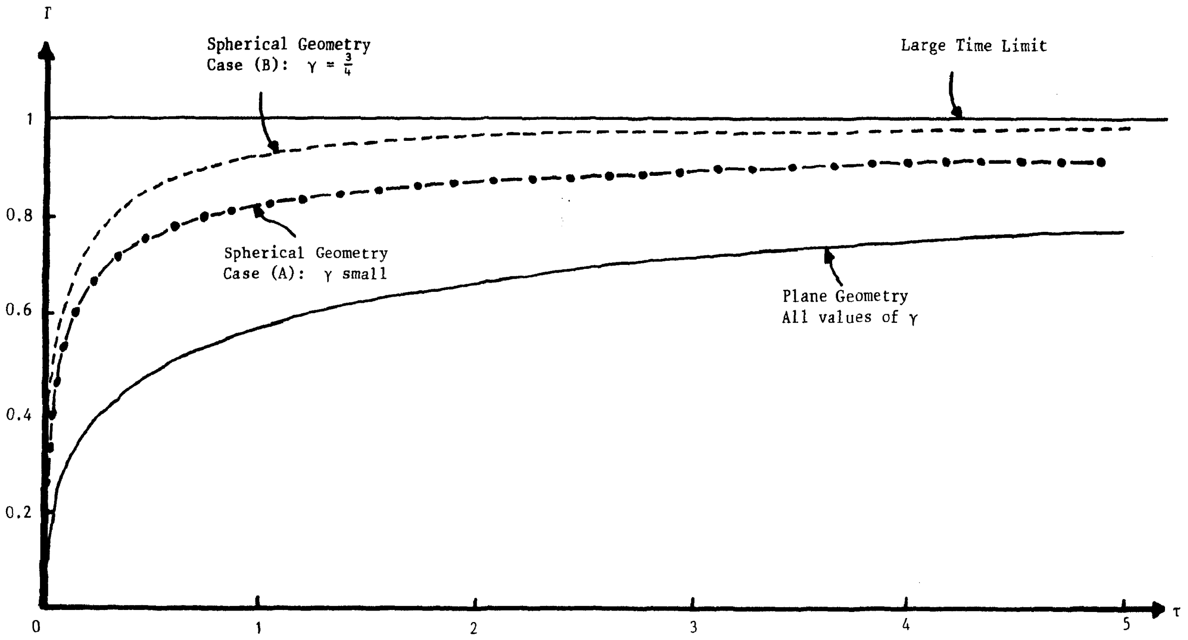

FIGURE 4. Graphs of non-dimensional concentration *(Γ)* against non-dimensional time (τ).

Two comments are in order. Unlike the plane geometry case of Figure 2, the results for the spherical geometry case of Figure 3 do not collapse onto a single curve when expressed in terms of r and τ; there is in fact a different curve for each value of γ[*] . (However the use of non-dimensional quantities, advocated in §2.4, still represents an enormous gain in efficiency. Without such use the plots of C_* against t would change if any of γ, C_0, D or a changed whereas, with non-dimensional quantities, only changes in γ matter.) The second comment is that, whatever the value of γ, the plot of r against τ is always above the curve labelled (A) in Figure 4. Thus, for a given value of τ, the value of r for the spherical geometry case of Figure 3 is never below that value given by curve (A), i.e. for this geometry, curve (A) represents the lowest migration - not surprising when it is recalled that curve (A) represents behaviour for small values of γ. Furthermore curve (A) is above the solid curve for all values of τ, i.e. for a given value of τ migration in the spherical geometry case is always more rapid (for given values of γ and C_0) than in the plane geometry case.

These comments illustrate that migration behaviour depends on the geometry of the food - package system. The literature pays little attention to this fact, and the actual (and proposed) legislation almost none at all. A recommendation of this report is therefore that explicit attention should be given, both in planning research and in drafting legislation, to this unfortunate omission. Suggestions as to how this recommendation can be implemented will be made later in this report.

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[*] Indeed this situation will be the norm. It can be shown that, whatever the geometry, a migration system satisfying the physical laws described in §2.3 will result in an equation of the form $r = f(\tau,\gamma)$, where the function f depends on the geometry. It has been shown in §2.4 that a peculiarity of the plane geometry of Figure 2 is that f, nominally a function of the two variables τ and γ, does not in fact depend on γ^{-} but this could not have been anticipated.

§2.6 Discussion III: The importance of boundary and initial conditions

In §2.3 it was emphasized that the diffusion equation (2.3) needed supplementation by additional boundary and initial conditions before precise predictions could be made. The same statement would be true whatever (differential) equation were used. Furthermore, the difference between curves (A) and (B) in Figure 4 can be ascribed entirely to a difference in the value of γ, which enters the mathematical formulation of the problem via the boundary condition (2.13). It can therefore be seen that accurate predictions can (in general) be made only if the proper boundary and initial conditions are known with adequate precision. In migration problems this statement has particular force in relation to conditions at the interface between food and plastic, and a further recommendation is that more research on this specific problem should be undertaken.

§2.7 Summary

It is emphasized again here that the point of this chapter has been to discuss, and therefore bring out, certain basic physical and mathematical principles that will be crucial in the evaluation of mathematical models in Chapter 3 of this report, and in the recommendations for development in Chapter 4.

§2.8 References

Abramowitz, M. and Stegun, I.A. 1965 "Handbook of Mathematical Functions", Dover Publications Inc., New York. 1046pp.

Crank, J. 1979 "The Mathematics of Diffusion", Second Ed. (paperback), Oxford University Press. 414pp.

Katan, L.L. 1979 Migration units and dimensions. Plastics & Rubber: Mats. & Applies. 4, 18-24.

Reid, R.C., Sidman, K.R., Schwope, A.D. and Till, D.E. 1980 Loss of adjuvants from polymer films to foods or food simulants. Effect of the external phase. Ind. Eng. Chem. Prod. Res. Dev. 19, 580-587.

CHAPTER THREE: CRITICAL DISCUSSION OF IMPORTANT MODELS

§3.1 Introduction

In the course of preparing this report several hundred papers and books have been consulted, of which about 90 have been identified as of particular importance, and studied in depth. This chapter provides a coherent, but critical, account of those mathematical models in this literature that have proved most useful or appear to be most promising; there are also some original contributions. The discussion will not be a piecemeal annotated list of all papers that have quoted mathematical formulae but, instead, an attempt at a logical development in which important work is quoted where appropriate. (Consistent with this approach and also to avoid useless repetition, not all the 90 or so sources will be referred to in the text, but a full list is provided in §3.8.) Naturally the account will be consistent with the principles laid down in Chapter 2; in particular the great potential importance of geometry will be continually emphasized.

Before beginning the bulk of this Chapter, it is helpful to make a few remarks about mathematical models and their use, additional to those in the footnote on page 1/2/3. As there indicated, a mathematical model of a migration process involves a set of hypotheses about the underlying physics and chemistry which, when expressed in mathematical terms, enable quantitative predictions to be made. The value of any mathematical model can be assessed only by comparison with data. It requires separate judgement, involving perhaps such matters as the costs of refining and developing the model as well as obtaining data, and the perception of the degree of discrepancy that is acceptable, to decide whether or not a given model is a satisfactory predictor for a given set of migration phenomena. (Such judgement of what is acceptable as a discrepancy does not involve science alone; however this study aims to describe some factors relevant to the exercise of this judgement.) It is important to note also that any comparison between the predictions of a mathematical model and appropriate data is not a test of any one of the set of several individual hypotheses that, together, comprise the model. A single hypothesis (e.g. that the contaminant concentrations on either side of a food-plastic interface are in a constant ratio throughout the migration process as in

(2.7)) must be tested directly since such an hypothesis may be invalid even though the model as a whole is judged acceptable (and vice versa). Of course, if a model is judged to be unacceptable, it is then sensible to re-examine each of the individual hypotheses on which it is based, but it is important also to note that errors in some hypotheses are likely to be more critical (in the sense of significantly altering the predictions of the mathematical model) than errors in others. There is an analogy here with the concept of <u>controlling factors</u>, i.e. errors in the modelling of the dominant process(es) are much the most significant. However it is also important to note that, in general, any one mathematical model has a limited range of validity. For example it may be valid only for certain (non-dimensional) times or for a plastic-food-contaminant system with certain physical properties. Outside the range of validity, other factors (not included in the model) may become important – even controlling - and an experimental test of a model ought to attempt assessment of this range. Unfortunately many workers have assumed wrongly that certain mathematical results (e.g. migration proportional to $t^{\frac{1}{2}}$) have universal applicability.

Given a mathematical model, it is sometimes possible to obtain quantitative predictions from it in the form of relatively simple formulae such as (2.8), (2.14a) and (2.14b). Sometimes the predictions can be obtained only in more complex mathematical form, e.g. as infinite series or complicated integrals. In general, it is rare (because of features like complicated geometry for example) for it to be possible to obtain mathematical formulae (simple or complex) for the solution of the set of equations forming the mathematical model*. In such a case the theory of the rapidly expanding branch of mathematics called <u>numerical analysis</u> (universally abbreviated to N.A.) would be employed to solve the set of equations numerically using a computer. (In practice it would also normally be sensible nowadays to use a computer to obtain <u>numerical</u> results in cases where the

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*In such circumstances a mathematician would normally write "The set of equations do not admit an <u>analytical</u> solution"; the word "analytical" in its technical mathematical sense has however been avoided in this report because of the different, also technical, meaning which it has in chemistry.

predictions of the mathematical model have been expressed in complex mathematical form.) The purpose of numerical analysis when used in this way is to ensure, as far as possible, that the numerical solution(s) are obtained efficiently and accurately; it is important to note not only that modern computers have greatly increased the potential usefulness of mathematical modelling of phenomena like migration but also, and as a warning, that their use introduces further potential errors, namely those associated with the numerical computation process. Such errors are inevitable and numerical analysis is (partly) concerned with their control. Despite this warning, it is certain that obtaining the accurate numerical solutions of many of the mathematical models of migration discussed below will be fairly routine provided the task is carried out by a person with appropriate training and skill. In this phase of the study time and resources have not permitted the development of new computer results but these should form a prominent part of the next phase. Therefore the mathematical predictions that will be discussed will be for simple geometries; fortunately such predictions, properly interpreted, allow one to understand the interaction of the various processes contributing to migration and therefore to anticipate, at least qualitatively, migration behaviour in the more complex geometries occurring in real life situations. This is the real value of simple mathematical solutions.

Comments on page 106 (and elsewhere) of Reid, Schwope and Sidman (1983) are relevant to the above discussion of mathematical models.

§3.2 An important test

It is sensible first to note some simple formulae that give the maximum possible concentration in food of a specific contaminant. The formulae have universal validity provided only that the contaminant does not undergo chemical change during the migration process. Suppose a plastic package of volume V contains food (or food simulant) of volume V_*, and that, when containment occurs, there is a mass M of a specific contaminant in the plastic at concentration C_0 where, by definition,

$$C_0 = \frac{M}{V} \tag{3.1}$$

Whatever happens to the package between initial containment and ultimate consumption of the food, the mass of the contaminant in the food-package system at no time exceeds M (making the reasonable assumption that no further contaminant is added to the system). Although some contaminant may in practice be lost (e.g. by handling or by migration to the atmosphere), it is simplest and safest to ignore any such loss; if required, corrections can always be made later. The total mass of this specific contaminant in the system is therefore taken to be M for all time.

Irrespective of the mechanism of mass transfer, migration acts to equalise the contaminant concentrations between the two different parts of the system; provided an ultimate steady temperature T is reached, the system will approach an equilibrium whose properties depend, in general, on T. In this equilibrium, the concentrations C and C_* of the contaminant in the plastic and food respectively are uniform and, since mass is conserved,

$$CV + C_*V_* = M. \tag{3.2}$$

At equilibrium the ratio of C_* to C is equal to the partition coefficient γ, i.e.

$$\frac{C_*}{C} = \gamma. \tag{3.3}$$

Elimination of C from (3.2) and (3.3) gives

$$C_* = \frac{\gamma M}{V + \gamma V_*} = \frac{\gamma C_0}{1 + \gamma(V_*/V)} = \frac{C_0}{\gamma^{-1} + (V_*/V)}, \tag{3.4}$$

where (3.1) has been used to express C_* in terms of C_0 rather than M.

Equation (3.4) and close equivalents have a long history in migration research. A special case was apparently first introduced by Garlanda and Masoero (1966), and other workers who have discussed this result include Sanchez (1979), Katan (1979), Senich (1981) and Reid, Schwope and Sidman (1983). Since (3.4) gives the maximum possible concentration C_* of the contaminant in the food, it is easy, provided γ is known, to use it to assess in a specific case whether the concentration of the contaminant in the food will ever exceed a specified limit (e.g. legal or toxic). Only if the value of C_* given by (3.4) exceeds such a limit will it be necessary to use more complex mathematical models of migration like those discussed in later sections of this Chapter. This point is made by Katan (1979). Reid, Schwope and Sidman (1983) also make the same point but for a special case of (3.4) with plane geometry; this restriction is quite unnecessary.

But it has been noted that (3.4) can be used, as it stands, only if the value of the partition coefficient γ is known for the particular trio of plastic, food and contaminant and this is, in practice, often not so. Many authors, including Sanchez (1979), Sanchez, Chang and Smith (1980) and Keinhorst and Niebergall (1986b)have discussed the dependence of γ on temperature and other properties. In particular Sanchez discusses how γ can be estimated for Class III systems, and Keinhorst and Niebergall demonstrate good agreement between theory and experiment for some particular sets of materials. For aqueous foods and lyophilic plastics (which are the majority and include polyolefins) values of γ are typically very small; thus Reid, Schwope and Sidman (1983) quote $\gamma \approx 7.1\times10^{-3}$ for styrene monomer migrating from polystyrene into 50% aqueous ethanol and $\gamma \approx 2\times10^{-4}$ for BHT migrating from HDPE into a water gel. On the other hand much higher values, some greater than unity, have been measured, especially with oily foods and lyophilic plastics. In view of the importance of γ, but the uncertainty about its value in many circumstances, a major conclusion of this report is that a suggestion of Schwartz (1983) should be given high priority, namely that "a data base for parameters such as diffusion and partition coefficients" should be "developed".

Fortunately, use can be made of (3.4) even when the value of γ is not known because, whatever the value of γ, the value of C_* in (3.4). never exceeds C_{**}, where

$$C_{**} = C_0\left(\frac{V}{V_*}\right). \tag{3.5}$$

The concentration of the contaminant in the food must always be <u>less</u> than C_{**} since such a concentration would be achieved only in the physically unrealistic circumstances when the plastic is completely denuded of contaminant. Neverthless C_{**} can easily be calculated in any specific case since it does not involve γ, and this should always be done since, when C_{**} is less than the specified limit, no further use of mathematical models is required. The difference, in practice, between (3.4) and (3.5) can be illustrated by a numerical example. Suppose a 50g bottle holds 1 litre of liquid food so that $V/V_* = 0.05$ if both substances have the density of water. Table 2 shows values of C_*/C_0 obtained from (3.4) for several values of γ, and of C_{**}/C_0 obtained from (3.5). It will be noted, in particular, that there is little difference between C_{**}/C_0 and the value of C_*/C_0 when $\gamma \geq 1$. Equation (3.5) can also be used in an inverse design sense. Suppose there is a specified legal or toxic limit C_L on the concentration of a specific contaminant in a specific food. According to (3.5) this is bound not to be exceeded provided the initial concentration C_0 of the contaminant in the plastic is less than $C_L(V_*/V)$, and there is presumably some scope in designing plastic containers so that (V_*/V) can be made as large as possible (bearing in mind other constraints such as cost, strength and, above all, consumer acceptability.)[*] Pursuing this point a little further is instructive, and illustrates again the potential importance of geometry. Suppose a plastic film of fixed thickness h is to be used to make a container for a fixed volume V_* of liquid food. In line with the discussion above it is desirable, other things being equal, to make

γ	C_*/C_0 Eqn. (3.4)
10^{-4}	10^{-4}
10^{-2}	0.0083
1	0.0476
	C_{**}/C_0 Eqn. (3.5)
	0.05

TABLE 2: Numerical examples from equations (3.4) and (3.5). Other examples are given by Reid, Schwope and Sidman (1983).

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[*] Conversely problems are most likely to occur when V_*/V is small as in miniature bottles of spirits.

the shape of the container such that (V_*/V) is as large as possible, i.e. such that V is as small as possible. The best possible shape from this point of view is a sphere, and it can be shown that the value of (V_*/V) for a sphere is about $0.207_{(V_*^{\frac{1}{3}}/h)}$. The best possible cylinder has its radius equal to half its height and (V_*/V) about $0.181_{(V_*^{\frac{1}{3}}/h)}$, and the best possible cuboid is a cube with (V_*/V) about $0.167_{(V_*^{\frac{1}{3}}/h)}$.

In concluding this section it is worth noting that, according to (3.4), $C_* \approx \gamma C_0$ when (V_*/V) is small, i.e. when the volume of the plastic is effectively infinite. Reference to (2.8), (2.14a) and (2.14b) in Chapter 2 will confirm that the model problems there considered satisfy this result. This simple result can also be very useful in estimating C_{**} when V_*/V is not known precisely.

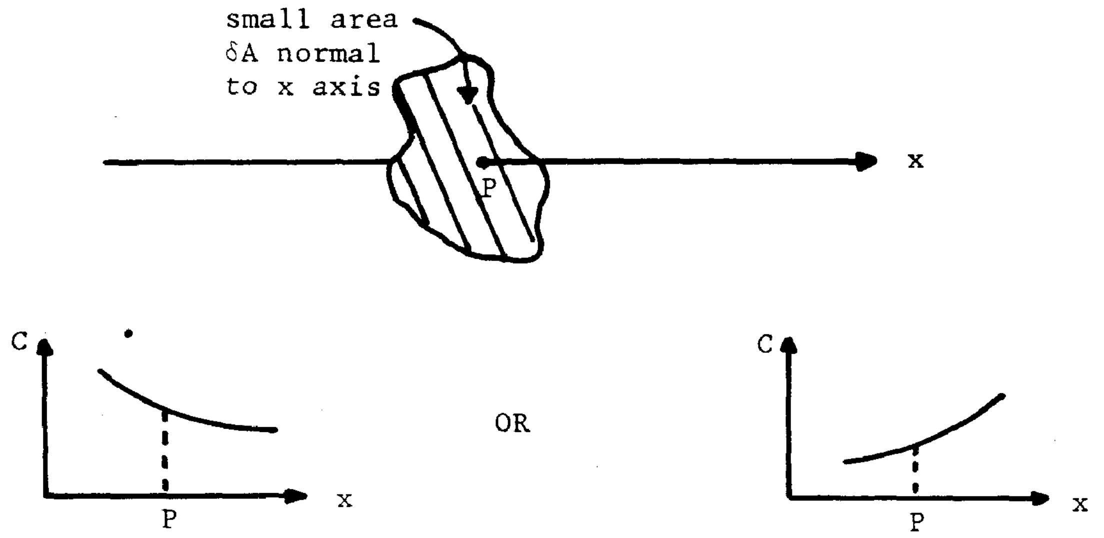
§3.3 Mathematical models of Class II systems

Scientific basis of the models

As noted in Chapter 1, Class II systems are those where migration properties do not depend on penetration of the plastic by the food. Almost all the mathematical models of these systems that appear in the literature are based on classical diffusion theory, and this section begins with some background to that subject. More substantial treatments do of course exist; the most familiar of these is likely to be the book by Crank (1979). It should be noted that, historically, many of the models considered here for Class II systems were intended for application in all systems.

The models in the literature all make simplifying assumptions about the structure of both the plastic and the food. In particular they assume that the length scales of concern in migration are much larger than those which characterise the micro-molecular structure. This is the continuum hypothesis which is explained in, for example, Chapter 1 of Batchelor (1967), and its satisfaction enables the definition of properties like concentration (temperature, density, ...) as continuous functions of position and time (except - perhaps - at discontinuities between different media). Such properties are defined as spatial averages over regions large enough to contain many molecules but with dimensions smaller than those of direct concern for migration. The characteristic length scale of such regions is known as the <u>continuum scale</u>. Two further assumptions are universally made. First, it is assumed by modellers that the structure in both media is <u>isotropic</u> on the continuum scale (except at boundaries and interfaces), i.e. when the media are in equilibrium all directions are equivalent at every point. The second assumption concerns the geometry of migration systems. Although the boundaries and interfaces between different media are not smooth and sharp in real life, it is hypothesised that adequate predictions can be obtained by supposing that they are. It might be reassuring to note that the assumptions described in this paragraph have been universally applied to almost all motions of solids, liquids and gases for over 100 years with excellent results.

Consider the migration of a specific contaminant. Consistent with the notation in §2.3 and §3.2, the concentrations of this contaminant in the plastic and the food will be denoted by C and C_* respectively, where (in general) C and C_* depend on time t and all three space coordinates x,y,z. (Note that in the special examples considered in §2.3, C_* happened to be uniform, i.e. independent of x,y,z.) On the basis of the continuum hypothesis, it is legitimate to suppose that C and C_* are well-behaved functions. Consider a small surface in the interior of the



$\frac{\partial C}{\partial x} < 0$ at P => flux positive (left to right)

$\frac{\partial C}{\partial x} > 0$ at P => flux negative (right to left)

FIGURE 5. Schematic sketch illustrating equation (3.6)

plastic whose area is δA and whose normal (perpendicular) is in the direction of the x axis. If C depends on x in the neighbourhood of this surface there will be a net *flux* of contaminant across it; According to Pick's first law or on the basis of more general phenomenonological arguments given in Chapter 3 of Batchelor (1967), the rate of transfer of contaminant mass across this surface in the direction in which x increases is

$$-D\frac{\partial C}{\partial x}.\delta A, \tag{3.6}$$

where D is known as the *diffusion coefficient* (or mass transfer coefficient) . The minus sign in (3.6) is necessary because transfer takes place from regions where C is larger to regions where C is smaller. The units of the important parameter D are m^2s^{-1}, and D is an intrinsic property of the plastic-contaminant system and of the position where the flux is evaluated. In particular D may depend on C and properties like temperature for example; however the dependence on C is likely to be small when C is small, and most modellers have ignored such dependence for Class II systems (even in cases where C is not small). The philosophy adopted is that such dependence should be included only if the results of models that assume D is independent of C are unacceptable. If there is systematic variation of structure on the continuum scale D will also depend on x,y,z, but – again - modellers have not considered the influence of such variation, i.e. they have assumed that the media can be regarded as *homogeneous* on the continuum scale. For the moment, however, it is not necessary to assume that D is constant and uniform. The flux in the food will also be assumed to be given by (3.6), but with C and D replaced by C_* and D_*; the flux across small surfaces normal to the y and z axes is likewise given by (3.6) but with $\partial/\partial x$ replaced by $\partial/\partial y$ and $\partial/\partial z$ respectively. In mathematical terms it is actually most efficient to use *vector notation*, and the flux across a small surface of area δA is written $- D \underset{\sim}{n} . \nabla C \, \delta A$, where ∇C is the concentration gradient and $\underset{\sim}{n}$ is a unit vector normal to the surface. (The assumption of isotropy ensures that D has the same value for all surface areas whatever their orientation.)

It is a straightforward exercise now to show that Fick's first law is consistent with conservation of mass provided C satisfies the partial differential equation

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(D\frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z}\right). \tag{3.7a}$$

One derivation of this equation is given on pages 2 to 4 of Crank (1979). In the language of vectors (3.7a) can be written in either of the following two forms:

$$\frac{\partial C}{\partial t}=\nabla.(D\nabla C), \tag{3.7b}$$

or (Crank 1979, page 5)

$$\frac{\partial C}{\partial t}=\mathrm{div}(D\,\mathrm{grad}\,C), \tag{3.7c}$$

and the shortness of either of (3.7b) or (3.7c) compared with (3.7a) shows why mathematicians prefer vector formulations. It may happen for geometrical reasons in an application that C (and D) are independent of one or more of x,y,z. In such a case the general equation (3.7a) simplifies; suppose, for example, that C (and D) are independent of y and z. Then (3.7a) reduces to

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right). \tag{3.8}$$

It has also been noted earlier that many modellers have assumed that D is constant and uniform; in such a case (3.7a) becomes

$$\frac{\partial C}{\partial t}=D\left(\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}+\frac{\partial^2 C}{\partial z^2}\right), \tag{3.9a}$$

or (in vector notation)

$$\frac{\partial C}{\partial t}=D\nabla^2 C, \tag{3.9b}$$

and (3.8) becomes

$$\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2}, \tag{3.10}$$

Crank (1979) points out that (3.10) is usually referred to as Fick's second law. It is hoped that the account here will make clear two points:

(a) Fick's second law is a direct consequence of his first law and of conservation of mass together with - in the case of (3.10) - certain simplifying assumptions. It therefore hardly merits identification as a separate law.

(b) Fick's second law in the form (3.10) is valid only when the geometry of the problem being considered is particularly simple. In real life this will be so only very rarely and it is then necessary to use (3.7a) or - perhaps - (3.9a). Unfortunately many users of mathematical models in migration have ignored this fact, already highlighted in §2.5 and §3.2, with the consequence that many formulae in the literature, though valuable for understanding, do not apply quantitatively to real-life situations.

Boundary and initial conditions

The task of the modeller is to find - normally nowadays by use of a computer as explained in §3.1 - the solution of (3.7a) or (3.9a) that applies to the problem with which he/she is concerned. As explained and stressed in §2.3 and §2.6, this cannot be done without the specification of boundary and initial conditions that contain information additional to (3.7a) and (3.9a), and specific to the problem.

Initial conditions are easy to state for migration problems. Let the time when containment occurs be designated as $t = 0^*$. The initial conditions give the distribution of the contaminant within the plastic and the food at $t = 0$. All modellers assume that the contaminant is distributed uniformly within the plastic; denoting this uniform concentration by C_0 as in §2.3 gives

$$C(x,y,z,0) = C_0 \tag{3.11}$$

for all values of (x,y,z) corresponding to points within the plastic.

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[*] Other choices, e.g. $t = t_0$, simply complicate the algebra without - in any way - changing the results.

Similarly it is supposed that, initially, there is no contaminant within the food. Thus

$$C_*(x,y,z,0) = 0 \tag{3.12}$$

for all points within the food. Amendments to (3.11) and (3.12) will have to be made should other conditions occur initially, e.g. the contaminant is not distributed uniformly within the plastic or there is some contaminant within the food.

Boundary conditions are required at all boundaries with the medium (e.g. the atmosphere) external to the food-package system and at the interface (or interfaces) between the food and the plastic package. Consider the former conditions first. In real life there is undoubtedly some loss of contaminant to the external medium; however this is difficult to quantify (and - even if done - would lead to great complications). As explained in §3.2, it is simplest from the mathematical point of view and safest from the hazard assessment point of view to assume that no such loss occurs. Mathematically this is expressed either as

$$\frac{\partial C}{\partial n} = 0, \frac{\partial C_*}{\partial n} = 0 \text{ at all external boundaries ,} \tag{3.13a}$$

where $\partial/\partial n$ denotes differentiation in the direction along the local normal to the external boundary, or (in vector form) as

$$\underset{\sim}{n} \; .\nabla C = 0, \underset{\sim}{n} \; .\nabla C_* = 0 \text{ at all external boundaries .} \tag{3.13b}$$

In some circumstances, it is possible to express the same physical condition in another way. Usually diffusion of the contaminant in the plastic is a slow process and, as a consequence, the period of time for which migration predictions are required may be (relatively) short enough for little of the contaminant near the external boundaries of the plastic to have migrated. From the point of view of migration, it is then possible to regard the plastic as of <u>infinite</u> extent with no change in the concentration of contaminant far away from the food-package interface(s), i.e.

$$C(x,y,z) \to C_0 \text{ as } (x^2+y^2+z^2)^{\frac{1}{2}} \to \infty . \tag{3.14}$$

It is important to emphasize that (3.14) replaces the first condition in (3.13a) - or (3.13b) - but that the condition on C_* is unchanged, and also that (3.14) is an <u>approximation</u> to the first condition in (3.13a). It is possible to assess the periods of time for which (3.14) is a good approximation since, in a time t, the thickness of the region of the plastic that has lost contaminant has order of magnitude $(Dt)^{\frac{1}{2}}$. Provided this is much less than the thickness h of the plastic film forming the packaging, equation (3.14) will be a valid approximation. Thus, for example, consider a film of thickness 5×10^{-5}m (50 microns) and a value of D of $5 \times 10^{-16} m^2 s^{-1}$ ($5 \times 10^{-12} cm^2 s^{-1}$), typical of the migration of styrene monomer in polystyrene. For t = 86400s (1 day), $(Dt)^{\frac{1}{2}}$ is about 6.6×10^{-6}m, i.e. about h/8 , and (3.14) is likely to be reasonable. On the other hand $(Dt)^{\frac{1}{2}} = h$ when t = 5×10^6s, i.e. about 58 days. Use of (3.14) in this case is therefore likely to give acceptable results for migration times not exceeding a day or two, but (3.13a) should be used for longer times.

Most difficulty concerns the specification of the boundary conditions at the interface between the food and the plastic - and this is very important. It is assumed to be valid, as explained above, to regard this interface as sharp and smooth - at least for the Class II systems that are currently under consideration. At this interface the rate at which contaminant leaves the plastic must be equal to the rate at which it enters the food. By Fick's first law - equation (3.6) – this requires

$$D\frac{\partial C}{\partial n} = D_*\frac{\partial C_*}{\partial n} \text{ at every point on the interface .} \tag{3.15}$$

There is a widely used alternative to (3.15), based on the fact that for many systems diffusion in. the food is much more rapid than diffusion in the plastic; this is normally true, for example, when the food is liquid. In those circumstances it is consistent to suppose that the concentration C_* of contaminant in the food is <u>uniform</u> at all times. Any internal bulk motion in the food, caused e.g. by convection, would of course greatly accelerate this tendency of C_* to approach uniformity. This is discussed later. The rate of increase of contaminant mass within the food is therefore $d/dt(C_*V_*)$, and this must be equal to the rate at which contaminant is leaving the plastic. This is equal to the surface integral of $D(\partial C/\partial n)$ over the interface where $\partial/\partial n$ denotes differentiation along the local normal to the interface in the direction from the food into the plastic. Thus

$$V_*\frac{dC_*}{dt} = \iint_A D\frac{\partial C}{\partial n}dA\,, \tag{3.16a}$$

or, in vector notation,

$$V_*\frac{dC_*}{dt} = \iint_A D\nabla C.\underset{\sim}{dA} \quad . \tag{3.16b}$$

In fact, this condition has been used in all models in the literature in simplified form, appropriate for the idealized geometries of the problems that have been studied. For example, suppose the interface is a plane, and take its equation as $x = 0$ with plastic occupying the region $x > 0$. If, in addition, D and C are independent of y and z (and thus depend only on x and t), the integral on the right-hand side of (3.16a) or (3.16b) can be evaluated with the result that

$$V_*\frac{dC_*}{dt} = DA\left.\frac{\partial C}{\partial x}\right|_{x=0}, \tag{3.17}$$

where A is the area of the interface. The special case of (3.17) when the food has the shape of a cuboid with cross-sectional area A and thickness a (so that $V_* = Aa$) is equation (2.6). Another special case of (3.16a), for a spherical interface, is equation (2.12).

Before the mathematical model is (at least in principle) soluble, more information is needed about conditions at the interface. At equilibrium, the concentrations C_* and C have a fixed ratio (the partition coefficient) at points very close to the interface (but on opposite sides). Users of mathematical models of migration have invariably assumed that this equilibrium condition holds throughout the migration process, i.e. they have assumed that there is a constant γ such that

$$\frac{C_*}{C} = \gamma \text{ at all points of the interface for all time, i.e. } \frac{C_*(0,t)}{C(0,t)} = \gamma\,. \tag{3.18}$$

This extension of the partition coefficient concept to non-equilibrium situations is central to the whole problem of modelling migration. Roughly speaking, the assumption can be justified on the grounds that migration is normally a (relatively) slow process and that, therefore, at each time during the migration process, conditions on either side of the interface are in quasi-equilibrium. (This type of argument is common in fluid mechanics; for example, the equilibrium gas laws are used to link pressure, density and temperature in the atmosphere with good results.) More particularly, it should be noted that γ is the ratio of chemical activities and these do not change greatly with concentrations if these are well removed from saturation concentrations. This is not always so, and the authors of this report wish to stress that real progress in migration research requires that the validity of (3.18) should be tested experimentally; they are unaware of any such tests having been conducted. Obviously such experiments will not be easy to design or execute, given also that they should aim at discovering the correct interfacial condition should (3.18) be found to be invalid.

It was mentioned in §1.1 that, in general, packaged food is exposed to a wide and fluctuating range of temperatures between containment and consumption. From the point of view of the model equations discussed in this section, changes in temperature T cause changes in the values of γ and D. Other effects (such as volume changes due to thermal expansion/contraction) are likely to be much less significant - probably negligible – for practical prediction purposes. References for the dependence of γ on T were given in §3.2, and the dependence of D on T is mathematically similar (van Amerongen 1965; Garlanda and Masoero 1966). It would be possible, but extremely expensive in terms of computer resources and also much more difficult in terms of controlling numerical errors, to use the model equations with the explicit dependence of γ and D on T included; one reason for the expense and difficulty is that it would then be necessary to include partial differential equations for T in the model. No authors have so far included such dependence in their mathematical models and it is therefore necessary to adopt the hypothesis, consistent with the philosophy of mathematical modelling outlined in §3.1, that there are some constant values of γ and D which give, on comparison of the mathematical/numerical results with data, acceptable predictions of migration from the practical point of view. If so, it would be necessary to regard these constants as appropriate averages over the relevant temperature range. For the sake of completeness and clarity, it is necessary to emphasize one point in connection with temperature dependence. Nearly all experiments have been conducted under isothermal conditions, and legislative standards specify a constant temperature for the analytical tests of migration that they include*. In these ideal cases there are no changes in γ and D during the migration process and these parameters therefore have constant values (dependent on the specified/controlled temperature). The complications discussed in the first part of this paragraph are then irrelevant. However, this remark suggests to the authors of this report that inadequate attention may so far have been paid to the possible effects of temperature changes during migration, and it is therefore recommended that some migration tests be conducted under non-isothermal conditions typical of those that real foods and packaging undergo. For example, tests should examine cases where the food changes phase during the migration process due, for instance, to freezing.

A few authors have used an empirical "mass transfer resistance" law instead of (3.18). This will be dealt with when their models are discussed below. With this exception, all the equations that have been used in the formulation of mathematical models of migration in Class II systems have been given.

Remark

The remainder of this section will highlight some special solutions of the equations discussed above that have already been used in migration research. However, in the view of the authors of this report, the most important part of this section has already been seen by the reader.
The point is that the special solutions that follow apply only in specific circumstances and cannot be used in other circumstances (e.g. different geometries), except - perhaps - approximately; then proper justification must be given. On the other hand, the model equations derived and discussed above apply (at least as a promising hypothesis) to all Class II systems and, for any given geometry, it is a matter of technique (often routine technique) to derive the appropriate solution in numerical form

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*Strictly isothermal tests are of course impossible because of "come-up" and "come-down" times.

using a computer. Perhaps an analogy with chemical analysis is useful. The migration characteristics for each trio of food/polymer/contaminant in a given geometrical configuration have to be measured in a specifically designed experiment; likewise, for a specific situation, the solution of the set of equations forming the mathematical model has, in general, to be derived ab initio. (A difference is that the mathematical solution is expressible for given geometry in non-dimensional form and this reduces the potential labour as explained in §2.4.) The point above is important, and experience shows that it is often not understood by non-mathematicians who attach too much significance (and often the wrong significance) to special solutions.

Special solutions for well-mixed food

It has already been noted that one of the most comprehensive accounts of special solutions of the mathematical model equations for Class II systems is given by Crank (1979). Many of those solutions have been known for many years, and van Amerongen (1965) discusses some of them from the particular viewpoint of migration from rubber and the determination of the diffusion coefficient D.

The first specific application of mathematics to migration from plastic packaging into food is by Garlanda and Masoero (1966). The special solutions are for three situations of ascending complexity but each is one-dimensional, i.e. diffusion takes place only in the direction of one axis - taken to be the x-axis. In the first, illustrated in Figure 6, both plastic and food have infinite extent. The initial concentration of contaminant in the plastic is C_0 and in the food is zero. Garlanda and Masoero suppose that diffusion in the food is so rapid that the concentration of contaminant within the food is uniform throughout migration, i.e. they assume the conditions leading to (3.17). However, since the volume V_* of the food is infinite, the boundary condition (3.17) can be further reduced to $C_* = 0$ for all t. The interpretation of this is that, in an infinite extent of food, a uniform concentration can never be detectably different from zero, given that at any time the food contains a finite mass M_* of contaminant. Garlanda and Masoero show that

$$M_* = 2C_0 A\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}, \qquad (3.19)$$

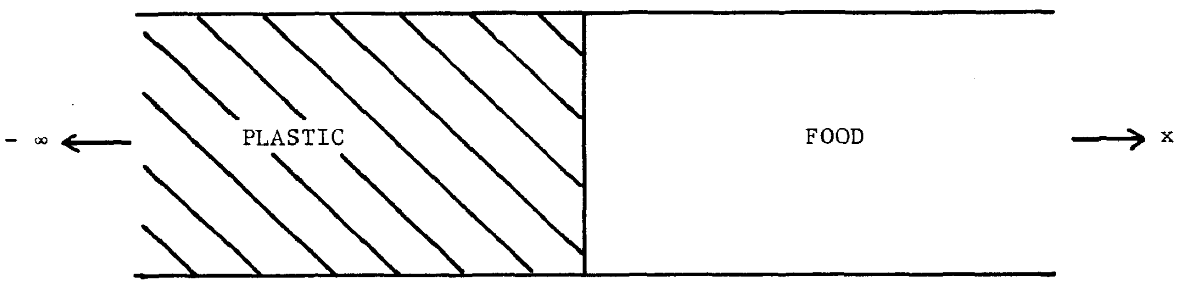

FIGURE 6

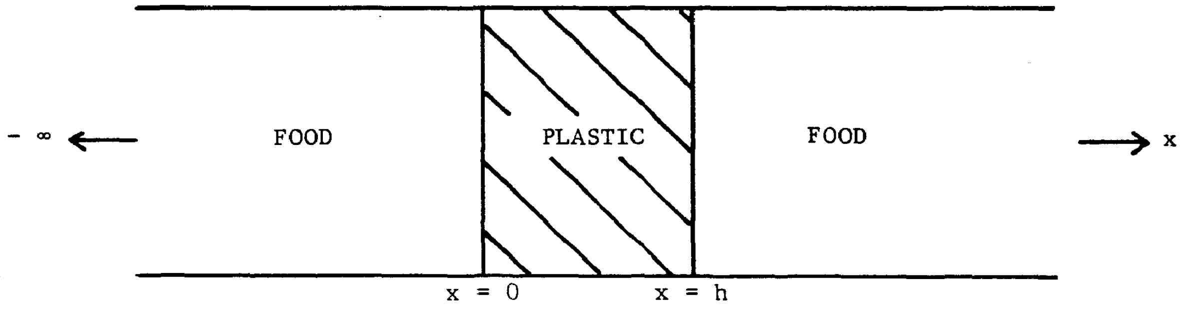

FIGURE 7

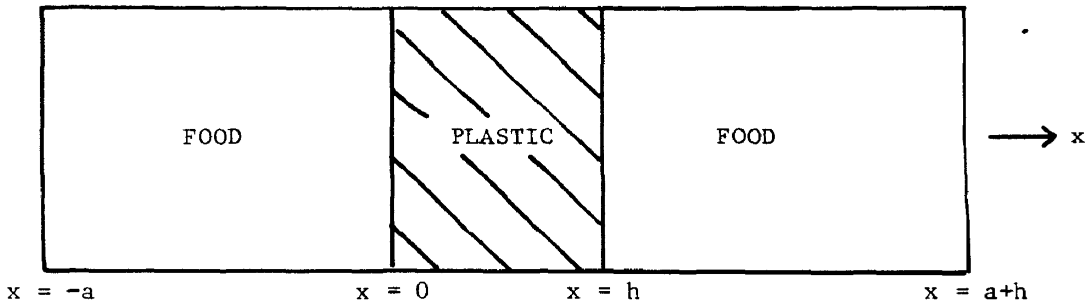

FIGURE 8

where A is the area of the interface and D is the diffusion coefficient of the contaminant in the plastic.

Despite the unrealistic nature of the geometry in Figure 6, there are two features of (3.19) that happen to apply in all situations where the model equations are as given in the earlier sub-section. First of all, M_* is proportional to C_0, the initial concentration of contaminant within the plastic. (This important result is also illustrated by the work in §§2.3 - 2.5 and in §3.2.) Secondly, M_* in (3.19) is proportional to $t^{\frac{1}{2}}$. This is <u>not</u> true for all t in more realistic situations than that illustrated in Figure 6 but, in fact, in all situations covered by the model equations, M_* is proportional to $t^{\frac{1}{2}}$ for sufficiently short times after migration starts. (This is illustrated by (2.15) in §2.4.)

The next situation considered by Garlanda and Masoero is shown in Figure 7. The plastic now has thickness h so that migration takes place across two interfaces ($x = 0$ and $x=h$). The food is still supposed to have infinite extent so that $C_* = 0$ for all t, where, as always, C_* is the concentration of contaminant within the food. The major difference from the situation of Figure 6 is that now there is only a finite mass of contaminant available for migration into the food. Indeed all the contaminant initially in the plastic eventually migrates into the food so that, finally, the total mass $M_{*\infty}$ of contaminant within the food is given by

$$M_{*\infty} = C_0 A h . \tag{3.20}$$

Garlanda and Masoero show that, at time t after migration starts, the mass M_* of contaminant within the food is given by the formula

$$M_* = M_{*\infty} \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-(2n+1)^2 \pi^2 \tau_+}}{(2n+1)^2} \right\}, \tag{3.21}$$

where τ_+ is a non-dimensional time defined by

$$\tau_+ = \frac{Dt}{h^2}, \tag{3.22}$$

i.e. like the second definition in (2.16), but with $\gamma = 1$ and h replacing

a. It can be shown that, for small values of τ_+, a good approximation to (3.21) is

$$M_* \approx M_{*\infty}.4\left(\frac{\tau+}{\pi}\right)^{\frac{1}{2}} = 4C_0A\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}. \qquad (3.23)$$

Given that there are now <u>two</u> interfaces, this is what would have been predicted from (3.19), and the interpretation of (3.23) is, of course, that in the early stages of migration, the fact that the plastic has finite thickness is irrelevant since it is contaminant near the interfaces that passes into the food.

Finally Garlanda and Masoero consider the situation shown in Figure 8. Now the food has finite extent, with total width 2a, and is symmetrically distributed about the plastic. They also assume that, at the interface, (3.18) holds, i.e. $C_*/C = \gamma$ for all t where γ is assumed to be the equilibrium partition coefficient. Eventually the concentration C_* of contaminant within the food is given by (3.4) with $V_*/V = 2a/h$. Thus $M_{*\infty}$, the total mass of contaminant that is finally in the food, satisfies

$$M_{*\infty} = \frac{C_0.2\gamma Aa}{1+\beta} = \frac{C_0Ah}{1+\beta^{-1}}, \qquad (3.24)$$

where the non-dimensional constant β is defined by

$$\beta = \frac{2\gamma a}{h}. \qquad (3.25)$$

It will be seen later that β can be interpreted as the ratio of the capacities of the food and the plastic for containing contaminant. It is the product of $\frac{2a}{h}$, the volume ratio, and γ, which is a measure of the relative "attraction" of the two media for the contaminant. For this case, Garlanda and Masoero do not give the formula for M_* for arbitrary t. This is rather surprising since they remark, quite correctly, that it has wider application than either (3.19) or (3.21). However the formula is given by Crank (1979), and is discussed in the specific context of migration by Reid, Schwope and Sidman (1983) and others. The result can be written in many forms, of which two are recorded here. First

$$M_* = M_{*\infty}\left\{1 - 2\beta(1+\beta)\sum_{n=1}^{\infty}\frac{\exp(-4q_n^2\tau_+)}{1+\beta+\beta^2q_n^2}\right\}, \qquad (3.26)$$

where τ_+, $M_{*\infty}$ and β are defined in (3.22), (3.24) and (3.25) respectively, and the q_n (n=1,2,...) are the positive roots in ascending order of magnitude of the equation

$$\tan q_n = -\beta q_n . \qquad (3.27)$$

Secondly, replacing τ_+ by $\tau = Dt/(\gamma^2 a^2)$ as in (2.16), (2.17) and (2.18) gives

$$M_* = M_{*\infty}\left\{1 - 2\beta(1+\beta)\sum_{n=1}^{\infty}\frac{e^{-\beta^2 q_n^2 \tau}}{1+\beta+\beta^2 q_n^2}\right\}, \qquad (3.28)$$

where the q_n continue to be defined by (3.27). (Note that (3.26) and (3.28) are not different results but a single result expressed in two slightly different ways.)

The result in (3.26), or (3.28), may well appear complicated to a non-mathematician but it is as straightforward to him/her as the formula of a protein expressed in terms of individual atoms is to a chemist. In both cases the symbolism used leads to a rather long expression in detail, but the professional can "see" the structure and form. The description of a typical house in terms of individual components would need much more length. The authors ask the reader to accept that the expressions do not involve very advanced or novel mathematics, and to continue into the discussion that follows which should clarify their meaning. The same comment applies to later expressions like (3.37).

Since e^{-s} tends to zero as s approaches infinity, it can be seen immediately from either formula that M_* tends to $M_{*\infty}$, as of course it should. Less obvious perhaps is the fact that (3.26), or (3.28), includes many of the earlier results given in this report as special cases. For example, consider the situation of Figure 7 which results from that of Figure 8 by letting a, i.e. β in. (3.25), approach infinity while keeping h fixed. For large β, the solutions of (3.27) are approximately those of $\cos q_n = 0$, remembering that $\tan q_n = \sin q_n/\cos q_n$. Thus $q_n \approx (2n+1)\pi/2$ (n = 0,1,2, ...). Moreover, when β is large, $2\beta(1+\beta) \approx 2\beta^2$ and $1+\beta+\beta^2 q_n^2 \approx \beta^2 q_n^2$. Thus, for large 6, (3.26) becomes (3.21) after some routine algebra. It has already been seen that (3.19) is a special case of (3.21), and therefore of (3.26). It can also be shown that when h approaches infinity keeping a fixed, i.e. when β in (3.25) approachess zero, the result in (3.28) approaches that in (2.8) which applies to the situation illustrated in Figure 2. In summary therefore, (3,26) – or (3.28) - includes all the cases of one-dimensional migration so far considered in this report. In particular, it may be noted here that for small values of τ or τ_+, and irrespective of the value of β, the result in (3.26) gives

$$M_* \approx 4C_0A\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}, \tag{3.29}$$

which would have been predicted from (3.23) - an approximation to (3.26) for large β - and from (2.15) - an approximation to (3.26) for small β when it is multiplied by 2 (because there are two interfaces in Figure 8). Equation (3.29) can be rewritten $M_* \approx C_0.2A.(4/\pi)^{\frac{1}{2}}(Dt)^{\frac{1}{2}}$ when it can be seen that in the early stages of migration, the material that passes into the food is from surface layers of thickness of order $(Dt)^{\frac{1}{2}}$. This result extends to plastic containers of arbitrary shape in the early stages of migration. It also has important implications in its own right, e.g. for repeat extraction tests with the same container. The result (3.29) eventually ceases to be valid because these surface layers increase in thickness and coalesce in the centre of the plastic; once that occurs the concentration in the plastic is everywhere less than C_0. These remarks apply directly to total immersion tests of e.g. global migration. Similarly (3.19) can be applied to one-sided extraction from a plastic film (with the other interface impermeable to contaminant) only for short times. It ceases to be applicable once $(Dt)^{\frac{1}{2}}$ becomes comparable with the film thickness and, consequently, when the contaminant concentration in the plastic is everywhere less than C_0.

Plotting results in dimensignless form

For the reasons given in §2.4, all the graphs in this report will be given in non-dimensional form. There remains some choice about the exact non-dimensional variables to use in a plot, and two possibilities are given in Figures 9 and 10. Crank (1979) points out that β, defined in (3.25), is simply related to the proportion of the total quantity of contaminant that is eventually in the food. This proportion is $M_{*\infty}/(C_0Ah)$, which from (3.24), is given by

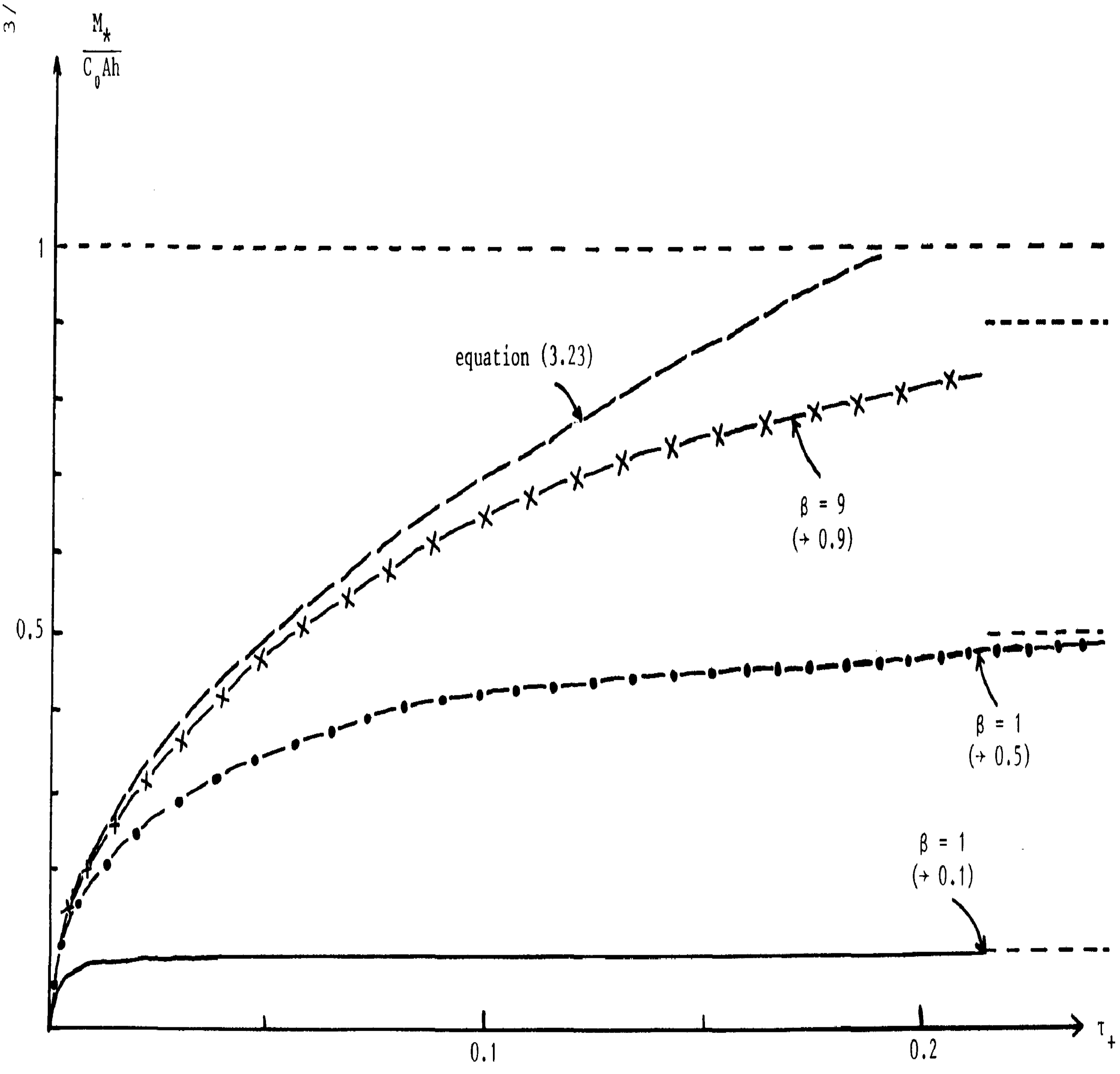

FIGURE 9. The behaviour of $M_*/(C_0Ah)$ predicted by (3.26) for 3 values of β, where τ_+ and β are defined in (3.22) and (3.25) respectively. Note that $M_{*\infty}$ in (3.26) is equal to $C_0Ah/(1+\beta^{-1})$ - see (3.24). Also shown is the approximate behaviour predicted by (3.23); evidently the accuracy of this approximation depends on β (as well as τ_+).

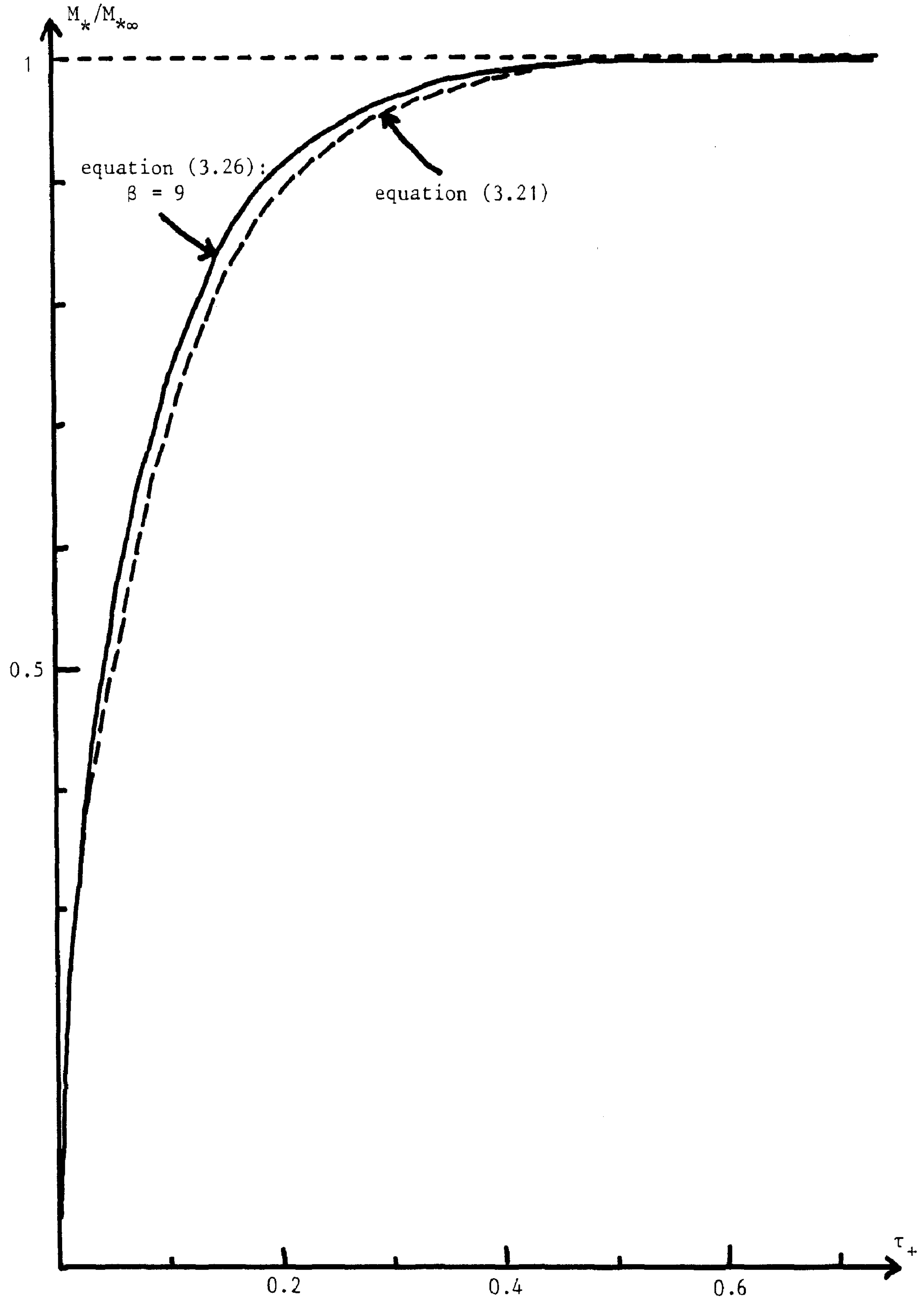

FIGURE 10. A comparison, for β = 9, of the exact result (3.26) with the approximation (3.21).

$$\frac{M_{*\infty}}{C_0Ah}=\frac{\beta}{1+\beta}. \tag{3.30}$$

(Recall, as noted before (3.24), that (3.30) is consistent with the discussion in §3.2 and with (3.4) in particular.) Figure 9 gives plots of $M_*/(C_0Ah)$ against τ_+ as predicted by (3.26) for three values of β, viz. 9, 1 and 1/9 corresponding to final uptakes of 90%, 50% and 10% respectively. Reid, Schwope and Sidman (1983) give more extensive graphs of the same relationship in Figures 4, 5 and 6 of their work. (There are certain differences between these figures and Figure 9 of this report. Their axes have logarithmic scales and there are trivial changes in notation. For example Reid, Schwope and Sidman use a for the present β and ψ for the present $4\tau_+$.) Figure 9 illustrates well the importance of the parameter β. For large values of β (which could be caused by a large value of the partition coefficient γ, or by a large value of the ratio a/h of the volumes of the food and plastic, or by both possibilities), the food is effectively a large reservoir for the contaminant so that equilibrium takes a long time to be achieved and a large proportion of contaminant is eventually transferred to the food. The converse statements hold when β is small as Figure 9 well illustrates. Also shown on Figure 9 is the approximation (3.29), and it is clear that it is adequate for a range of non-dimensional times τ_+ whose length increases with β, consistent again with the interpretation that the size of β is a measure of the capacity of the food as a reservoir for the contaminant.

Figure 10 compares the dependence of $M_*/M_{*\infty}$ on τ_+ for β =9 (as predicted by (3.26)) with that predicted by (3.21), already noted as an approximation to (3.26) for large β. Even for this relatively small value of β, the agreement is remarkably good.

In contrast with the presentation in §§2.3 - 2.6, the discussion above has been in terms of M_*, the mass of contaminant in the food, rather than C_*, its concentration. However the difference can be trivially accounted for because C_* approaches $C_{*\infty}$, where

$$C_{*\infty}=\frac{M_{*\infty}}{V_*}=\frac{\gamma}{1+\beta}C_0. \tag{3.31}$$

(It can easily be verified that this formula for $C_{*\infty}$ is, in the different notation, identical with (3.4). It will also be noted that $C_{*\infty}/C_0$ can be reduced, for a fixed γ, by increasing β, i.e. by increasing $V_*/V = 2a/h$.) Thus (3.26) can be rewritten as

$$\frac{C_*}{C_0} = \frac{\gamma}{1+\beta}\left\{1 - 2\beta(1+\beta)\sum_{n=1}^{\infty}\frac{e^{-4q_n^2\tau_+}}{1+\beta+\beta^2 q_n^2}\right\}, \qquad (3.32)$$

and other formulae above can be rewritten using the same technique. Among the many authors who have quoted one or more of the formulae above are Briston and Katan (1974), vom Bruck, Eckert and Rudolph (1976), Sanchez, Chang and Smith (1980), Messadi, Taverdet and Vergnaud (1983), Miltz and Rosen-Doody (1980) and Keinhorst and Niebergall (1986a). In most cases, many of the experimental results are apparently consistent with the quoted formulae. (Cases where there is clearly disagreement are not Class II systems, or there is chemical change.) We say "apparently" because, having quoted the formula(e), most authors do not give the experimental values of the parameters in the formulae, and the reader is consequently unable to check the agreement (or otherwise) between theory and experiment. This point has been made previously by one of the authors of this report (Katan 1979); unfortunately that recommendation has not been generally followed and practice that is (frankly) unprofessional continues, although there are welcome signs of recent improvement. A further criticism of many papers, including those cited above, is that the graphs are not plotted in non-dimensional form and therefore, as explained in §2.4, can only be used for the specific trio of food/polymer/contaminant for which the data were measured.

Fortunately there are exceptions to the strictures made above. These include Reid, Schwope and Sidman (1983) who give many practical numerical examples. In general, values of β for these examples are much less than 1. For one case (water/polystyrene/styrene monomer at 40°C(313K)) the values of γ, a and h were 3.3×10^{-4}, 3.1×10^{-3}m and 1.2×10^{-4}m, giving $\beta = 2\gamma a/h \approx 1.7 \times 10^{-2}$. Sometimes higher values of β occur; in another case (50% aqueous ethanol/polystyrene/styrene monomer at 40°C(313K)) γ, a and h were 7.1×10^{-3}, 1.05×10^{-2}m and 9.3×10^{-5}m,

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[*] Reid, Schwope and Sidman actually quote a value of 1.6×10^{-2} for β; while this is not consistent with the values they give for γ, a, h (which are quoted above), the difference is not important.

giving $\beta \approx 1.6$. A value of β of order 10 can be inferred from experiments reported by Messadi, Taverdet and Vergnaud (1983) in which 20 circular discs of a commercial PVC compound containing dioctyl phthalate as a plasticiser were immersed in 2×10^{-4} m^3(200ml) of two food simulant liquids (n-heptane and peanut oil). It is stated that γ "was found to be about 1", and each disc had radius 9×10^{-3}m and thickness 3.4×10^{-3}m, giving $\beta \approx V_*/V \approx (2 \times 10^{-4})/(20 \times \pi \times 81 \times 10^{-6} \times 3.4 \times 10^{-3}) \approx 11.6$.

Results for immobile foods

All the models considered so far have assumed that the food is "well-mixed", i.e. that the concentration C_* of contaminant in the food is uniform. As noted above in the discussion following (3.15), this can occur because the diffusion coefficient D_* of the contaminant in the food is much greater than D, or because the food is liquid and is in convective motion. (Messadi, Taverdet and Vergnaud (1983) and others discuss the effect of stirring and show it to be significant.) For completeness, we record now another special solution which applies when there is no motion in the food, and when no assumption is made about the relative magnitudes of D and D_*. For example, this solution is likely to apply to many cases where the food is solid. The geometry is that of Figure 8 and, for clarity, the equations, and boundary and initial conditions, will on this occasion be listed in full. As usual the concentrations of contaminant in the plastic and the food are denoted by C and C_* respectively where, now, C_* (as well as C) depends on x. Both C and C_* still of course depend on t. The equations governing C and C_* are

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \text{ for } 0 < x < h ; \quad \frac{\partial C_*}{\partial t} = D_*\frac{\partial^2 C_*}{\partial x^2} \text{ for } -a < x < 0 \text{ and } h < x < a + h . \tag{3.33}$$

No contaminant is lost from the system so that - see (3.13a) -

$$D_*\frac{\partial C_*}{\partial x} = 0 \text{ at } x = -a \text{ and } x = a + h . \tag{3.34}$$

At each interface (x = 0 and x =h) we have - see (3.15) and (3.18) -

$$D\frac{\partial C}{\partial x} = D_*\frac{\partial C_*}{\partial x} \text{ and } C_* = \gamma C . \tag{3.35}$$

Finally there is the normal initial condition, viz.

$$C = C_0 \text{ and } C_* = 0 \text{ at } t = 0 . \tag{3.36}$$

It can then be shown after some algebra that

$$M_* = M_{*\infty}\left\{1-2\left(\frac{1+\beta}{\beta}\right)\sum_{n=1}^{\infty}\frac{\tan^2 q_n . e^{-4q_n^2\tau_+}}{q_n^2[(1+\beta)+(1+\alpha^2\beta)\tan^2 q_n]}\right\}, \qquad (3.37)$$

where $M_{*\infty}$, β and τ_+ have their usual meanings and are defined in (3.24), (3.25) and (3.22) respectively, and α is another non-dimensional constant defined by

$$\alpha = \frac{1}{\gamma}\left(\frac{D}{D_*}\right)^{\frac{1}{2}}. \qquad (3.38)$$

Finally, it is necessary to know that the q_n ($n = 1,2,...$) in (3.37) are the positive roots in ascending order of magnitude of the equation

$$\alpha \tan q_n + \tan \alpha\beta q_n = 0. \qquad (3.39)$$

One of the outcomes of the algebra leading to (3.37) is an expression giving the dependence of C_* on x (and t). This is more complicated than (3.37) and will not be given here. It is sufficient to note now that the <u>average</u> concentration $\overline{C_*}$ of contaminant in the food at time t is $M_*/V_* = M_*/(2Aa)$.

Whilst it seems unlikely that (3.37) is an original result, we are not aware of a previous derivation, nor has it apparently been used in work on migration. (However Carslaw and Jaeger (1959) discuss many solutions of the same type in the context of heat conduction.) It is useful briefly to note certain properties of (3.37). The value of $M_{*\infty}$ is, of course, given by the simple theory of §3.2 and is independent of D and D_*. For small values of τ_+, it can be shown that

$$M_* \approx \frac{4C_0A}{1+\alpha}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}; \qquad (3.40)$$

this result is given by Reid, Sidman, Schwope and Till (1980). Comparison of (3.40) with (3.29) shows that when D_*/D is large, i.e. when $\alpha << 1$, these results are approximately the same as, indeed, they should be. For larger values of α, the diffusion in the food is less rapid and M_* is a factor $(1+\alpha)^{-1}$ less than when the food is well-stirred. In the extreme case, when α is very large, the early time approximation (3.40) can itself be approximated by

$$M_* \approx 4(\gamma C_0)A\left(\frac{D_* t}{\pi}\right)^{\frac{1}{2}}, \tag{3.41}$$

and this is a result which forms an interesting counterpoint to (3.29) since, in this limit, the concentration in the plastic is uniform and the migrated contaminant (with concentration γC_0) occupies a layer of thickness of order $(D_* t)^{\frac{1}{2}}$ within the food (Reid, Sidman, Schwope and Till 1980). A possible practical application of (3.41) is to the migration of plasticiser from PVC film into cheese (Sandberg and Vaz 1984; Ashby 1986). In discussing (3.26) above, it was noted that it included many earlier results as special cases; likewise (3.37) is the most general result so far obtained and can be shown to include (3.26) as a special case for $\alpha \ll 1$.

There is a separate special case of (3.37) that is given explicitly by Reid, Sidman, Schwope and Till (1980, equations (23) to (25)[*]). This special case is when the plastic is effectively infinite in extent, i.e. the set-up at each interface is as in Figure 2, and can be obtained from (3.37) by letting $\beta \to 0$ appropriately. (The reader should note once more that there are differences of notation between the present report and Reid, Sidman, Schwope and Till's work. In particular our parameter β plays no role in their 1980 paper since the plastic is there taken to be effectively infinite throughout, and our parameter α is the reciprocal of what they call β.) In the present notation, the special case of (3.37) when the plastic is effectively infinite (very small β) is written in the following form by Reid, Sidman, Schwope and Till (1980):

$$M_* = M_{*\infty}\left(\frac{2\alpha}{1+\alpha}\right)\left(\frac{\tau_*}{\pi}\right)^{\frac{1}{2}}\left\{1-\left(\frac{2\alpha}{1+\alpha}\right)\sum_{n=1}^{\infty}\left(\frac{1-\alpha}{1+\alpha}\right)^{n-1} f\left[\frac{n}{\tau_*^{\frac{1}{2}}}\right]\right\}, \tag{3.42}$$

where τ_+ is another non-dimensional time defined by

$$\tau_* = \frac{D_* t}{a^2}, \tag{3.43}$$

and, for any quantity u (where, in (3.42), $u = n/\tau_*^{\frac{1}{2}}$),

$$f(u) = e^{-u^2} - \pi^{\frac{1}{2}} u \operatorname{erfc} u, \tag{3.44}$$

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[*] Unfortunately this result is misquoted in equation (36) of Reid, Schwope and Sidman (1983).

with the function erfc defined in (2.2). Actually, in the course of deriving and investigating (3.37), an alternative (and more elegant) way of writing (3.42) was discovered, namely

$$M_* = M_{*\infty}\left\{1-\frac{2\alpha}{\pi}\int_0^\infty \frac{\sin^2 u}{u^2(\sin^2 u+\alpha^2\cos^2 u} e^{-u^2\tau_*} du\right\}. \qquad (3.45)$$

(It may reassure the reader who is not a mathematician to learn that it is *not* obvious to a mathematician that (3.42) and (3.45) are different ways of expressing the *same* result, or that either is a special case of (3.37). Establishing these results requires fairly sophisticated mathematical techniques.) In practice, (3.42) and (3.45) are of complementary value since they will be useful for small and large values of τ_+ respectively.

Reid, Sidman, Schwope and Till (1980) discuss typical values of the parameter α, and argue that (3.37) - or (3.42) - should be used instead of (3.26) (or one of its special cases) for values of a *greater* than about 0.1 or 0.2. They base.this conclusion on graphs of (3.42) in Figure 2 of their paper and they remark that α is normally much less than 0.1 for *solid* oily foods, but that (because of low values of γ) values of α greater than 0.1 are often encountered with *solid* "watery" foods. Time has not permitted use of a computer to obtain numerical results from (3.37) and it is recommended that this task should be undertaken, with the major aim of refining (if necessary) the estimates by Reid, Sidman, Schwope and Till (1980) of the values of a for which (3.37) should be used instead of (3.26). (In this context it will be noted that the term in curly brackets in (3.37) is a function of *two* non-dimensional constants α and β, as well as of non-dimensional time τ_+, whereas - for geometrical reasons - (3.42) involves only one non-dimensional constant α. It would therefore be expected in general that the values of α for which (3.37) is significantly different from (3.26) would depend on β.)

Models involving a mass transfer coefficient

The concept of a "well-mixed" *liquid* food is discussed further by Reid, Sidman, Schwope and Till (1980) and by Reid, Schwope and Sidman (1983). On the basis of the immediately preceding work, it would seem natural to argue that a liquid food is "well-mixed" (in the sense that the contaminant within it can be regarded as being of uniform concentration) if $\alpha = \gamma^{-1}(D/D_*)^{\frac{1}{2}}$ is less than about 0.1 or 0.2. However these authors adopt another criterion. They assume that the degree of resistance of the food to the migrating contaminant can be quantified by a constant mass transfer coefficient k (a quantity with the units of velocity). Suppose that the food occupies the region x > 0 and is of infinite extent so that, as discussed above before (3.19), the concentration in the bulk of the food can be taken as zero for all t. Then instead of (3.13a) and (3.18), the interface condition at x = 0 is taken to be

$$D\frac{\partial C}{\partial x} = -k\gamma C \text{ at } x = 0 \text{ for all } t\ . \tag{3.46}$$

This is an empirical relationship with little support from fundamental scientific principles. It is explained by reference to the motion of the liquid food and, in particular, to the concept of a boundary layer of thickness δ adjoining the interface where $k = D_*/\delta$. The size of δ is dependent on the liquid motion in an unspecified way and it is stated that "values of k are normally estimated from generalized correlations"(Reid, Schwope and Sidman 1983) . The boundary layer inhibits the transfer of migrated contaminant into the bulk of the food so that large values of δ (small values of k) represent the case of large resistance to migration. Other authors who have used the same concept include Chan, Anselmo, Reynolds and Worman (1978), Sanchez, Chang and Smith (1980), and Zieminski and Peppas (1983a).

For the geometry of Figure 6 (infinite plastic and food with one interface), use of (3.46) gives (Crank 1979)

$$M_* = \frac{DC_0A}{k\gamma}\left\{\exp\tau_k \operatorname{erfc}\tau_k^{\frac{1}{2}} + 2\left(\frac{\tau_k}{\pi}\right)^{\frac{1}{2}} - 1\right\}, \tag{3.47}$$

where the new non-dimensional time τ_k, is given by:

$$\tau_k = \frac{k^2\gamma^2 t}{D}. \tag{3.48}$$

(In the notation of Reid, Sidman, Schwope and Till (1980) and Reid, Schwope and Sidman (1983), our τ_k is their γ^2.) For small values of τ_k, it is easy to show that (3.47) reduces to

$$M_* \approx K\gamma C_0 At\,. \tag{3.49}$$

The expression for M_* for the geometry of Figure 7 (finite plastic and infinite food with two interfaces) is also given but will not be recorded here. It is sufficient to note that (3.49) again holds (when multiplied by 2 because there are now two interfaces) for small values of τ_k. For large τ_k, on the other hand, (3.47) becomes

$$M_* \approx 2C_0 A\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}, \tag{3.50}$$

which is exactly (3.19). For large times therefore the extent of the migration is independent of the value of k.

Reid, Schwope, Sidman and Till (1980) and Till, Reid, Schwartz, Sidman, Valentine and Whelan (1982) discuss some experimental evidence to support (3.47) which, in particular, illustrates that M_* is proportional to t, rather than $t^{\frac{1}{2}}$, for small τ_k, but that the rate of growth slows down for larger τ_k, consistent with (3.50). On the basis of this limited evidence, Reid, Schwope and Sidman (1983) propose that solutions like (3.47) that are derived by use of (3.46) - rather than (3.13a) and (3.18) - should be employed for predicting migration in liquid foods only for values for τ_k such that $\tau_k^{\frac{1}{2}} < 10$. They indicate that this condition is rarely encountered in practice but one important exception is noted, namely aqueous food/plasticized PVC/adipate (or phthalate) esters. The numerical examples quoted show furthermore that the differences between (3.47) and the corresponding solutions based on (3.13a) and (3.18) are noticeable only when the concentrations of contaminant in the food are extremely low. Given the empirical nature of (3.46) and the difficulty of *a priori* estimation of k, the authors of this report conclude that the use of (3.46) in practical predictions of migration into liquid food for Class II systems simply introduces unnecessary complications, and we believe that this conclusion could only be changed if it were contradicted by substantially more data than are currently available*.

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*There can be no dispute in qualitative terms with the basic physical idea that motivates (3.46), namely the influence of a liquid boundary layer. Our scepticism is about the practical importance of this phenomenon and, incidentally, about the quantitative accuracy of (3.46). For instance, there is little reason why k should be a constant; this is in fact acknowledged by Reid, Sidman, Schwope and Till (1980,p.586).

Concluding comments on models of Class II systems

Essentially all the mathematical models that have appeared in the literature have now been presented and discussed; in addition a new solution, viz. (3.37), that includes many others as special cases has been derived. In concluding this section of the report, there are two recurrent points that, even at the risk of undue repetition, we wish once more to emphasize. In the first place, all the solutions are for plane geometries only, i.e. they have quantitative relevance to very few real migration problems since commercial plastic containers are rarely plane. Exceptions exist, e.g. some flat packets of cooked meat and cheese; furthermore the results of the models seem likely to apply reasonably well to migration in many of the test cells used in laboratories. Nevertheless it is difficult to understand - and impossible to condone - the failure of mathematical modellers of migration to derive results for more realistic geometries. The work in §§2.3 - 2.5 shows unambiguously that different geometries lead to significant differences in migration behaviour even when there are no changes in the materials involved. Whilst there would be no real difficulty in deriving the analogues of most of the results in this section for cylindrical and spherical geometry, these results would also be special. The real need is for numerical solutions of migration models for realistic geometries. Secondly, most of the papers on migration that have been studied in preparing this report contain very little, if any, mathematics and, in general, the few to which this comment does not apply have inadequate connections between the mathematics and the experimental results. The latter are not usually plotted in non-dimensional form, and it deserves emphasis that this should be done even when the authors of the papers have no direct or immediate concern with mathematical models. Also insufficient details are given to enable the reader to make his/her own comparison between theory and experiment. In some papers the situation is even worse; some mathematical formulae are given but are not used, nor even referred to, subsequently!

§3.4 Mathematical models of Class III systems

Introductory remarks

In §1.2 Class III systems were defined (Katan 1971) as those in which the migration of the contaminant is controlled by the food. While the implication of this definition is that migration is negligible in the absence of food, it is possible in this report on mathematical models of migration to be slightly more flexible by requiring simply that the presence of the food substantially increases migration. In fact all models of Class III systems have dealt with one type, namely that in which the food (or food simulant) is liquid and penetrates the plastic, with consequent changes in its physical properties. The penetration may, or may not, be accompanied by substantial swelling of the plastic. In what is apparently the first paper on the theory of Class III systems, Knibbe (1971) describes the features that all subsequent modellers have incorporated. There is a "sharp front" between the part of the plastic (adjacent to the original food/plastic interface) that has been penetrated by food, and the part that has not. This front advances into the plastic as time increases, and within the penetrated plastic (i.e. behind the front) the transfer of contaminant is greatly enhanced relative to what occurs in the original. Whilst Knibbe (1971) and Katan (1971) both assume that no migration takes place in the absence of penetration (i.e. that $D = 0$ or $\gamma = 0$ in the notation of §3.3), this assumption is unnecessarily restrictive and has not been made by some subsequent modellers. Other useful qualitative discussions of migration in Class III systems are given by Figge (1980)[*] and Shepherd (1982).

Mathematical models

Figure 11 illustrates the situation considered by Knibbe (1971) and Katan (1971), where b(t) denotes the penetration distance at time t after migration starts[†]. Both authors cite experimental evidence which is stated

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[*] However Figge's paper contains an instructive non-sequitur in its discussion of its Figures 3 and 4 on its pp.190-192. On the abscissae are plotted times in units of hours and days, and not non-dimensional times. Understandably therefore the graphs in these Figures of migration for different systems are different, but it cannot be judged from these Figures whether the graphs would be different if plotted in appropriate non-dimensional form. Therefore these Figures cannot legitimately be used to claim that certain food simulants are unsuitable (although that conclusion may well be correct).

[†] It is actually unclear what the precise definition of b(t) is. The point of this remark is that in certain circumstances the penetration front is not "sharp" in the mathematical sense, whereas in others it is. See p. 122 of Crank (1979).

to support the theoretical prediction that

$$b(t) \ \infty (Kt)^{\frac{1}{2}} \qquad (3.51)$$

where K is a constant with the same units (m^2s^{-1}) as an ordinary diffusion coefficient. Knibbe assumes without discussion that the penetration is a diffusion process, and emphasizes that the diffusion coefficient is "strongly dependent" on the concentration of the food in the plastic. He does not state what he assumes about this dependence but writes that K in (3.51) is proportional to the maximum value of the diffusion coefficient. It seems unlikely that (3.51) holds for all possible dependencies, especially in more realistic geometries than that of Figure 11, but a full mathematical treatment of the point would be very difficult, if not impossible. Some of the later models use different formulae than (3.51).

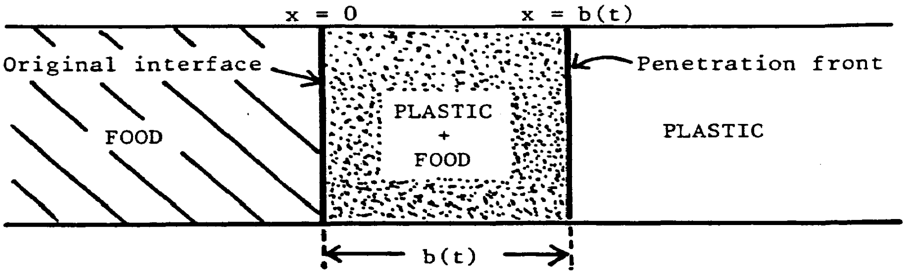

FIGURE 11

Knibbe now supposes that the migration of contaminant in the penetrated plastic is a diffusion process with diffusion coefficient D_+, where D_+ depends on the concentration of the food in the plastic. He considers two possibilities. When D_+ is much less than K, the penetration front advances much more rapidly than the migration front so that all the migrated contaminant originates in the penetrated region. Provided D_+ can be regarded as constant, it is then possible to use (3.19) so that

$$M* = 2C_0 A\left(\frac{D+t}{\pi}\right)^{\frac{1}{2}} \quad , \qquad (3.52)$$

where - as usual – M_* is the mass of contaminant in the non-penetrated food at time t. (For two-sided extraction (3.52) has of course to be doubled, and it is assumed both that the food is well-mixed and that the food and the plastic are effectively infinite.) Knibbe discusses the assumption that D_+ in (3.52) is constant, arguing that, although D_+ increases with the quantity of penetrated food, so also does the thickness of the penetrated plastic due to "swelling" and that these two effects are in balance so that both D_+ and the thickness of the penetrated plastic can be regarded as constant. Unfortunately when $D_+ << K$ the thickness of the penetrated plastic does not enter the expression for M_* in (3.52) and this argument seems invalid. (Expansion does of course cause a reduction in the concentration of the contaminant but this can be incorporated trivially into (3.52) by redefining C_0 to be the concentration in the penetrated plastic rather than the original plastic.) Katan (1971) avoids use of (3.52) by arguing that it is prudent for safety evaluation to suppose that all the contaminant in the region of penetrated plastic has migrated into the food; this gives

$$M * C_0 \, Ab(t) \quad , \tag{3.53}$$

and is obviously (and deliberately) an over-estimate. The second case considered by Knibbe is when D_+ is comparable with or greater than K. In this case migration occurs relatively fast and contaminant from all the penetrated plastic is involved in migration. Some graphs in Knibbe's paper illustrate the type of migration behaviour then expected. Penetration becomes unimportant for values of D_+ much greater than K, and predictions can be made as for Class II systems.

The basic ideas used in the work by Knibbe and Katan were incorporated in. two more complicated models by Frisch (1978) and Rudolph (1979). These models have differences of approach but, in our judgement, both merit further attention here. Unfortunately neither Frisch nor Rudolph seems aware of the work of the other!

Both authors consider the geometry of Figure 11, and suppose that all the mass transfer processes are diffusion processes. Frisch (1978) assumes that the region occupied by pure food ($x < 0$) is well-mixed, and also treats the region occupied by plastic, and by plastic plus food, as one single region within which the concentration of food c varies from its equilibrium solubility value c_s at the interface $x = 0$ to zero far away from the interface (i.e. $x \rightarrow \infty$). (Where necessary in this section lower case letters will be used to denote properties of the food in the plastic that have been denoted by the corresponding upper case letters for properties of the contaminant; in particular c and d will denote the concentration and diffusion coefficient, respectively, of the food in the plastic.) Thus Frisch's model does not include the sharp front as an <u>explicit</u> feature. However it could be obtained from his general model equations by considering appropriate limits. The model includes variable diffusion coefficients so that the equation for c(x,t) is (3.8) in the present report, viz.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(d \frac{\partial c}{\partial x} \right) , \qquad (3.54)$$

with the obvious boundary and initial conditions which are

$$c(0,t) = c_S , \; c(\infty,t) = 0, \; c(x,0) = 0 \qquad (3.55)$$

Similarly the equation used for the contaminant concentration C(x,t) is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right) , \qquad (3.56)$$

With

$$C(0,t) = 0 \; , C(\infty,t) = C_0 \; , \; C(x,0) = C_0 \qquad (3.57)$$

The first condition in (3.57) is the same as that used for the geometry of Figure 6 and applies because $C_* = 0$ throughout the food for all t for the reason given in the discussion preceding (3.19). Frisch now supposes that d and D are functions of c; specifically he takes

$$d = d_0 \exp\left[\sigma(\frac{c}{c_S} - 1) \right] \; , D = \mu d_0 \; \exp\left[\sigma \nu (\frac{c}{cs} - 1) \right] \; , \qquad (3.58)$$

where d_0 is the value of d when $c = C_S$, and σ, μ, ν are positive dimensionless constants whose values, like d , depend on the specific materials in the system. (Frisch uses the notation D_S , β, α and a for what in our notation are d_0 , $\frac{\sigma}{C_S}$, μ and ν respectively.) Justification for (3.58) is given in the paper. Wagner (1952) showed how the solution of (3.54) and (3.55) could be obtained numerically (no simple formula exists), and Crank (1979, pp.112-117) gives a lengthy summary of Wagner's work with a table (Table 7.3 on p.384) from which good approximations can be obtained. When c(x,t) is known so is D via the second equation in (3.58). Hence (3.56) can be solved for C(x,t) as Frisch shows; of course the results are available only in numerical form. It is then possible to determine the flux (i.e. the rate of transfer) of contaminant into the food, and Frisch gives an expression for this. By integrating this expression with respect to t it follows that

$$M_* = \phi(\sigma,\mu,\nu)\, AC_0(d_0 t)^{\frac{1}{2}} \quad , \qquad (3.59)$$

where the function ϕ can be determined from Wagner's and Frisch's work for any values of α, μ, v. Whilst it is not appropriate nor necessary to give numerical details here, there is one interesting special case that is worth attention. Frisch suggests that contaminant molecules are sometimes much larger than food molecules so that $D/d = \mu$ is small; he therefore states that, in certain special cases, μ is less than 10^{-2}, and shows that $\phi(\sigma,\mu,\nu) \approx 2(\mu/\pi)^{\frac{1}{2}}$ for such small values of μ, so that (3.59) reduces to

$$M_* \approx 2C_0 A \left(\frac{\mu d_\circ t}{\pi}\right)^{\frac{1}{2}} . \qquad (3.60)$$

Since, according to (3.58), μd_0 is the value of D at the interface (where $C = C_S$), this result is very reminiscent of (3.52) and of earlier results for Class II systems like (3.19), as would be expected. Frisch shows further that (3.60) can be written

$$M_* \approx M_{*0} e^{\frac{1}{2}\sigma} \quad , \qquad (3.61)$$

where M_{*0} is the value of M_* when the food is insoluble in the plastic, i.e. when the system is behaving as a Class II system. Since $e^{\frac{1}{2}\sigma} > 1$ for all positive α, (3.61) shows clearly that food penetration enhances the migration, and this provides a consistency check on his model. Frisch considers some other special cases in his paper but gives no comparison with any data, and we are not aware of any subsequent attempt - which seems unfortunate.

There are several differences between Frisch's work and that of Rudolph (1979), but, as already noted, Rudolph also assumes the geometry is that in Figure 11. However Rudolph supposes that the diffusion coefficient d of the food in the plastic is a constant and the appropriate solution of (3.54) then has the well-known form

$$C(x,t) = k_1 \operatorname{erf}\left\{\frac{x}{2\sqrt{dt}}\right\} + k_2 \quad , \tag{3.62}$$

where k_1 and k_2 are constants to be determined by the boundary conditions. Rudolph supposes that at x = 0, the concentration of the food in the plastic is a constant, say γ_0, times the concentration, say C_0 , of the uncontaminated food. He thus extends the partition coefficient concept of (3.18) to the food. This yields $k_2 = \gamma_0 C_0$ on substitution in (3.62). The position of the sharp front at x = b(t) - see Figure 11 - is determined by assuming that there is an abrupt discontinuity there at which c falls from C_1 to zero. This leads to $k_1 = -C_1\lambda\sqrt{\pi}\exp(\lambda^2)$ where the non-dimensional constant λ is the solution of the equation

$$\gamma_0 C_0 - C_1 = C_1 \lambda \pi^{\frac{1}{2}} \exp(\lambda^2) \operatorname{erf}\lambda \quad , \tag{3.63}$$

and the position of the front is given in terms of λ by

$$b(t) = 2\lambda(dt)^{\frac{1}{2}} \quad . \tag{3.64}$$

Before proceeding it is important to make two comments. First, there is a sign error in equation (20) of Rudolph's paper; this is the equation in his paper that corresponds to (3.63) . Secondly, while (3.63) has to be solved numerically for λ for given values of c_0 and c_1 , Rudolph does not indicate how c_1 is to be determined. (Of course c_0 is fixed by the food.) This seems to us to be a severe shortcoming of his work. It is more satisfactory to adopt a second possibility which Rudolph refers to on p.1710 of his paper, namely to suppose there is no jump in concentration. This means that $c_1 = 0$ and that

$$C(x,t) = \gamma_0 C_0 \left[1 - \operatorname{erf}\left\{\frac{x}{2\sqrt{dt}}\right\}\right] . \tag{3.65}$$

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*The differences in notation between Rudolph's original paper and this report are so numerous that they are not listed here; it is hoped that no confusion results.

In mathematical terms there is now no sharp front. However, in practical terms, there is at any time t only a region of finite thickness within which c is effectively non-zero. The point is that for any given method of chemical analysis there is a limit, say c_L , such that concentrations below c_L are undetectable and are therefore recorded as zero. From (3.65) it now follows that c is detectably non-zero only for $x < b_L(t)$, where

$$b_L(t) = 2\lambda_L(dt)^{\frac{1}{2}} \quad , \tag{3.66}$$

and the non-dimensional quantity λ_L is the solution of the equation

$$\operatorname{erf} \lambda_L = 1 - \frac{C_L}{\gamma_o C_0}. \tag{3.67}$$

Therefore, even when there is no sharp front, measurements would, in effect, indicate the existence of one, and its rate of advance depends on d and t exactly as if there were a sharp front and (3.64) held. (The reader may wish to refer again to the footnote associated with the text immediately before (3.51).) In summary, the question of whether a sharp front exists is much less important than the order of magnitude in practical terms of the thickness of the penetrated region, and all models so far considered predict that this is proportional to t , as in (3.51) and (3.64).

Rudolph (1979) now deals with the concentration of contaminant. He assumes standard diffusion processes, with constant diffusion coefficients in the non-penetrated food and in the unpenetrated plastic, and a diffusion coefficient in the penetrated plastic that depends on c(x,t), the concentration of food in the plastic discussed above. His boundary and initial conditions are standard, i.e. they are based on (3.18) and conservation of mass. In formal mathematical terms the distribution of contaminant concentration can be found everywhere; naturally the formula contains an integral involving the variable diffusion coefficient in the penetrated plastic which can be evaluated only when the dependence of this coefficient on c is prescribed. The algebraic details are routine, but fairly lengthy and complicated, and reference can be made to the original paper if required. From the point of view of migration, the important result is that $M*$, the mass of migrated contaminant at time t, satisfies

$$M* = 2\psi C_0 A\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \quad , \tag{3.68}$$

where D is as usual the diffusion coefficient of the contaminant in the pure plastic, and ψ is a non-dimensional constant which depends on all the material properties (e.g. diffusion and partition coefficients, C_0/C_1) and can be determined when these are known (and when the dependence of the diffusion coefficient on c is prescribed) by the methods given by Rudolph. Some typical graphs are given in Rudolph's paper.

More importantly the Hamburg group to which Rudolph belongs has made extensive comparisons of his theory with their experimental data (vom Bruck, Rudolph, Figge and Eckert 1979; Figge and Rudolph 1979; Figge 1980; vom Bruck, Figge and Rudolph 1981). It was found that the migration results for a wide range of systems in which the food penetrated the plastic could be fitted by curves predicted from Rudolph's theory. Figge (1980) explains that the measurements were used to select the unknown constants in Rudolph’s theory, using trial and error, so that the resultant theoretical curves gave a good fit to the data. Such constants included the partition coefficients, the diffusion coefficients of the food and the contaminant in the unpenetrated plastic, and the constant λ in (3.63). Of course this method of selecting unknown theoretical parameters from data is commonly used, but it does nothing to solve the major problem of how the theory can be used subsequently to make acceptably accurate predictions for new systems. In particular the method, when adopted in the present situation, does nothing to explain how the concentration c_1 in (3.63) is determined. Careful study of Figure 34 in Figge (1980) shows in fact little evidence that there is a <u>sharp</u> front between the penetrated and unpenetrated plastics, thus providing support for the earlier remarks associated with (3.65) and (3.67). In particular, Rudolph's algebra, like that of Knibbe (1971), Katan (1971) and Frisch (1978), supports the comment after (3.67) above that what matters in practice is the order of magnitude of the thickness of the penetrated region, not whether there is a sharp front. There is one other general point that ought to be made, namely that the <u>number</u> of unknown constants that have to be selected is so high that reasonable agreement between theory and experiment is almost guaranteed. Figge (1980) does not explain how the dependence of D, the diffusion coefficient of the contaminant in the penetrated plastic, on c, the concentration of food, is determined, but he indicates that the curves shown in his Figure 34, for the system tricaprylin/HDPE/BHT, were obtained by using the formula

$$D = D_0 + kc \quad , \qquad (3.69)$$

where the values of the constants D_Q (the diffusion coefficient of BHT in the unpenetrated HDPE) and k were determined from the data. The expression in (3.69) is of course derived in standard fashion from the Taylor series expansion of D about c = 0; this technique is widely used throughout physics, e.g. in using virial coefficients for gases. All the data of the Hamburg group using tricaprylin/HDPE or plasticized PVC/additive could be fitted by Rudolph's theory.

However Figge (1980) notes that the theory could not fit data taken with any system of the form tricaprylin/HIPS/additive, a system in which penetration of the food was stated to be accompanied by significant swelling of the plastic. (See Figure 32 and the bottom of p. 234 of Figge's paper.) In a later theoretical paper Rudolph (1980) extended his earlier work to allow the penetrated plastic to swell into the region originally occupied by pure food. Mathematically, the model has very similar structure to the earlier one by Rudolph that was summarized immediately above, and it can be criticized in the same way. Vom Bruck, Figge and Rudolph (1981) appear to indicate (although the wording is not clear) that Rudolph's (1980) model can be fitted to the data from the tricaprylin/HIPS/additive system that the earlier model could not allegedly cope with.

In essence all authors since 1971 have extended, but not developed in any significant way» the basic framework laid down then by Knibbe and Katan. For completeness, it should also be noted that some papers (Peterlin 1977; Enscore, Hopfenberg and Stannett 1977; Astarita and Sarti 1978; Joshi and Astarita 1979) have dealt with the penetration of the plastic by the food and the consequent swelling, but did not consider the implications for migration. It seems to the authors of this report that the work in some of these papers may ultimately provide a more useful framework for predicting migration in Class III systems than does, for example, that of Rudolph, but much more research (both theoretical and experimental) needs to be done to establish the truth (or otherwise) of this opinion.

A phenomenon, not strictly in Class III behaviour as defined above, that has certain similarities with penetration of the plastic by the food is change in the plastic structure due entirely to migration of an additive; any penetration of the plastic by food is relatively minor, or a secondary effect which can be considered separately. The phenomenon is important because it occurs with plastic softeners (plasticizers, impact modifiers etc.), e.g. PVC flexible film and RCF, but is scientifically exceptional and should not be allowed to influence unduly development of a model (or models) applicable to all Class III systems.Zieminski and Peppas (1983a) postulate the existence of an advancing interface in the plastic separating a glassy region (plastic from which the plasticizer has migrated into the food) from a rubbery region (plastic that retains its plasticizer either wholly or substantially). Migration is modelled by an equation with a variable diffusion coefficient, i.e. (3.56), but, in addition, migration in the glassy region contains a convection term. This is difficult to understand. Zieminski and Peppas (1983a) present some numerical solutions of their model equations and some experimental data for water/ PVC/DEHP (di(2-ethyl hexyDphthalate) or BBP (benzyl butyl phthalate) systems. Unfortunately they are unable to compare their theory with their data.

§3.5 The PIRA model

Work undertaken at the PIRA Laboratories (Adcock, Hope and Paine 1980a, 1980b; Adcock, Hope, Sullivan and Warner 1984) included the development of an extremely novel physical model ("pictorial concept") for the assessment of the migration of additive(s) in Class III systems. This model, described fully in Adcock, Hope and Paine (1980b), is based on the representation of the plastic as a matrix of molecules of different sizes. A typical molecular weight distribution curve for plastics produced by free-radical polymerization is represented by a histogram with 19 groups containing a total of 857 molecules. (These figures are arbitrary.) Molecules in each group are modelled as squares whose area is proportional to the molecular weight for that group; the 857 squares are then arranged randomly in a rectangle, but the precise method of arrangement is such that the squares of different areas fit tightly together within this rectangle. It is then assumed that one of the longer edges of the rectangle is the interface between the plastic and the food. A food is divided into 19 groups, one for each range of molecular weights. Food group 1 is capable of "penetrating" all molecules in group 1, but not those in any higher group; food group 2 can penetrate all molecules in groups 1 and 2 but not those in any higher group, and so on. (Group 1 consists of the lightest molecules, group 2 of. the next lightest etc.) Food of a given group actually penetrates all those molecules which (a) it is capable of penetrating, and (b) are reachable from the interface by pathway(s) through penetrable molecules. Given a particular rectangle representation of the plastic, it is then a simple (but very time-consuming) task to evaluate, for each of the 19 groups of food, the proportion of the area of the rectangle that is penetrated. Note that the model contains no prescription for predicting time evolution so that the 19 proportions are estimates of equilibrium penetration.

It is assumed that the contaminant (additive) molecules (which play no part in the rectangular representation of the polymer matrix) are distributed uniformly within the rectangle and that all those within the penetrated region migrate into the uncontaminated food. It follows that the mass of contaminant that ultimately migrates, denoted elsewhere in the present report by $M_{*\infty}$, is proportional to the area of the penetrated region according to the PIRA model. A graph of $M_{*\infty}$ against group number is stated to be of the "same shape" as curves obtained from data, and given in Adcock, Hope and Paine (1980a).

Unfortunately no attempt is made to quantify the shape similarity or to calibrate the model against data. It appears that it can be used for predictive purposes only if the following information is known (or can be estimated):

(a) the initial concentration C_0 of contaminant within the plastic;
(b) the true molecular weight distribution within the plastic;
(c) the "group" to which the food belongs;
(d) the corrections needed to the model to account for the fact that migration really occurs in three dimensions not two, i.e. cubes and cuboids should replace the squares and rectangles of the model.
(e) how to account for other structural factors such as polarity and crystallinity which affect penetration, i.e. replacement of molecular weight by compatibility/solubility.

Nevertheless the PIRA model provides an interesting qualitative explanation of the likely role of the plastic structure on migration, an explanation that is lacking in other accounts.

§3.6 Some complications

Introduction

Some complications like temperature dependence and spatial inhomogeneity due to penetration have been discussed above. For completeness, it is desirable to mention others that are important and which, in some cases, have received attention.

Chemical change

None of the "mainstream" models of Class II and III systems that have been summarized earlier consider the possibility of chemical change either within the plastic (before migration) or in the food (after migration). We are unaware of any mathematical treatment of the former important aspect of migration. Several workers allude to the latter; for example Schönert and Monshausen (1978) model certain "abnormal diffusion patterns" of a polyacid in aqueous solution by assuming a step change in the diffusion coefficient as the polyacid structure changes suddenly from a statistical coil formulation to one involving the α-helix. It is our opinion, however, that for practical purposes the abrupt change in the value of the diffusion coefficient in situations of this sort probably has relatively little effect on behaviour in the sense that satisfactory predictions could be obtained using standard Class II models with an appropriate average (but constant and uniform) diffusion coefficient.

Reid, Schwope and Sidman (1983) discuss some experiments with more serious implications for mathematical modelling. They noted that the migration of BHT and of Irganox 1010 from polyolefines into certain aqueous solutions showed no sign of approaching any asymptotic limit, such as that illustrated by their Figures 9 and 10 for large values of τ_+, even though such behaviour had been anticipated. Analysis of the aqueous solution after the experiments had terminated showed significantly less BHT or Irganox 1010 there than had been lost from the plastic so that chemical degradation of the contaminant must have occurred in the solution after migration. Thus the concentration $C_*(t)$ of contaminant in the aqueous solution was always less than the equilibrium value of γC_0 predicted by (3.18) for effectively infinite plastic but finite food. Hence the aqueous solution was never saturated with the original contaminant. This effect was modeled by assuming that the degradation occurred by a first-order mechanism with C_* satisfying $dc_*/dt = -k_r c_*$ for some chemical reaction rate constant k_r. A slightly different model was presented in a later paper (Schwope, Till, Ehntholt, Sidman, Whelan, Schwartz and Reid 1987) and further data were presented and discussed. However, mainly because of substantial experimental scatter (see next paragraph), the available data were not sufficient to test either model adequately. It should be noted that, even in this situation, migration must eventually approach a limit because, in practice, there is only a finite amount of contaminant within the plastic. Hence $M_{*\infty}$ can never exceed C_0V (where V is the volume of the plastic), but this may of course be a substantial overestimate, although the limit is reached very nearly in some important practical cases. Note finally that the occurrence of chemical change requires separate assessment of the degradation products for hazard.

Repeatability, reproducibility and variability

Many workers have noted that the results of several, nominally identical, migration experiments are not the same and that the differences between the results of separate experiments are unpredictable even when the whole set of experiments is conducted within a single laboratory. For example, in the last paper referred to in the previous paragraph Schwope, Till, Ehntholt, Sidman, Whelan, Schwartz and Reid (1987) comment (p.320) that "satisfactory replication of results could not be achieved in migration measurements of BHT from LDPE into water at 49°C" and "the results show a disconcerting scatter". The degree of scatter is evident in their Figure 4.

A major study of the repeatability (which refers to experiments within a single laboratory) and reproducibility (which refers to experiments in different laboratories) of the results of migration tests was undertaken under the auspices of the EEC with the work centred at their Joint Research Centre, Petten in the Netherlands. A full report of the study is given in Karcher, Haesen and Le Goff (1983), and the main findings are also in Haesen, Le Goff and Karcher (1984). A total of nine laboratories (including that at Petten) participated in the work which included four phases. For present purposes it is sufficient to concentrate on the findings of the first two phases. In the first phase eight laboratories from six European countries (including Switzerland) analysed, using high performance liquid chromatography, samples (centrally prepared at Petten) of two test liquids (water and HB307) containing two plastic additives (Irganox 1010 and DHBP) at three different concentrations. The concentrations were in the p.p.m. range, i.e. of the order of 10^{-3}kgm^{-3}. There was considerable scatter in the results with standard deviations ranging from 10 - 16% for DHBP in HB307 to greater than 70% for Irganox 1010 in HB307. Haesen, Le Goff and Karcher (1984) summarize the conclusions of this phase as follows: "The considerable scatter observed showed a major problem. It was clear that the overall objective was not being achieved, and another identification method had to be found to obtain satisfactory repeatability and reproducibility"*. A second phase was undertaken with the principal aim of determining the repeatability and reproducibility of migration data. (The first phase did not deal with migration.) Analytical problems arising in the first phase of the study were said to be "eliminated" by use of ^{14}C - labelled additives. The laboratory at Petten distributed samples of centrally prepared HDPE, each sample containing one of the same two additives used in phase one, to the participating laboratories. Migration tests, each for 10 days at 40°C (313K), were conducted in Petri dishes with three test liquids (90: 10 v/v water-ethanol; HB 307; olive oil). Samples of the resulting liquid were, in each case, analysed both at the laboratory conducting the test, and at Petten. There were some problems with evaporation of ethanol for the water-ethanol mixture, and some "outlying" results were rejected. (It is noted later that the proper statistical treatment of outlying results - <u>outliers</u> - is a controversial topic, and not one to be taken lightly.) The standard deviations for repeatability (within laboratory) ranged from 2 - 9% and this was judged to be acceptable. However the standard deviations for reproducibility (between laboratory) were generally much higher, ranging from 5 - 47% with an average of about 28% (Haesen, Le Goff and Karcher (1984), Table 3). Karcher, Haesen and Le Goff (1983) find these values surprisingly high. Further phases of the study were concerned with one-sided test cells (in phase two the

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*No comment was made on an even more striking feature of the results than the degree of scatter, namely that in all cases the average measured concentration was below the actual (nominal) concentration by amounts between 10 and 50%.

plastic laminates were totally immersed in the test liquid) and with measurements of migration under tightly controlled conditions. The results of these phases are like those of phase two, in terms of the orders of magnitude of the standard deviations for repeatability and reproducibility.

This important study, and earlier ones conducted under EEC auspices (Rossi, Waibel and Vom Bruck 1980), have serious implications both for drawing up legislation and for surveillance of foods. For one thing, the reductions in standard deviations between phases one and two were achieved by use of scintillation counters with radioactively labelled additives, and this technique cannot be used for practical surveillance.

It follows, for the authors of this report at least, that legislative standards for migration in foods, and consequent monitoring procedures, should take explicit account of statistical fluctuations if they are to be scientifically satisfactory. The EEC studies provide abundant evidence of the existence of such fluctuations even when test conditions are carefully controlled. In real life the fluctuations will have much greater magnitudes. There is an important point to be made here. Much scientific work (both experimental and theoretical) is conducted on the basis of an implicit premise, namely that the process(es) being investigated is(are) deterministic and that, consequently, fluctuations of any sort must be no more than annoying imperfections. Occasionally this view may be acceptable in practice, but this is rare. Most scientific processes of any degree of complexity have associated with them unavoidable and inherent variability. The causes of such variability may be intrinsic to the process (e.g. turbulent flow in the atmosphere) or they may arise for practical reasons. For example, in migration in real food with real packaging, the amount of migration occurring for any one package will depend on a host of factors such as the exact structure of both media, the exact original distribution of the contaminant in the plastic, the detailed geometry (including air pockets for example) of the contact region between food and plastic, the history (including temperature) of the package between containment and consumption etc. It is obvious that, practically (or even ideally), these factors cannot be precisely quantified nor, since each package is unique, would there be any point in attempting such quantification. It inevitably follows that, practically at least, migration has to be regarded as a statistical phenomenon, a stochastic (or random) process. It may be, for certain foods in certain packages, that the degree of variability, as measured by the magnitude (e.g. the standard deviation) of the fluctuations, is so small that it is negligible in practice, but the evidence of the EEC studies suggests that this will be rare. Since the ultimate aim of all migration estimation is health safety, it should also be noted that the degree of variability associated with toxicity data is as large as (if not larger than) that associated with migration data.

One of the major recommendations of this report is therefore that, in order to establish legislation and monitoring procedures that are scientifically satisfactory, assessment of the degree of variability in the migration occurring in real life should be undertaken. Furthermore success in this major task will require statistical expertise to be available at all stages from planning onwards. Unfortunately this did not occur in the EEC studies*; consequently the full potential of these was not realized.

In view of these conclusions it is proper to enquire into the status of the mathematical models discussed elsewhere in this Chapter. With the exception of the PIRA model (§3.5) these have all been deterministic. Indeed, the fact that this is so is one example of the implicit assumption of determinism referred to earlier. More positively, the predictions of such models can be regarded as predictions of the mean (expected) migration over a population of migration phenomena or, less specifically, as estimates of the order of magnitude of the expected migration. It is very likely, in any case, that such models provide accurate indications of the dependence of the order of magnitude of the migration on key parameters like D and key variables like t. Only further experiments will tell whether these beliefs are correct.

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*This is immediately apparent from perusal of the cited references. For examples (there are many), note that there is no discussion of the statistical significance (a technical term) of the results nor of the decisions taken about outliers. The latter point is both important and controversial (see e.g. Barnett and Lewis 1984).

§3.7 Summary

At the end of this Chapter it is appropriate to emphasize that among its conclusions are that, hitherto, the mathematical modelling of migration has been rather restricted in its range. Realistic geometries have, wrongly, been ignored and almost all models have assumed that migration is, for practical purposes, a deterministic process. Given these provisos, it may be claimed that there is substantial theoretical support for the modelling of Class II systems but rather less for that of Class III systems and those in which there are additional complications. However there has been inadequate comparison between the predictions of existing models and experimental data; systematic use of non-dimensional numbers and variables would facilitate such comparisons and also enhance their value.

§3.8 References

Adcock, L.H., Hope, W.G. and Paine, F.A. 1980a The migration of non-volatile compounds from plastics: Part I . Some experiments with model migration systems. Plastics and Rubber: Materials and Applications February 1980, 37-43.

Adcock, L.H., Hope, W.G. and Paine, F.A. 1980b The migration of non-volatile compounds from plastics: Part II. A descriptive and a pictorial concept of migration. Plastics and Rubber; Materials and Applications May, 1980 71-77.

Adcock, L.H., Hope, W.G., Sullivan, D.A. and Warner, A.H. 1984 The migration of non-volatile compounds from plastics. Part 3 - Further experiments with model systems and development of the descriptive and pictorial concept of migration. Plastics and Rubber Processing and Applications **4** ,53-62.

Asby, R. 1979 The problems of testing. Paper presented at CDC Conference, London.

Ashby, R. 1986 Plasticisers migrating from PVC cling film. Comments (with a limited circulation) on "Cling Film Risk Probe", At Your Service magazine, Spring 1986, West Midlands County Council, 4-5.

Astarita, G. and Sarti, G.C. 1978 A class of mathematical models for sorption of swelling solvents in glassy polymers. Poly. Eng. & Sci. **18**, 388-395.

Barnett, V. and Lewis, T. 1984 "Outliers in Statistical Data", 2nd Ed., John Wiley & Sons, Chichester. 463pp.

Batchelor, G.K. 1967 "An Introduction to Fluid Dynamics", Cambridge University Press. 615pp.

Berens, A.R. 1977 Diffusion and relaxation in glassy polymer powders: 1. Fickian diffusion of vinyl chloride in poly(vinyl chloride). Polymer 18, 697-704.

Berens, A.R. 1978 The diffusion of gases and vapors in rigid PVC. Proc. SPE Meeting on Plastics in Packaging, Chicago. 73-77.

Bishop, J.R. 1972 Considerations of how representative are present rather simple extraction tests. Ann. 1st. Super. Sanitá, 8 337-343.

Brighton, C.A. 1968 The extractability of additives from PVC compounds. Plastics & Polymers December 1968, 549-554.

Briston, J.H. and Katan, L.L. 1974 "Plastics in Contact with Food", Food Trade Press Ltd., London. 466pp.

Brown, W.R. and Park, G.S. 1970 Diffusion of solvents and swellers in polymers. J. Paint Technol. 42. 16-25.

Calvert, P.D. and Billingham, N.C. 1979 Loss of additives from polymers: a theoretical model. J. Appl. Poly. Sci. 24, 357-370.

Carslaw, H.S. and Jaeger, J.C. 1959 "Conduction of Heat in Solids", 2nd Ed., Oxford Univ. Press. 510pp.

Chan, R.K.S., Anselmo, K.J., Reynolds, C.E. and Worman, C.H. 1978 Diffusion of vinyl chloride from PVC packaging material into food simulating solvents. Poly. Eng. & Sci. 18, 601-606.

Chudy, J.C. and Crosby, N.T. 1977 Some observations on the determination of monomer residues in foods. Fd. Cosmet. Toxicol. 15, 547-551.

Crank. J. 1979 "The Mathematics of Diffusion", 2nd Ed. (paperback), Oxford Univ. Press. 414pp.

Crider, L.B., O'Mara, M.M. and Bowles, R.L. 1978 A model for the diffusion of vinyl chloride monomer from PVC under various conditions of storage. Proc. SPE Meeting on Plastics in Packaging, Chicago. 195—199.

Doremus, R.H. 1979 Chemical durability of glass. In "Treatise on Materials Science and Technology", edited by M. Tomazawa and R.H. Doremus, Academic Press, New York, 41-69.

Enscore, D.J., Hopfenberg, H.B. and Stannett, V.T. 1977 Effect of particle size on the mechanism controlling n-hexane sorption in glassy polystyrene microspheres. Polymer 18, 793-800.

Figge, K. 1980 Migration of components from plastics - packaging materials into packed goods - test methods and diffusion models. Prog. Polym. Sci. 6, 187-252.

Figge, K., Cmelka, D. and Koch, J. 1978 Problems involved in and a comparison of methods for the determination of total migration from packaging materials into fatty foods. Fd. Cosmet. Toxicol. 16, 165-175.

Figge, K. and Leimgruber, R. 1976 On the physical chemical behaviour of low molecular substances in the system packaging material/contained product. Lecture given at Second Int. Symp. on Migration, Hamburg.

Figge. K. and Rudolph, F. 1979 Diffusion im System Kunstst of fverpacknng/ Füillgut. Die Angew. Makromol. Chemie 78, 157-180.

Frisch, H.L. 1978 Simultaneous nonlinear diffusion of a solvent and organic penetrant in a polymer. J. Polym. Sci.; Polym. Phys. Ed. 16, 1651-1664.

Garlanda, T. and Masoero, M. 1966 Considerazioni sulla migrazione di componenti di materie plastiche in solventi a contatto. La Chimica e 1'Industria 48, 936-943.

Garlanda, T. 1971 Theoretical aspects concerning the migration of components from packaging materials. Paper written for Montecatini Edison S.p.A., 1 February 1971.

Ghisolfi. G. 1986 Advanced chemical-physical procedure to decrease acetaldehyde level during production of PET bottles. Paper given at 7th Conf. on High Performance Plastic Containers, Dusseldorf.

Gilbert, S.G. 1979 Modeling the migration of indirect additives to food. Food Technol. 33, 63-65.

Haesen G. and Schwarze, A. 1978 Migration phenomena in food packaging. Report No. EUR 5979, Community Reference Bureau series, Office for Official Publications of the European Communities: Luxembourg. 46pp.

Haesen, G., Le. Goff, B. and Karcher, W. 1984 Reproducibility aspects in specific migration measurements: a collaborative study. Food Adds. & Contaminants 1, 53-61.

Institute of Packaging, The. 1970 The leaching of substances from packaging materials into food. Proceedings of Conf. at National Coll. of Food Technol., Weybridge.

Ishiwata, H., Inoue, T. and Tanimura, A. 1986 Migration of melamine and formaldehyde from tableware made of melamine resin. Food Adds. & Contaminants 3, 63-70.

Jackson, R.A., Oldland, S.R.D. and Pajaczkowski, A. 1968 Diffusion of additives in polyolefins. J. App. Poly. Sci.12, 1297-1309.

Joshi, S. and Astarita, G. 1979 Diffusion-relaxation coupling in polymers which show two-stage sorption phenomena. Polymer 20, 455-458.

Karcher, W., Haesen G. and Le Goff, B. 1983 Collaborative study on the methodology for specific migration studies. Report No. EUR 8286 EN, Commission of the European Communities, Directorate-General for Science, Research and Development, Luxembourg. 88pp.

Katan, L.L. 1971 Migration from packaging materials to foodstuffs: a new approach. Paper presented at a conference arranged by The Institute of Packaging, Eastbourne, 2.1-2.35.

Katan, L.L. 1976 Migration and legislation. Abstract of a lecture given at Second Int. Symp. on Migration, Hamburg.

Katan, L.L. 1979 Migration units and dimensions. Plastics and Rubber; Materials and Applications February 1979, 18-24.

Keinhorst, A. and Niebergall, H. 1986a Untersuchungen zur Vorausberechnung der Migration von Zusatzstoffen aus Kunststoffverpackungen in Lebensmittel. I. Mitteilung. Einleitung, Diffusions- und Verteilungskoeffizienten in den Systemen Polyamid-12/Wasser und Polystyrol/Wasser. Deutsche Lebens.-Runds. 82, 254-256.

Keinhorst, A. and Niebergall, H. 1986b Untersuchungen zur Vorausberechnung der Migration von Zusatzstoffen aus Kunststoffverpackungen in Lebensmittel III Mitteilung. Verteilungskoeffizienten, Vorausberechnung von Migrations - Zeit - Verläufen. Deutsche Lebens.-Runds. 82, 390-397.

Klahn, J., Figge, K. and Freytag, W. 1982 Process for calculating the migration of low molecular-weight constituents from plastics into test foodstuffs. English translation from Deutsche Lebens.-Runds. 78, 241-254.

Knibbe, D.E. 1971 Theory of extraction of additives from plastics by swelling solvents. Plastica 24, 358-363.

Kochmann, R., Kutzki, R. and Neibergall, H. 1985 Modelluntersuchungen zur Migration von Inhaltsstoffen aus Verpackungsmaterialien in Lebensmittel. V. Mitteilung: Migrationsmessungen in gequollenen Polymersystemen. Lebens.- Wiss. und - Technol. 18, 148-153.

Koros, W.J. and Hopfenberg, H.B. 1979 Scientific aspects of migration of indirect additives from plastics to food. Food Technol. 33, 56-60.

Koros, W.J. and Hopfenberg, H.B. 1979 Small molecule migration in products derived from glassy polymers. Ind. Eng. Chem. Prod. Res. Dev. 18, 353-358.

Lox, F. 1983 Migration of components from plastic packaging materials into food simulants. Unpublished manuscript.

Lox, F., Walden, A., De Smet, R. and Machiels, J. 1986 Procedures for the evaluation of the maximum global migration of plastic packaging components into food. Paper presented at IAPRI Conf., Oslo.

Messadi, D. and Vergnaud, J.M. 1981 Simultaneous diffusion of benzyl alcohol into plasticized poly (vinyl chloride) and of plasticizer from polymer into liquid. J. App. Poly. Sci. 26, 2315-2324.

Messadi, D. and Vergnaud, J.M. 1982 Plasticizer transfer from plasticized PVC into ethanol-water mixtures. J. App. Poly. Sci. 27, 3945-3955.

Messadi, D., Taverdet, J.L. and Vergnaud, J.M. 1983 Plasticizer migration from plasticized poly (vinyl chloride) into liquids. Effect of several parameters on the transfer. Ind. Eng. Chem. Prod. Res. Dev. 22, 142-146.

Messadi, D., Vergnaud, J.M. and Hivert, M. 1981 A new approach to the study of plasticizer migration from PVC into methanol. J. App. Poly. Sci. 26, 667-677.

Miltz, J. and Rosen-Doody, V. 1984 Migration of styrene monomer from polystyrene packaging materials into food simulants. J. Food Proc. & Pres. 8, 151-161.

Niebergall, H. and Kutzki, R. 1982 Model investigations on the migration of constituents from packaging materials into foodstuffs. Communication II. Procedure and evaluation of the migration measurements. English translation from Deutsche Lebens.-Runds. 78, 323-328.

Park, G.S. and Hoang, T.V. 1979 Diffusion of additives and plasticizers in poly (vinyl chloride)-I The 1:2 double disc method for obtaining the diffusion coefficient of additives in polymers. Eur. Poly. J. 15, 817-822.

Park, J.R. 1976 Migration studies and their relationship to dietary intake. Lecture given at Second Int. Symp. on Migration, Hamburg.

Peppas, N.A. and Zieminski, K.F. 1980 Migration of potentially toxic compounds from plasticized polymers. Proc. SPE Ann. Tech. Conf. on Plastics through Processing, New York. 589-590.

Peterlin, A. 1977 Diffusion with discontinuous swelling. III. Type II diffusion as a particular solution of the conventional diffusion equation. J. Res. NBS - A. Phys. & Chem. 81A, 243-250.

Pinnes, E.L. 1979 Time constants for moisture diffusion through a permeable barrier into an airspace. Poly. Eng. & Sci. 19, 525-529.

Reid, R.C., Sidman, K.R., Schwope, A.D. and Till, D.E. 1980 Loss of adjuvants from polymer films to food or food simulants. Effect of the external phase. Ind. Eng. Chem. Prod. Res. Dev. 19, 580-587.

Reid, R.C., Schwope, A.D. and Sidman, K.R. 1983 Modelling the migration of additives from polymer films to foods and food simulating liquids. Proc. Fourth Int. Symp. on Migration, Hamburg, 105-156.

Rossi, L., Waibel, J. and Vom Bruck, C.G. 1980 Repeatability and reproducibility of measurements of vinyl chloride concentrations in materials and articles made of polyvinyl chloride. Fd. Cosmet. Toxicol. 18, 527-535.

Rudolph, F.B. 1979 Diffusion in a multicomponent inhomogeneous system with moving boundaries. I. Swelling at constant volume. J. Polym. Sci.: Polym. Phys. Ed. 17, 1709-1718.

Rudolph, F.B. 1980 Diffusion in a multicomponent inhomogeneous multiphase system with moving boundaries. II. Increasing or decreasing volume (swelling or drying). J. Polym. Sci.; Polym. Phys. Ed. 18, 2323-2336,

Sanchez, I.C. 1979 Equilibrium distribution of a minor constituent between a polymer and its environment. In ACS Symposium Series 95 ("Durability of Macromolecular Materials", edited by R.K. Eby), 171-181.

Sanchez, I.C., Chang, S.S. and Smith, L.E. 1980 Migration models for polymer additives. Polym. News 6, 249-256.

Sandberg, E. and Vaz, R. 1984 Migration studies on plastic films used for cheese packaging in Sweden. English translation from VarFöda, 36, 279-288.

schönert, H. and Monshausen, F. 1978 Bimodal diffusion in polymer-solvent systems. Coll. & Polym. Sci. 256, 631-637.

Schwartz, P.S. 1983 Migration studies for regulation of indirect food additives: proposed changes. Proc. Fourth Int. Symp. on Migration, Hamburg, 157-171.

Schwope, A.D., Till, D.E., Ehntholt, D.J., Sidman, K.R., Whelan, R.H., Schwartz, P.S. and Reid, R.C. 1987 Migration of BHT and Irganox 1010 from low-density polyethylene (LDPE) to foods and food-simulating liquids. Fd. Chem. Toxicol. 25, 317-326.

Schwope, A.D., Till, D.E., Ehntholt, D.J., Sidman, K.R., Whelan, R.H., Schwartz, P.S. and Reid, R.C. 1987 Migration of Irganox 1010 from ethylene-vinyl acetate films to foods and food-simulating liquids. Fd. Chem. Toxicol. 25, 327-330.

Senich, G.A. 1981 Migration to and from plastics. Chemtech June 1981. 360-365.

Shepherd, M.J. 1982 Trace contamination of foods by migration from plastics packaging - a review. Food Chem. 8, 129-145.

Taverdet, J.L, and Vergnaud, J.M. 1983 Surface analysis of plasticized PVC packagings by attenuated total reflectance. Instr. Anal, of Foods, 1, 367-377.

Taverdet, J.L. and Vergnaud, J.M. 1986 Preparation of plasticized PVC samples with very low matter transfers. Eur. Poly. J. 22, 959-962.

Tester, D.A. 1976 The extraction of vinyl chloride from PVC containers. J. Soc. Cosmet. Chem. 49, 459-466.

Till, D.E., Ehntholt, D.J., Reid, R.C. , Schwartz, P.S., Schwope, A.D., Sidman, K.R. and Whelan, R.H. 1982 Migration of styrene monomer from crystal polystyrene to foods and food simulating liquids. Ind. Eng. Chem. Fundam. 21, 161-168.

Till, D.E., Ehntholt, D.J., Reid, R.C., Schwartz, P.S., Sidman, K.R., Schwope, A.D. and Whelan, R.H. 1982 Migration of BHT antioxidant from high density polyethylene to foods and food simulants. Ind. Eng. Chem. Prod. Res. Dev. 21, 106-113.

Till, D.E., Reid, R.C., Schwartz, P.S., Sidman, K,R., Valentine, J.R. and Whelan, R.H. 1982 Plasticizer migration from polyvinyl chloride film to solvents and foods. Fd. Chem. Toxicol. 20, 95-104.

van Amerongen, G.J. 1965 Diffusion in elastomers. J. Rubber Chem. Div. ACS, 37, 1065-1152.

Vergnaud, J.M. 1983 Scientific aspects of plasticizer migration from plasticized PVC into liquids. Polym.-Plast. Technol. Eng. 20, 1-22.

Vom Bruck, C.G., Eckert, W.R. and Rudolph, F.B. 1976 Migration von Vinylchlorid aus PVC-Packungen. Fette Seifen Anstrichmittel 78, 334-337.

Vom Bruck, C.G., Figge, K. and Rudolph, F. 1981 Interaction of fat-containing food with plastics packaging. JAOCS 58, 811-815.

Vom Bruck, C.G., Rudolph, F.B., Figge, K. and Eckert, W.R. 1979 Application of the diffusion theory to migration of plastics components into packed goods: survey of recent migration studies. Fd. Cosmet. Toxicol. 17, 153-157.

Wagner, C. 1952 On the solution of diffusion problems involving concentration-dependent diffusion coefficients. J. Metals 4, 91-96.

Wang, F.H.L., Duda, J.L. and Vrentas, J.S. 1980 Analysis of impurity migration in plastic containers. Poly. Eng. & Sci. 20, 120-127.

Zieminski, K.F. and Peppas, N.A. 1983a Diluent diffusion in polymer-diluent systems near T_g: migration of phthalic esters from PVC to water. J. App. Poly. Sci. 28, 1751-1765.

Zieminski, K.F. and Peppas, N.A. 1983b Migration of phthalic esters from poly (vinyl chloride) in the presence of alcohols. Die Angew. Makromol. Chemie 116, 77-88.

CHAPTER FOUR: RECOMMENDED FUTURE WORK AND CONCLUSIONS

§4.1 Introduction

The previous Chapters of this report have dealt with the features required for a successful practical model of migration, and have critically summarized what appear to be the most promising existing models with this in mind. That work responded directly to the first part of the remit for this report. The selection of models for discussion, the relative emphasis paid to them, and the comments made on them also took into account legislative need as expressed in the second part of our remit, namely "It is hoped that a limited number of models will cover the behaviour of most cases of practical interest leading to a basis for legislation". However some further attention to this need is appropriate.

In fact the points to be made in this context are closely linked both with our recommendations for future work, and with our conclusions. Moreover there is no clear or natural separation between the latter two points. Hence it is best to deal with all three matters in a single (and final) Chapter of the report.

§4.2 The use of mathematical models in formulating legislation

The scientific input to legislation

A fundamental assumption is central to the views expressed in this section, namely that legislation on matters (like migration) that involve science should be framed in terms that make sense, scientifically speaking. Obviously other factors, such as legal practicality, and mode and cost of implementation, are also important. Although we are not competent to express a profesional view on such matters, we are entitled to assert, both as scientists and as citizens, that we would never support legislation that was scientifically nonsensical. (An example of nonsensical legislation would be any that insisted that there should be zero migration in all circumstances.)

The first conclusion, of the present investigation (that should not be surprising) is that further work is needed before mathematical models can be used to anything like their full potential in framing (and monitoring) legislation. Nevertheless there are many positive points that can already be made about the proper place of mathematics (and physics) in this regard.

Perhaps the most immediate such point is that legislation must take account of the geometry, i.e. the shape and size, of the plastic package and the food it contains. Work in Chapters 2 and 3 shows why these factors are important, but further numerical examples will reinforce this very well-known argument. A draft proposal from the EEC (1978) (quoted for example by Ashby (1979)) is that "the value of the overall migration limit shall be equal to 10mg/dm^2 of the surface of the article in the following cases:- (a) containers greater than 250ml; (b) .....". For specificity suppose the food has a density of 10^3kg m^{-3} (the density of water), and consider two containers of different shape each containing 250ml, one a sphere (of radius about 0.039m) and one a cube (of side about 0.063m). Routine calculations, using equation (4.1) below, show that an overall migration limit of 10mg/dm^2 gives an overall average concentration $\bar{\theta}_*$ in the food of 77mg/kg* for the sphere and 95mg/kg for the cube. The difference is due entirely to the difference in shape of the containers. Lest it be argued that the difference between 77 and 95 is so small that the effect of the shape of the container can be ignored in practice, it should be noted that shapes that are more realistic for actual packages give much higher values of $\bar{\theta}_*$. For example a cuboid containing 250ml with length, width and depth in the ratio 10:5:1 gives $\bar{\theta}_* = 152\text{mg/kg}$. Changing the <u>size</u> of the container without changing

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*In this section it seems appropriate in view of existing and draft legislation to express concentration as a mass-ratio (mass of contaminant per unit mass of food). Elsewhere in this report the symbol C (with suffixes etc. where appropriate) has always been used to denote concentration expressed in the units of mass per unit volume. This explains the use of the new symbol θ. Consistent with Table 1, the Greek symbol indicates that concentration, expressed as a mass-ratio, is a non-dimensional quantity. The conversion from θ to C is simple since $C = \rho_*\theta$ as explained on page 2/2/14, where ρ_* is the density of the food. As usual the asterisk suffix on θ in $\bar{\theta}_*$ denotes concentration <u>in the food</u> and the overbar denotes the average over the whole volume occupied by the food.

its shape also changes $\bar{\theta}_*$ by, as it happens, a factor equal to the reciprocal cube root of the volume ratio (i.e. inversely proportional to the ratio of corresponding linear dimensions). Thus, still with the overall migration limit of 10mg/dm^2 and with the food density that of water, $\bar{\theta}_*$ is $(77/10^{\frac{1}{3}}) \approx$ 36mg/kg for a spherical container holding 2500ml and $(77 \times 10^{\frac{1}{3}}) \approx$ 166mg/kg for one holding 25ml. (The draft proposal does not of course apply to containers holding less than 250ml but that fact in no way negates the point of principle.)

Further discussion of the illogical effects of a migration limit of 10mg/dm^2 is given by Katan (1980). Table 3 is taken from this reference, and applies to foods with densities equal to that of water.

Volume of cube (ml)	Concentration (mg/l)
200	103
250	95
1000	60
10000	28

TABLE 3: The concentration of contaminant in food for cubes of different volumes with a migration limit of 10mg/dm^2 (Katan 1980).

These numerical examples also illustrate another fundamental point, namely that the reporting of scientific investigations of migration - and, therefore, the wording of legislation on migration - should be in terms that are dimensionally sensible. (This point has recurred frequently in this report in the different, but equivalent, guise of the importance and usefulness of non-dimensional quantities.) For this reason, the use of a quantity with units of mass per unit area, i.e. the overall migration limit of 10mg/dm^2, in draft legislation is scientific nonsense since the size and shape of the container (and the food) to which it applies are not precisely specified[*]. The following arguments demonstrate the validity of this severe criticism.

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[*] But were such precise specification to be provided, the legislation would be totally impractical since separate specification would be required for each separate container shape and size (as well as - perhaps - for each food and plastic).

Suppose a package contains a volume V_* of food of density ρ_* and that there is a surface area A of the package in contact with the food. Let the transfer of contaminant from the plastic to the food be S (where S = 10mg/dm^2 for the numerical examples above). Then $\bar{\theta}_*$ is obviously given by the formula

$$\bar{\theta}_* = \frac{AS}{V_* \rho_*}. \tag{4.1}$$

The aim of legislation is to ensure that, for each harmful contaminant, $\bar{\theta}_*$ is below a limit determined by health safety considerations. Legislation which attempts to ensure this by controlling S is doomed to failure since, whatever legal limit is imposed on S, the <u>shape</u> of a container of fixed volume V_* can always be found so that $\bar{\theta}_*$ is arbitrarily <u>high</u>. In fact, consider a cuboid of square base of side b and of depth d; then $V_* = b^2 d$ and $A = 2b^2 + 4bd$ (assuming both top and base are in contact with the food but, otherwise, $A = b^2 + 4bd$ and the argument is changed only in algebraic detail but not in its important conclusion). Use of (4.1) then leads, after a few lines of elementary algebra, to

$$\bar{\theta}_* = \frac{S}{\rho_*}\left\{\frac{2b^2}{V_*} + \frac{4}{b}\right\} = \frac{S}{\rho_*}\left\{\frac{2}{d} + 4\left(\frac{V_*}{d}\right)^{\frac{1}{2}}\right\}. \tag{4.2}$$

Thus $\bar{\theta}_*$ tends to infinity for fixed S, ρ_* and V_* both when b tends to infinity and d tends to zero (short flat cuboid), and when b tends to zero and d tends to infinity (tall narrow cuboid). The same conclusion is reached if a circular cylinder (like a bottle), or - indeed - any one of a set of more complicated geometrical structures - is investigated instead of a cuboid.

This fault, which is fundamental, has been exposed previously and its continued tolerance is inexcusable.

Before discussing possible formats of satisfactory legislation, it is necessary to make a further critical comment about the wording in the part of the draft proposal that was quoted above, and which is still present in many current legislative instruments and proposals. These assume that the transfer S of contaminant (e.g. 10mg/dm^2 for global migration) is the <u>same</u> at all points on that part of the surface of the plastic that is in contact with food. This is true only in idealized mathematical models such as those in §3.3. and §3.4, and may be approximately true in some migration test cells (in the sense that those parts of the plastic/food interface where the transfer differs markedly from the average form a small proportion of the total interfacial area). In real packages the implied assumption is unlikely to be true because of factors like changes in surface curvature and the occurrence of an air/food interface. The proposal should therefore refer to an average migration limit, where the average is over the area of plastic in contact with the food. (For this reason, it would have been more correct to have replaced S in (4.1) by $\bar{S}$; this was not done because replacement might have caused confusion.)

Much legislation includes reference to a "limit value" expressed as a mass ratio (e.g. mg/kg). For the reason given above, it should have been made clear that this also can only be an average concentration (in this case over the volume occupied by food or uniformly mixed food simulant)., and this omission has led to confusion in at least one case highlighted by Ashby 1986. In fact, such a limit is a limit value of $\bar{\theta}_*$ and there is no objection on dimensional grounds to legislation expressed (exclusively) in terms of this non-dimensional quantity. It is therefore recommended that all legislation be framed in terms of $\bar{\theta}_*$, and the remainder of this Chapter will assume the acceptance of this recommendation*. (Use of a concentration expressed in other, not non-dimensional, units in legislation can be criticized on the same scientific grounds as those adduced against use of 10mg/dm^2. The detailed argument will not be given here but involves the fact that different foods have different densities. Although the variation of density across the range of food and drink is small enough for this point to have relatively minor practical significance, the scientific argument is important enough for the use of concentrations expressed as mass per unit volume (e.g. 60mg/l) in (draft) legislation to be discouraged.)

Before discussing frameworks for legislation it is necessary to state one further assumption that will be made in this report. This is that when two (or more) contaminants migrate from a single container, they do so

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*It is recognized that the precise value of the legal limit on $\bar{\theta}_*$ will have to recognize, for semi-solid foods, that there are great variations in concentration within the food. See the earlier discussion on immobile foods beginning on p3/29/56.

independently. This may well be a good assumption when each migration process is as in a Class II system. But in a Class III system, it is much less clear that the assumption will be valid since most models are non-linear, and there is little experimental evidence available. Further laboratory studies are desirable.

Mathematical models and legislation

Consider as before a plastic package of given shape containing food, and suppose that containment occurs at time $t = 0$ when a contaminant is distributed uniformly throughout the plastic with concentration C_0 (where as throughout this report the units of C_0 are mass per unit volume). Suppose that there is no contaminant within the food at time $t = 0$ and (for simplicity and safety) that subsequently no contaminant is lost to the environment outside the food/package system. After containment the contaminant migrates into the food. Let C_* denote the concentration of the contaminant in the food in units of mass per unit volume, and let θ_* denote the same concentration as a mass-ratio. As noted above, C_* and θ_* are very simply related by the equation

$$\theta_* = \frac{C_*}{\rho_*}. \tag{4.3}$$

In general C_* and θ_* vary both with time and with position in the food. It was advocated above that legislation should be framed in terms of $\bar{\theta}_*$, the average of θ_* over the region occupied by food. Obviously

$$\bar{\theta}_* = \frac{\bar{C}_*}{\rho_*} = \frac{M_*}{\rho_* V_*}, \tag{4.4}$$

where M_* is the mass of contaminant that has migrated into the food and V_* is the volume occupied by food (so that $\rho_* V_*$ is the mass of the food). In (4.4), $\bar{\theta}_*$ (and M_*) depend on time t; this can, and will, be emphasized when required by writing $\bar{\theta}_*(t)$. For the same reason the notation $\theta_*(\underset{\sim}{x},t)$ or $\theta_*(x,y,z,t)$ will be used to highlight the dependence of θ_* on position in the food when required, where the vector $\underset{\sim}{x}$ (or - equivalently – the Cartesian coordinates x, y, z) pinpoints a particular point in the food.

A mathematical model, as defined in §3.1, is capable of predicting $\theta_*(\underset{\sim}{x},t)$, and then $\bar{\theta}_*$ by averaging (integrating) over all $\underset{\sim}{x}$, provided:

(a) The set of equations, including both differential equations and boundary and initial conditions, that constitutes the model is an adequate (in practical terms) representation of the important physical and chemical processes.

(b) The values of the relevant parameters are known. Which parameters are relevant depends on the model but important examples are diffusion and partition coefficients and those that define the size and shape (i.e. the geometry) of the system.

(c) The model is sufficiently simple (in mathematical structure) for it to be solvable, either in the form of an exact formula or by use of a computer, and hence to be capable of giving numerical predictions of $\bar{\theta}_* (t)$.

Most mathematical models discussed in this report do not conform with one or more of the above conditions, especially (b) .

There are two related roles for mathematical modelling in framing and obeying legislation on migration. These are:

(i) formulating legislation and, specifically, providing the means of calculating the composition of a plastic in terms of $\bar{\theta}_*$;

(ii) assisting in conforming with legislation and, specifically,
    (1) design of food/package systems;
    (2) quality control;
    (3) surveillance and policing.

Provided conditions (a), (b) and (c) above are satisfied it is possible to test any proposed design for a food/package system to ensure, or show otherwise, that, if the design is implemented, the value of $\bar{\theta}_*$ will be less than the legislative limit for all times t of practical interest. This test will in general require use of a computer to solve the full set of model equations for the proposed geometry. In certain circumstances however this will be unnecessary.

It will be recalled that, in §3.2, some simple formulae for the equilibrium value of C_* were derived. In equilibrium the concentration in the food is uniform so that $\overline{C}_* = C_*$ and $\overline{\theta}_* = \theta_*$. It then follows from (3.2), (3.5) and (4.3) that $\overline{\theta}_* = (t)$ satisfies

$$\overline{\theta}_*(t) \le \frac{(C_0/\rho_*)}{\gamma^{-1} + (V_*/V)} < \frac{C_0 V}{\rho_* V_*}\,, \qquad (4.5)$$

where γ is the true partition coefficient and V is the volume of the plastic in the package. The procedure to be adopted is to calculate $(C_0V)/(\rho_*V_*)$ for the proposed design. If this is less than the legislative limit, the design can be accepted forthwith. If not, and if it is known that chemical changes do not occur, the second term in (4.5) should be calculated. Once more no further testing is required if this is less than the legislative limit. However further work is necessary if both of the limits in (4.5) are greater than the legislative limit.

Several sets of workers (Katan 1971; Chang, Senich and Smith 1982; Reid, Schwope and Sidman 1983) have argued that the type of testing discussed here should be conducted via a decision tree or algorithm, and this approach is endorsed by the authors of this report. The previous paragraph has discussed the first two branches or gates in this decision-tree. Unfortunately the later branches in existing schemes all assume one-dimensional diffusion and this is not adequate for realistic geometries. However there is no doubt of the structure of the next gate, at least for Class II systems. All the models discussed in §3.3 predict the same type of behaviour for $M_*(t)$, the mass of contaminant that has migrated into the food after time t, for sufficiently small values of non-dimensional time. The most general formula for this behaviour is obtained from (3.40) by dividing by 2 since extraction from real closed packages is one-sided. Hence for sufficiently small values of non-dimensional time,

$$M_*(t) \approx \frac{2C_0A}{(1+\alpha)}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}, \qquad (4.6)$$

where D is the diffusion coefficient of the contaminant in the plastic, A is the surface area of the package that is exposed to food, and α is the non-dimensional parameter defined in (3.38)*. Use of (4.4) then gives

$$\bar{\theta}_*(t) \approx \frac{2C_0A}{(1+\alpha)\rho_*V_*}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \quad . \qquad (4.7)$$

(The distinction between θ_* and $\bar{\theta}_*$ is important in (4.7); when (4.6) applies the contaminant is less likely to be distributed uniformly within the food.) Arguments given following (3.14) and (3.29) in §3.3 show that (4.7) can be used only when $(Dt)^{\frac{1}{2}}/h$ is sufficiently small. Whilst Reid, Schwope and Sidman (1983) derive precise criteria for assessing what constitutes "sufficiently small" in one-dimensional geometry, there is no justification for assuming that these criteria are correct for real package situations. The same comment applies even more forcibly to later gates in the Reid, Schwope and Sidman (1983) scheme, where decisions are all based on formulae derived from the one-dimensional solutions discussed in §3.3.

It will be clear also from work in §3.4 and §3.6 that there is at present inadequate knowledge for a precise decision tree approach to be adopted now, even in one-dimensional geometries, for Class III systems and for situations where chemical change and/or variability are important. Note however that Katan (1971) describes a complete decision tree aimed not at precise estimates of migration but at safe upper limits.

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*To avoid interrupting the development of the argument, several small but important points about (4.6) are considered in this footnote. Although (3.40) was derived only for one-dimensional geometry, it is clear that

§4.3 Recommendations for future work and conclusions

Many isolated recommendations and conclusions have been made in the body of this report. In this final brief section the authors attempt a coherent summary of these points.

Our principal overall recommendation is that further research be undertaken with the aim of using mathematical models to their full potential in:

(a) planning experiments and analysing data;
(b) formulating legislation;
(c) designing food/package systems that meet legal limits.

Several shortcomings of previous work on migration that uses mathematics have been identified. It is recommended that these should be rectified in all future work. The most serious faults are (i) exclusive emphasis in both experiments and mathematical modelling on one-dimensional geometries which are not representative of real packages; (ii) a failure to. express experimental results and legislative proposals in terms of non-dimensional variables and parameters; (iii) the reluctance of some experimentalists to give sufficient details for it to be possible to assess whether their results are consistent, or otherwise, with a proposed model; (iv) limitation, either of model or of experimental verification, to a narrow range of applicability.

The work in §3.3 suggested that, on available evidence, an adequate set of equations for predicting migration in Class II systems exists. Following comments in the previous paragraph, it is important to develop solutions for more realistic geometries and to compare these solutions with data. Other urgent needs are to test the validity of (3.18) experimentally and to develop a data base for parameters such as diffusion and partition coefficients. The situation with Class III systems, and with those exhibiting other complications such as chemical change or variability, is much less satisfactory, and we recommend that (relatively) more attention be given to such systems in future by both experimentalists and modellers. We hope that this report gives clear guidelines for such studies.

4/11/11

§4.4 References

Ashby, R. 1979 The problems of testing. Paper presented at CDC Conference, London.

Ashby, R. 1986 Plasticisers migrating from PVC cling film. Comments (with a limited circulation) on "Cling Film Risk Probe", At Your Service magazine, Spring 1986, West Midlands County Council, 4-5.

Chang, S.S., Senich, G.A. and Smith, L.E. 1982 Migration of low molecular weight additives in polyolefins and copolymers. Report No.NBSIR 82-2472, National Bureau of Standards, US Dept. of Commerce, Washington DC. 110pp.

EEC 1978 Official J. 21 (No. C141), 4-9.

Katan, L.L. 1971 Migration from packaging materials to foodstuffs: a new approach. Paper presented at a conference arranged by The Institute of Packaging , Eastbourne, 2.1-2.35.

Katan, L.L. 1980 Plastics overall migration directive. Plastics in Retail Packaging Bulletin, 3 (No.7), 5.

Reid, R.C., Schwope, A.D. and Sidman, K.R. 1983 Modelling the migration of additives from polymer films to foods and food simulating liquids. Proc. Fourth Int. Symp. on Migration, Hamburg, 105-106.