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Volume 11

Methodology for Estimating the Migration of Additives and Impurities from Polymeric Materials

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FOREWORD

This document is one of a series of volumes, developed for the U.S. Environmental Protection Agency (EPA), Office of Toxic Substances (OTS), that provides methods and information useful for assessing exposure to chemical substances. The methods described in these volumes have been identified by EPA-OTS as having utility in exposure assessments on existing and new chemicals in the OTS program. These methods are not necessarily the only methods used by OTS, because the state-of-the-art in exposure assessment is changing rapidly, as is the availability of methods and tools. There is no single correct approach to performing an exposure assessment, and the methods in these volumes are accordingly discussed only as options to be considered, rather than as rigid procedures.

Perhaps more important than the optional methods presented in these volumes is the general information catalogued. These documents contain a great deal of non-chemical-specific data which can be used for many types of exposure assessments. This information is presented along with the methods in individual volumes and appendices. As a set, these volumes should be thought of as a catalog of information useful in exposure assessment, and not as a "how-to" cookbook on the subject.

The definition, background, and discussion of planning exposure assessments are discussed in the introductory volume of the series (Volume 1). Each subsequent volume addresses only one general exposure setting. Consult Volume 1 for guidance on the proper use and interrelations of the various volumes and on the planning and integration of an entire assessment.

The title of the nine basic volumes are as follows:

Volume 1	Methods for Assessing Exposure to Chemical Substances (EPA 560/5-85-001)
Volume 2	Methods for Assessing Exposure to Chemical Substances in the Ambient Environment (EPA 560/5-85-002)
Volume 3	Methods for Assessing Exposure from Disposal of Chemical Substances (EPA 560/5-85-003)
Volume 4	Methods for Enumerating and Characterizing Populations Exposed to Chemical Substances (EPA 560/5-85-004)
Volume 5	Methods for Assessing Exposure to Chemical Substances in Drinking Water (EPA 560/5-85-005)
Volume 6	Methods for Assessing Occupational Exposure to Chemical Substances (EPA 560/5-85-006)
Volume 7	Methods for Assessing Consumer Exposure to Chemical Substances (EPA 560/5-85-007)

Volume 8	Methods for Assessing Environmental Pathways of Food Contamination (EPA 560/5-85-008)
Volume 9	Methods for Assessing Exposure to Chemical Substances Resulting from Transportation-Related Spills (EPA 560/5-85-009)

Because exposure assessment is a rapidly developing field, its methods and analytical tools are quite dynamic. EPA-OTS intends to issue periodic supplements for Volumes 2 through 9 to describe significant improvements and updates for the existing information, as well as adding short monographs to the series on specific areas of interest. The first of these monographs are as follows:

Volume 11	Methodology for Estimating the Migration of Additives and Impurities from Polymeric Materials (EPA 560/5-85-015)
Volume 13	Methods for Estimating Retention of Liquids on Hands (EPA 560/5-85-017)

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TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

Page No.

TABLE OF CONTENTS (continued)

Page No.

TABLE OF CONTENTS (continued)

Page No.

LIST OF TABLES

LIST OF FIGURES

1. SUMMARY

--- NOTE TO USERS ---

This report contains extensive documentation concerning the migration of additives from polymers to the environment. However, for those users who only wish to use the computer to predict migration, it is recommended they proceed to Section 6 for instructions dealing with the computer program, as well as a list of the input data required for implementation. Should one then need to estimate any of the input parameters, references are given to direct the user to the appropriate section.

1.1 Background

Plastic and elastomeric products are used in virtually all segments of the U.S. economy. These products are based on polymers that are high molecular weight chains of low molecular weight monomers such as vinyl chloride, ethylene, styrene, and so forth. Although polymerization and subsequent purification processes have been greatly improved, in some cases the polymer product may contain impurities such as catalyst residues, unreacted monomer, and relatively low molecular weight polymer molecules (i.e., oligomers). Furthermore, most polymers are compounded with a variety of relatively low molecular weight chemicals to yield products with useful physical properties and service lives. Examples include plasticizers, UV and thermal stabilizers, antioxidants and biocides; other additives may be used to facilitate processing the plastic compound into its final form. New technology is under development to eliminate or minimize additive migration, and processing stages can sometimes be added to remove impurities. Performance enhancing additives can often be covalently bonded to the polymer to provide a non-migrating performance additive.

It is well-documented, however, that additives and monomer residues can migrate from the plastic or elastomer over time. The rate and extent of migration is dependent on many factors, such as temperature, the compatibility of the migrant with the polymer, the molecular size of the migrant, the compatibility of the migrant with the phase external to the polymer, and the interactions that may occur between the external phase and the polymer.

The Exposure Evaluation Division (EED) of the Office of Toxic Substances is frequently required to assess the potential for exposure to chemicals that are used as additives in polymeric materials or are the monomers or low molecular weight oligomers contained in polymers. Historically this task has been difficult because, (1) the chemicals of concern are new or complex molecules for which there are no migration data in the literature, and (2) a consistent model with which to make preliminary estimates of migration has not been available.

1.2 Scope

This task was undertaken with the objective of developing and documenting a defensible approach to assess the potential for release of chemical additives and reaction residues from polymeric materials. (Throughout this report, additives and reaction residues such as monomers, oligomers, catalysts, etc., are collectively referred to as "additives" or "migrants.")

A family of mathematical models was developed and/or adapted for describing the migration of additives to gases, liquids and solids in contact with polymeric materials. Emphasis was placed on air and water as external phases. The models are based on diffusion and convection mass transfer theories and have been organized to treat migration to fluids (air, water) or to solids. With the family of models, the user has an option to develop worst case (total loss of additive) scenarios, to allow partitioning to occur between the polymer and the external phase, or to consider external mass transfer resistances and their effect on rates of loss. The more complex models require more input data.

In all cases, the user must specify the physical situation (external phase, one- or two-sided extraction, and polymer thickness), as well as an estimate of the diffusion coefficient of the additive within the polymer. Should partitioning effects be of interest, data or estimates of the additive solubilities in the polymer and external phase must be provided, as well as the volume of the external phase and the polymer surface area for migration. When external mass transfer resistances are introduced, data must be given to define flow velocities and physical properties of the external phase.

Background material addressing these factors, as well as others which may influence migration, are presented in Section 2. These discussions provide a basis for the models which are developed in Section 3. As noted above, the models require various data inputs in order to yield migration estimations. It is highly unlikely that such data would be available at the time of a premanufacture notification review. For systems for which the necessary data are incomplete, methods, figures and/or tabulations have been provided in Section 4 to approximate missing values.

Example calculations using the various models are provided in Section 5. Finally, the computer program developed to implement these models is described in Section 6. The FORTRAN code and flow diagram for the AMEM computer model is provided in Appendix A. Appendix B provides a limited validation of the AMEM computer program by comparing AMEM predictions with migration data from the literature for 13 example cases.

1.3 Conclusions and Recommendations

Mathematical models have been developed to estimate the migration of additives and impurities from polymeric materials to air, water, and solids. A thorough validation of the models, however, has not been conducted. We recommend, therefore, that the models be tested against the considerable amounts and variety of data in the literature. The validation process would serve to establish practical limitations for the models that may not be addressed by the model assumptions. Furthermore, the process is likely to identify key areas for experimental study that might include frequently encountered migration scenarios for which there are little or no data.

The models require the input of several physical properties of the migrant, the polymer, and the external phase. Where values for these inputs are not available, they must be estimated. For those parameters that historically have been of interest to a large community of scientists and engineers, techniques for estimating the inputs are fairly well developed and substantiated. These would include solubilities and diffusion coefficients in water and air. Tabulations of, and methods for estimating, partition coefficients and solubilities of additives in polymers are lacking. Since values for these parameters are of critical importance to several of the models presented herein, we recommend that further investigation of these parameters be conducted. The first step would be a focussed review of the literature.

The methodology developed in this study is based on two key assumptions: (1) the additive is initially distributed uniformly throughout the polymer and (2) penetration or swelling of the polymer by the external phase does not occur to a significant extent. That is, absorption of an external phase by the polymer does not affect the diffusion coefficient or the solubility of the migrant in the polymer. These assumptions greatly simplify the mathematics but, in fact, may not always apply. Furthermore, when these assumptions are not valid, it is likely that migration will occur at a rate higher than that predicted by the models. In the case of a non-homogeneous additive distribution, the concentration at the surface may be higher due to blooming or incompatibility. In the case of external phase penetration of the polymer, the polymer may be swollen and the glass transition temperature lowered (essentially the polymer is plasticized). Thus, we recommend that the methodology be extended to cover non-uniform additive concentrations (e.g., blooming) and external phase effects on migration.

Finally, we suggest that the computer programs presented herein be further developed and integrated with other exposure models, for example those for indoor air quality. Further development of the programs could also be directed towards making them more adaptable to the various forms of data commonly received in Premanufacture Notifications. An additional possibility is to tailor the models for specific polymers or migrants that are of particular interest to the EPA.

2. FACTORS THAT AFFECT MIGRATION

2.1 Overview

The rate and extent of migration of an additive, monomer, or oligomer from a polymeric material depends upon the properties of the polymer, the migrant, and the external phase. Interactions between these entities are also important. System variables such as the geometry of the polymer-external phase contact, temperature, and time must also be considered.

The migration process involves the diffusion of the migrant through the polymer to its surface, transfer of the migrant across the polymer/external phase interface and assimilation of the migrant into the bulk of the external phase. Movement within the polymer depends upon the gradient in migrant concentration and upon an interaction parameter between the polymer and migrant termed the diffusion coefficient.

Once the migrant reaches the polymer/external phase interface, several factors affect the rate of transfer into the bulk of the external phase. These include the relative solubilities of the migrant in the polymer and external phase, the capacities of both phases for the migrant, and the mechanism for movement of the migrant in the external phase, e.g., by diffusion or by convection.

In this section, we discuss a variety of factors that influence migration. Most of these factors do not enter directly into any model calculation, but they are important in determining model parameters. In many ways, this section provides a background for those interested in migration processes from polymer sheets. Migration model development and applications are described in Sections 3, 4, and 5.

2.2 Polymer

A single polymer molecule is composed of a repetition of simpler molecular units called monomers. A polymeric material is typically envisioned as a mass of intertwined polymer molecules. A key consideration in the migration process is the mobility of the polymer molecules within the mass. Depending upon the polymer, the conditions under which it was fabricated and the temperature, the polymeric material contains varying fractions of crystalline and amorphous regions. In the amorphous regions, the molecules (or parts thereof) exhibit some degree of mobility. A consequence of their combined movements is the formation, dissipation and reformation of "holes" through which migrant molecules may move. There are several polymer properties and characteristics that relate directly or indirectly to the ease of migrant movement or loss during contact of the polymer with the environment. Some of the more important are discussed below.

2.2.1 Glass Transition Temperature

The segmental mobility of a single polymer molecule in a polymeric material is dependent on temperature. At a certain temperature, the material changes from one in which there is segmental motion and the polymeric material is flexible to one in which the segments of the molecules become immobile and the polymeric material is "stiff." This temperature is called the glass transition temperature T_g (Rodriguez, 1982). For any given polymer, the potential for migration of an additive is larger at temperatures greater than T_g.

This effect becomes more pronounced as the size of the migrant molecule increases (Crank and Park, 1968), and there may be discontinuous increase in the diffusion coefficient as one raises the temperature above T_g. Glass transition temperatures are shown for several polymers in Table 1.

2.2.2 Crystallinity

Polymers may exist in amorphous, partially crystalline, or crystalline states or regions. Crystalline regions, as the name suggests, are highly ordered domains in which there is no segmental mobility. Migration, therefore, can occur only through the amorphous regions of the polymer material. The tendency to crystallize is enhanced by regularity and polarity in the polymer molecule (Rodriguez, 1982). For example, trans- and cis-1,4-polybutadiene have crystallinities of 40% and 30% respectively. However, a random mixture of the two isomers has no crystallinity. Similarly, a nonpolar polymer such as atactic polypropylene has no crystallinity whereas the polar polymer Nylon 6 is very crystalline. The degree of crystallinity can be influenced by the thermal and processing history of the polymer.

It should be noted that crystallinity is different from glassiness although both are indicative of loss of chain mobility. Polymeric materials with crystalline regions exhibit melting points (a first-order transition) associated with the crystallites that are always higher than the glass (second-order) transition temperature.

2.2.3 Crosslinking

Crosslinks are covalent bonds between two or more polymer molecules. In the vulcanization of rubber, sulfur is commonly used as the crosslinking agent. Crosslinking reduces polymer chain segmental motion and, therefore, decreases migration rates.

2.2.4 Branching

Some polymer molecules are linear chains of monomers, while other polymer molecules contain side chains branched from the main chain. Branches hinder close ordering of the polymer molecules and result in a more open network of polymer molecules. Higher migration rates would be expected from branched polymers (Flynn, 1982). With reference to Section 2.2.2 above, branched molecules are also less likely to form crystalline regions. A good example of this is a comparison between high- and low-density polyethylenes. The high-density material (HDPE) is composed of linear molecules that pack well and has a 70% crystallinity whereas low-density polyethylene (LDPE) is branched and exhibits about 40% crystallinity. Data for the migration of the antioxidant 3,5-di-t-butyl-4-hydroxytoluene (BHT) from LDPE and HDPE are compared in Table 2 (Till et al., 1983).

2.2.5 Molecular Weight

The average molecular weight of the molecules composing a polymeric material can have a significant influence on many of its properties. Molecular weight effects on migration, however, are generally only a factor with relatively low-molecular weight polymers. Such polymers generally have properties that prevent their use as commercial

TABLE 1. APPROXIMATE GLASS TRANSITION TEMPERATURES (T_g) FOR SELECTED POLYMERS

(Seymour and Carraher, 1981)

Polymer	T_g (degrees kelvin)
Cellulose acetate butyrate	323
Cellulose triacetate	430
Polyethylene (LDPE)	148
Polypropylene (atactic)	253
Polypropylene (isotactic)	373
Polytetrafluoroethylene	160,400[a]
Polyethyl acrylate	249
Polymethyl acrylate	279
Polybutyl methacrylate (atactic)	339
Polymethyl methacrylate (atactic)	378
Polyacrylonitrile	378
Polypropylene (isotactic)	263
Polyvinyl acetate	301
Polyvinyl alcohol	358
Polyvinyl chloride	354
Cis-poly-1,3-butadiene	255
Polyhexamethylene adipamide (nylon-66)	330
Polyethylene adipate	223
Polyethylene terephthalate	342
Polydimethylsiloxane (silicone rubber)	150
Polystyrene	373

[a] Two major transitions observed.

TABLE 2. MIGRATION OF BHT FROM LDPE AND HDPE
(Till et al., 1983)

External Phase	Time (days)	Temperature (°C)	Migration* (μg/dm^2)	
			LDPE	HDPE
Milk	14	4	65	--
	21	4	--	1.5
Orange Juice	21	4	96	--
	28	4	--	7.1
Margarine	98	4	114	--
	99	4	--	2.4

* (--) Indicates no test data were reported for these conditions.

(solid) products. Consequently, the molecular weight of the polymeric material is not addressed further in this report.

There are, in addition, polymeric products that are available in the form of moisture activated or reactive, two-component systems. These include various adhesives and sealants [e.g., epoxies and room temperature vulcanizing silicones (RTV) and coatings (urethanes)]. In these systems, a relatively low-molecular weight polymer reacts either with moisture in the air or with a second, reactive component that is mixed with the low-molecular weight polymer at the time of use to form a high-molecular weight polymer. During the reaction (i.e., curing) period, carrier solvents and/or reaction products are released. They migrate through the polymer network that is increasing in molecular weight with time. Furthermore, it is likely that a dynamic molecular weight gradient exists across the polymer during the cure period. The modeling of migration in reacting systems is not considered in this report.

2.2.6 Plasticization

Plasticizers are additives, usually liquids, that are used to make rigid polymers more flexible. As opposed to solvents that also increase the flexibility of polymers, plasticizers have low volatility and therefore remain in the polymer for longer periods so that stable, plasticized products are possible. One example is the use of phthalate esters to increase the flexibility of polyvinyl chloride (PVC).

Plasticizers lower the glass transition temperature of the polymer. They act similar to a solvent in that they increase the spacing between polymer molecules and thereby increase segmental chain mobility. Diffusion rates of additives, including the plasticizer, are very dependent upon the plasticizer concentration.

2.2.7 Degradation

Polymeric materials may be subject to degradation by the external phase. In such a process, polymer molecules are broken at points along their length (i.e., chain scission) or attacked at side groups or at the end of the chain. In these cases the molecular weight of the polymer may be decreased such that the physical integrity of the material is reduced; there may also be an increase in the diffusion rates of migrants in the polymer.

2.2.8 Summary

In this brief discussion of polymers, we have emphasized several key properties that affect migration. None of these properties are employed directly in migration-rate model or calculations but are only employed indirectly as they affect a key parameter - the migrant diffusion coefficient (see Section 2.4).

2.3 Migrant

A migrant is, relative to the polymer, a low molecular weight species contained or dissolved within the network of polymer molecules. The migrant may be:

- unreacted monomer,
- molecules composed of a few monomer units, i.e., oligomers,

- additives purposefully formulated with the polymer to improve properties (e.g. stability during processing and use, flexibility, or appearance),
- degradation products of certain additives, (e.g., antioxidants and thermal stabilizers), that are designed to react according to a mechanism that protects the polymer,
- impurities present in the monomers as well as additives and by-products formed during polymer production, including residual catalysts, inhibitors, etc.

The mobility of a migrant in a polymer is a function of the size and shape of the migrant molecule. Both linear and spherical low molecular weight (<100 g/mol) have mobilities that decrease as the size of the molecule increases. For molecular sizes larger than, for example, butane, elongated or flattened molecules exhibit more mobility than spherical molecules of approximately the same molecular weight (Barrens and Hopfenburg, 1982). Some of these effects are demonstrated by the data in Table 3.

Polymers are typically formulated with several additives to yield a compound that has processing and ultimate properties appropriate for the fabricated product. Potentially, two or more of these additives could interact in such a way that their mobility characteristics in the polymer are affected. Such interactions are not considered in this report.

Also, certain families of additives or migrants, such as antioxidants and thermal stabilizers, are formulated with the polymer for the purpose of protecting the polymer during processing or prolonging the service life of the material. These additives function by responding to external factors, e.g., heat, oxygen, sunlight, or by neutralizing reactive sites on the polymer chain. In so doing, products of reaction are generated. These would be subject to the same considerations relative to migration as the initial additive.

2.4 Migrant Diffusion Coefficient

Depending upon their size, shape and chemical properties, migrant molecules require different size holes in order to move through the polymer. Consequently, each polymer-migrant pair is characterized by a unique property that describes the ability of the migrant to move through that particular polymer. This property is termed the diffusion coefficient.

The use of diffusion coefficients in the mathematical models is covered in Section 3, but are considered here to note that they can vary by many orders of magnitude between rubbery polymers and rigid, highly crystalline polymers for the same migrant at the same temperature. Many of the factors noted in Section 2.2 have a large influence on the magnitude of the diffusion coefficient.

Diffusion coefficients can also be a function of the concentration of constituents or penetrants in the polymer. Concentration-dependent diffusion coefficients can impede the analysis of experimental data. Exact expressions for concentration-dependent diffusion coefficients are known for only a very limited number of polymer-migrant pairs. This problem is typically circumvented through the use of a so-called integral diffusion coefficient that serves to average the concentration effects. It is this "average" diffusion coefficient which is employed in this report. Methods to estimate this parameter are discussed in Section 4.2.

TABLE 3. DIFFUSION COEFFICIENTS IN NATURAL RUBBER AS A FUNCTION OF MOLAR VOLUME AT 40°C

(Crank and Park, 1975)

Permeant	Molar Volume cm^3/mol	Comment	Diffusion Coefficient x 10^8 (cm^2/s)
Methane	37.7	↓	145
Ethane	54.9	linear	54
Propane	75.7	increasing molecular size	34
Butane	100.4	↓	34
n-Pentane	115	linear	23
iso-Pentane	116	↓	9
neo-Pentane	122	spherical	7

2.5 Migrant Concentration Factors

Additives, monomers, and oligomers may be present in polymers at concentrations ranging from less than 0.1% to over 40%. These potential migrants may be present as discrete additive domains or, more usually, as dissolved material. Indeed, many additives and polymerization residues form solid solutions with the polymer. In general, the additives are present in concentrations below their solubility limit. Because the driving force for migration within the polymer is the concentration gradient of the additive (discussed later in Section 3.3.1), all other conditions being equal, higher migrations will be associated with higher concentrations of additives. In fact, Fick's diffusion laws predict that, for simple systems at or below the solubility limit, migration is directly proportional to concentration. Thus, for example, doubling the concentration would double the rate of migration.

In some cases where a certain additive concentration is required to achieve a desired effect but where the concentration is above the solubility limit, other additives may be formulated into the compound to increase the compatibility and, therefore, solubility of the additive. In other cases, additives may be purposefully added at concentrations above their solubility limit in order to achieve a desired effect. For example, lubricants which exude to the surface improve the processing of some polymers, and anti-fogging additives prevent condensation build-up on clear plastic films used to wrap meat and produce (Nah and Thomas, 1980).

2.6 External Phase

In this report, the external phase is defined as the material contacting the surface of the polymer. It may be air, water, soil, another polymer, body fluids, skin, etc. Regardless of the nature of the external phase, its interactions with the polymer (e.g., swelling) may have significant effects on migration. Equally important from the point of view of predicting migration is the degree of agitation of the external phase (Reid et al., 1980).

2.6.1 Physical State

Simplistically, the external phase may be considered vapor, liquid or solid. It is important to note that none of these external phases is more or less likely to be associated with high or low rates of migration. Rather, the degree to which these different phases influence migration is determined by: the compatibilities and mobilities of the migrant in the polymer relative to those of the external phase; the relative volumes and surface areas of the polymer and external phase; and the degree of agitation of the external phase. These factors are addressed in the remainder of this section.

2.6.2 Agitation

As migrant moves to the surface of the polymer, it must pass into the external phase in order for migration to continue. The overall rate at which the additive migrates is defined by both the rate of migration through the polymer and the rate of migration from the polymer surface into the external phase. In one extreme, when the external phase is highly agitated and well mixed, the rate of migration from the surface will be rapid compared to the rate of diffusion through the polymer. In this case, migration is controlled by the diffusion rate of the additive in the polymer.

In the other extreme, when the external phase is totally stagnant, the migrant can move into the external phase only by a diffusional process. The relative diffusivities of the migrant in the polymer and in the external phase determines whether the external phase controls the rate of migration. The external phase becomes controlling when the migrant diffusion rate within the external phase is much slower than that in the polymer. This may occur for certain combinations of diffusion coefficients and solubilities in the two phases.

An intermediate situation between the above extremes occurs when the external phase is only moderately agitated. In this case, a thin, stagnant layer (i.e., the boundary layer) exists at the polymer-external phase interface. The thickness of the boundary layer is a function of the degree of agitation of the external phase. Depending upon the rate of migration through the polymer relative to the rate of transfer through the boundary layer, the migration process can be controlled by the external phase, the polymer, or by a combination of both. The parameter that characterizes the resistance to transfer through the boundary layer is the mass transfer coefficient. Methods to estimate this parameter are discussed in Section 4.5.

2.6.3 Partition Coefficient

The partition coefficient is defined as the ratio of the migrant concentration in the external phase to the migrant concentration in the polymer at equilibrium. The partition coefficient may be calculated by dividing the saturation concentration of the additive in the external phase by its saturation concentration in the polymer. Thus, the partition coefficient is an indicator of the relative solubilities of the additive in the polymer and in the external phase.

Knowledge of the partition coefficient is necessary in order to calculate migration rates through a stagnant or poorly mixed external phase or to estimate the migration into an external phase that has a finite capacity for the additive. Techniques to calculate the partition coefficient are covered in Section 4.4.

2.6.4 Migrant Capacity in the External Phase

For this report, the external phase is always considered to be devoid of the migrant of interest at the start of the migration process. As migration occurs, the additive concentration in the external phase increases. As time passes, one of two situations will develop in the external phase that will depend on the volume of the external phase, the amount of additive available for migration, and the partition coefficient.

In one case, the volume of the external phase is sufficiently large so that it can accept all the additive without surpassing about 10% of the saturation concentration possible if equilibrium existed between the external phase and polymer. Below the 10% level, the external phase appears to the polymer as if its additive concentration is essentially zero, and the presence of additive in the external phase does not significantly affect the concentration driving force for migration.

In the other case, at higher concentrations of additive in the external phase, the driving force for additive migration into the external phase decreases. Migration rates drop below those that would have occurred in the large external volume case and may even eventually cease. At the point at which migration stops, a partition equilibrium exists between the additive in the polymer and the additive in the external phase. Techniques for estimating the saturation concentration of a migrant in air and water external phases are provided in Section 4.4.2.

2.6.5 Diffusion Coefficient in the External Phase

When the external phase is stagnant, migrant molecules enter the external phase by diffusion. In this case, similar to diffusion within the polymer, the migration rate becomes a function of the concentration gradient driving force and the diffusion coefficient of the additive in the external phase. The diffusion coefficient is a property of the migrant-external phase pair.

Diffusion coefficients of additives through vapor are relatively high, generally in the 10^{-1} to 10^{-2} cm^2/s range, because the molecules of the vapor are widely spaced and thus provide an open network for diffusion. The molecules of a liquid are closer together and therefore holes for diffusion are reduced relative to a vapor external phase. Typical diffusion coefficients for liquids are in the range of 10^{-5} to 10^{-6} cm^2/s. Diffusion coefficients for polymeric solids are lower still and cover a much broader range - from 10^{-7} to 10^{-20} cm^2/s. As noted earlier, the more flexible the polymer, the higher its diffusion coefficient. Estimation techniques for diffusion coefficients in air, water, and polymers are covered in Sections 4.3.1, 4.3.2, and 4.2, respectively.

2.6.6 Degradation

In the discussion of the migrant capacity of the external phase (Section 2.6.4), the additive was considered inert. The capacity of the external phase was determined solely by its capacity for the additive. The additive, however, may react in the external phase. For example, an antioxidant that is designed to react with oxygen may do so in an external phase such as air or water containing dissolved oxygen. In these cases, it is possible for higher levels of migration to occur than would have been expected on the basis of the partition coefficient of the unreacted antioxidant. The kinetics of the reaction may even control the migration process (Till et al., 1983; Gandek, 1986). Degradation of the additive in the external phase is not considered further in this report.

2.6.7 Surfactants

Another factor that can strongly affect migration is the presence of surface active agents (i.e., surfactants) in the external phase. Surfactants are molecules having both hydrophilic and oleophilic segments. As such, they promote the solubilization of oleophilic substances in, for example, water. In such cases, the effective capacity of the external phase can be greatly increased giving a large "apparent" partition coefficient. Surfactants can be effective at very low concentrations.

2.6.8 Penetration

Just as additives can migrate out of polymeric materials, the external phase may migrate into the polymer. In some cases, the amount of external phase penetration into the polymer is sufficient to influence migration significantly. This effect occurs principally with liquid external phases. As the polymer absorbs liquid, it may soften, swell, become a gel and, in the extreme, dissolve in the liquid. As this process develops, the molecules of the polymer become more mobile. This results in more and larger "holes" for diffusing molecules. Thus the migrant diffusion coefficient increases.

An interesting aspect of penetration is the case in which the external phase is a multicomponent liquid containing penetrants at relatively low concentrations. Such penetrants may be preferentially absorbed by the polymer. A possible consequence is that the polymer exhibits migration levels disproportionate with the nominal penetrant concentration in the external phase. This effect has been observed in the case of certain food packaging materials in contact with fruit juices that contain low concentrations of essential oils (Till et. al., 1983). Penetration of the external phase into the polymer is not considered further in this report.

2.7 Temperature

Migration increases strongly with temperature. The principal reason is that the diffusion coefficient follows an Arrhenius relationship (i.e., it increases exponentially with absolute temperature).

In addition, the physical state of the polymer is a function of temperature. As discussed earlier in Section 2.2.1, at temperatures below the glass transition value, the polymer molecules are relatively immobile and diffusion is slow. Diffusion is more rapid above T_g. As temperatures increase further, crystallites, if present, melt and the polymer becomes amorphous - a condition also associated with more rapid diffusion.

In the case of a liquid external phase, an increase in temperature also raises the diffusion coefficient of any penetrating liquid into the polymer, thereby raising the rate and extent of swelling and extraction. Temperature may also affect the solubilities of the additive in the polymer and external phase and, consequently, the partition coefficient. Techniques provided in Section 4 to estimate values for many of the required input parameters (e.g., the diffusion coefficient in the polymer, the partition coefficient) apply only at 25°C. The model can, however, be used to estimate migration at higher temperatures but requires the user to input values for the required parameters at the appropriate temperature.

2.8 Time

The dependence of migration on time is addressed in detail in Section 3 and is discussed only briefly here. In cases where migration is controlled by a diffusive process, initially, migration is proportional to the square root of time. Accordingly, migration occurs at an ever-decreasing rate. This applies to situations in which diffusion is the rate limiting step. In cases where the migration is controlled by mass transfer processes in the external phase, the initial migration is proportional to linear time. Thus the migration rate will be constant until the external phase begins to exhibit finite characteristics or there is a significant decrease in the additive concentration in the polymer.

2.9 Overall Summary

While it is unlikely that the history of a polymer product will be known, it is worthwhile to note that, over time, a product will be exposed to a variety of external phases (Ayres et al., 1983). Some of these may be penetrating and others inert; some may be well-agitated and others stagnant; some may be essentially infinite in volume and others finite. Migration occurs to greater or lesser extents to each of these external phases and, in so doing, affects the additive concentration profile within the polymer in a variety of ways that may impact subsequent migration. To take all these potential exposures into account in a mathematical model would be a very complex task. Furthermore, to attempt to do so is likely to be impractical given that generally not much is known about the basic properties of the polymer, additive, and external phase or their interactions. To circumvent these problems, simplifying assumptions and approximations are necessary. These assumptions address, for example, the concentration gradient across the polymer, the transfer at the interface, and the conditions within the external phase. Theoretical and experimental investigators have established a consistent set of assumptions that adequately correlate migration data. In Section 3 we present models based on these assumptions that provide procedures for estimating additive migration from polymeric materials to a variety of external phases.

3. MODELS FOR MIGRATION ESTIMATION

3.1 Introduction

In the preceding section, many of the complex factors influencing migration were discussed. An impractical level of testing would be required to examine all the parameters for the number of polymer-additive systems of interest to the EPA. Thus, there is a need for mathematical models to estimate the potential loss of additives to the environment.

Such models should require minimum input data and produce an estimate of the fraction of additive initially present in the polymer that might be lost from the polymer as a function of time. For various scenarios, different inputs are required. Several inputs are required to physically characterize a system (e.g., the polymer film thickness, the environment in contact with the polymer, etc.). Other inputs are required to define the basic migration parameters (e.g., the diffusion coefficient, the partition coefficient, solubilities of the additive, etc.). Should values for these inputs not be available, we present some techniques in Section 4 to estimate them.

3.2 Assumptions

The mathematical models presented in the section are based on the assumption of an ideal polymer-additive system having the following properties:

- the polymer is a flat sheet of uniform thickness with no edges,
- initially, the additive is homogeneously distributed throughout the polymer and there is no additive present in the external phase. The additive of concern is not affected by any other migration that may be occurring,
- swelling or penetration does not occur, or, if it does, it does not affect the physical dimensions appreciably nor does it affect the migration,
- the diffusion coefficient of the additive is a function only of temperature and not of position or time,
- the migration is isothermal, and
- Fick's laws apply.

3.3 General Rate Concepts in Migration

3.3.1 The Polymer Film

As noted in the assumptions above, the additive is initially distributed uniformly throughout the polymer film. At time zero, some change occurs at the film surface to allow additive to leave the film. This step establishes a lower additive concentration near the film surface and initiates a diffusion process in the polymer film that attempts to reestablish a new uniform concentration. Further movement of the additive to the external phase necessitates additional diffusion to occur within the polymer.

The movement of additive within the polymer towards the film surface and into the external phase is, therefore, a function of gradients in additive concentration. This generality is expressed in mathematical terms by Fick's first law.

$$\text{Diffusion flux} = D_p\ (\partial C_p/\partial x) \tag{3-1}$$

The flux (mass/area-time) is, therefore, proportional to the gradient in concentration and the coefficient of proportionality is the diffusion coefficient of the migrant in the polymer, D_p. x is the distance measured into the polymer film and, because the concentration is always larger in the film interior during migration, $\partial C_p/\partial x > 0$. The units of D_p are $(\text{length})^2/\text{time}$ and are usually expressed as cm^2/s.

To obtain the flux of additive leaving the film, Eq. (3-1) is employed with the gradient $(\partial C_p/\partial x)$ being evaluated at the polymer film interface (x=0). Thus one must know how C_p varies with x at different times. This is accomplished by employing Fick's second law which is Eq. (3-1) applied over a short distance dx in a short period of time dt.

$$\partial C_p/\partial t = D_p(\partial^2 C_p/\partial x^2) \tag{3-2}$$

All models developed in this section utilize Eq. (3-2) to determine $C_p = f(x,t)$. Since Eq. (3-2) is a partial differential equation, the solution requires two initial or boundary conditions. One of these conditions, common to all cases, is the assumption that the additive is, initially, homogeneously distributed. In mathematical terms,

$$C_p(x) = C_{p,o} \text{ for all } x \text{ at } t = 0 \tag{3-3}$$

The remaining condition relates to events occurring at the film-external phase boundary. Various physical situations lead to different boundary conditions and, therefore, to different $C_p = f(x,t)$ relations.

Before exploring the various types of boundary conditions, we note that there are two interpretations when defining the polymer thickness. The simplest case occurs for situations where the additive is lost from only one side of the film (i.e., the other side is somehow prevented from losing additive). In this case, the length variable x begins at zero on the side where loss takes place and increases to a value L at the side where no loss occurs. Thus, L is the true film thickness. The other case is when migration occurs from both faces of the polymer film. In this situation there is no flux across the mid-plane of the film and $\partial C_p/\partial x = 0$ at this plane. Thus, the system behaves as though the film were only one-half its true thickness and, in the models, the characteristic film thickness is only one-half the true thickness.

Therefore, in employing the models described later, it is necessary to provide the true film thickness and, also, to specify if migration occurs from only one or from both surfaces. When the variable L is employed in equations, it will represent the true film thickness for one-sided migration, but only one-half the film thickness for two-sided migration.

3.3.2 Migration into a Fluid External Phase

In cases where the additive leaves the polymer film and moves into a fluid external phase (e.g., air and water), there are two important considerations that determine the appropriate boundary condition that, with Eq. (3-3), may be used to solve Eq. (3-2).

3.3.2.1 Partitioning

It is generally assumed that during migration, the additive concentration within the polymer is in equilibrium with the additive concentration in the fluid at the interface. The ratio of the equilibrium concentrations is the partition coefficient K. (See Section 2.6.3.)

$$K = (C_e/C_p)_{\text{interface}} \tag{3-4}$$

The concept of equilibrium at the interface implies no rate restrictions (i.e., the additive can move from the polymer into the external phase without hindrance). Thus, any rate processes relate only to movement of the additive into the bulk of the external phase. The appropriate boundary condition is then:

$$\text{Flux into the fluid external phase} = k(C_{e,\text{interface}} - C_{e,\text{bulk}}) \tag{3-5}$$

where k is a mass transfer coefficient. Denoting

$$C_{p,\text{interface}} = C_{p,x=0} \tag{3-6}$$

and using Eqs. (3-1) and (3-4), the boundary condition becomes

$$D_p(\partial C_p/\partial x)_{x=0} = k(KC_{p,x=0} - C_{e,\text{bulk}}), \quad t > 0 \tag{3-7}$$

3.3.2.2 Variation of the Additive Concentration in the External Phase

Next, one must examine whether $C_{e,\text{bulk}}$ varies appreciably during the migration process. First, we note the limiting case where the volume of the external phase is very large or where flow processes occur so that $C_{e,\text{bulk}}$ is always essentially zero. That is, there is no measurable accumulation of migrant in the external phase, at least relative to $KC_{p,x=0}$. Under such circumstances, $C_{e,\text{bulk}}$ is set equal to zero in Eq. (3-7) to yield

$$D_p(\partial C_p/\partial x)_{x=0} = kKC_{p,x=0} \qquad (C_{e,\text{bulk}} \to 0) \tag{3-8}$$

Alternatively, for a smaller quantity of external fluid, one may have the situation where $C_{e,\text{bulk}}$ increases from an initial value of zero to approach C_e at the interface (i.e., equal to $KC_{p,x=0}$). In this case, the flux from the polymer is hindered by the low driving force to move additive away from the film surface. This situation often occurs when the additive solubility in the external phase is quite low (small K) so that the right-hand side of Eq. (3-7) is initially small and decreases even further as $C_{e,\text{bulk}}$ rises.

3.3.3 Migration into a Solid External Phase

If the external phase is a solid (or can be treated as one because there are no convective currents), the physical processes in migration may be described as follows. Within the polymer film, the flux of additive to the surface is identical to that occurring with a fluid external phase (Section 3.3.1). At the film surface, there again occurs a partitioning step as described in Section 3.3.2.1. However, the mechanism to move the additive from the interface into the bulk solid phase takes place by diffusion rather than by convection and the boundary condition given by Eq. (3-7) is replaced by

$$D_p(\partial C_p/\partial x)_{x=0} = -D_e(\partial C_e/\partial y)_{y=0} \qquad (3\text{-}9)$$

Here, y is the length variable in the solid external phase and is measured from the interface. C_e is the additive concentration in the external phase. D_e is the additive diffusion coefficient in the solid external phase. Since $\partial C_e/\partial y < 0$, a negative sign is required in Eq. (3-9).

Within the solid external phase, diffusion occurs and an equation comparable to Eq. (3-2) applies, i.e.,

$$\partial C_e/\partial t = D_e(\partial^2 C_e/\partial y^2) \qquad (3\text{-}10)$$

One has, in essence, a dual diffusion problem with Eqs. (3-4) and (3-9) relating the concentration in both solids. The effective thickness of the solid phase is normally set equal to the volume of the external phase (V_e) divided by the exposed surface area (A), V_e/A. For large values of V_e/A, the external solid phase is essentially infinite in effective thickness.

3.4 General Mathematical Models

3.4.1 Fluid External Phase

For the general case of migration into a fluid phase, the rate model may be formulated mathematically using Eqs. (3-2), (3-3), and (3-7) with a variation that $C_{e,bulk}$ may be set equal to zero [as in Eq. (3-8)] provided the external phase volume is sufficiently large or the additive solubility in this phase is such that $C_{e,bulk} << KC_{p,x=0}$. Thus, it is necessary to specify $C_{p,o}$, D_p, k, K, L, and A to compute $C_p = f(x,t)$ and, therefore, the migrant flux from Eq. (3-1) at $x = 0$.

Solutions have been obtained by Hatton and co-workers (1979, 1983) and explored by Gandek (1986) using the following dimensionless groups:

$$\tau = D_p t/L^2 \qquad (3\text{-}11)$$

$$\alpha = KV_e/AL \qquad (3\text{-}12)$$

$$\gamma = kKL/D_p \qquad (3\text{-}13)$$

where t is the time and, as noted earlier, L is the film thickness for one-sided migration and one-half the film thickness for two-sided migration.

We do not present the equations for $C_p = f(x,t)$ (see Gandek, 1986). Rather, we have utilized them with the flux equation [Eq. (3-1)] and, by integration, have obtained the final relation describing the total migration occurring at any time. That is, with $C_p = f(x,t)$,

$$\text{Migrant flux} = D_p(\partial C_p/\partial x)_{x=0} \tag{3-14}$$

and

$$\text{Total mass migrated/area} = \int_0^t (\text{flux})\, dt \tag{3-15}$$

Further, we have non-dimensionalized the mass of additive migrated as

$$M_\tau = (\text{total mass migrated/area})/LC_{p,o} \tag{3-16}$$

so that M_τ is the fraction of the original additive that has been lost from the polymer.

For the general case where one must be concerned with the variation of the concentration in the bulk of the external phase, $C_{e,bulk}$,

$$M_\tau = [\alpha/(1+\alpha)] + \sum_{n=1}^{\infty} (\alpha^2/Q_n)\exp(-\omega_n^2\tau) \tag{3-17}$$

with

$$Q_n = \alpha + \gamma^2[\omega_n + \sin(\omega_n)\cos(\omega_n)]/\{2\omega_n[\gamma\cos(\omega_n)-\omega_n\sin(\omega_n)]^2\} \tag{3-18}$$

and ω_n are the non-zero, positive roots of the characteristic equation

$$\omega_n\tan(\omega_n) = \alpha\gamma\omega_n^2/(\alpha\omega_n^2-\gamma) \tag{3-19}$$

If one is not concerned about variations in $C_{e,bulk}$ due to the large value of V_e/A or because $C_{e,bulk} << KC_{p,x=0}$, then the boundary condition given by Eq. (3-8) may be used. In this case,

$$M_\tau = 1 - 2\gamma^2 \sum_{n=1}^{\infty} [\exp(-r_n^2\tau)]/[r_n^2(r_n^2+\gamma^2+\gamma)] \tag{3-20}$$

where r_n are the roots of the equation

$$r_n\tan(r_n) = \gamma \tag{3-21}$$

3.4.2 Fluid External Phase with a Large Mass Transfer Coefficient

In some instances, one may desire to obtain an estimate of the migration in a worst-case analysis using a large value for the mass transfer coefficient, k. Eqs. (3-17) and (3-20) could still be employed by setting the dimensionless parameter γ [Eq. (3-13)] to be large. However, it is more expedient to resolve the basic differential equations with k (or γ) $\rightarrow \infty$.

Two boundary conditions are possible. If the external fluid phase is large in extent so that the additive concentration remains very low or at least small compared to any saturation solubility, then one can state:

$$C_{e,\mathrm{interface}} = C_{e,\mathrm{bulk}} = 0 = C_{p,x=0} \qquad (3\text{-}22)$$

For this simple case (Crank, 1975),

$$M_\tau = 1 - 2 \sum_{n=0}^{\infty} [\exp(-q_n^2\tau)]/q_n^2 \qquad (3\text{-}23)$$

where

$$q_n = (2n+1)\pi/2 \qquad (3\text{-}24)$$

On the other hand, if $C_{e,\mathrm{bulk}}$ is sufficiently large to affect the migration, then the appropriate boundary condition is

$$C_{e,\mathrm{interface}} = C_{e,\mathrm{bulk}} = K(C_{p,x=0}) \qquad (3\text{-}25)$$

where all the variables in Eq. (3-25) are functions of time except K. In this case,

$$M_\tau = [\alpha/(1+\alpha)] - 2\alpha^2 \sum_{n=1}^{\infty} [\exp(-p_n^2\tau)]/(1+\alpha+\alpha^2 p_n^2) \qquad (3\text{-}26)$$

and p_n are the non-zero, positive roots of

$$\tan(p_n) + \alpha p_n = 0 \qquad (3\text{-}27)$$

3.4.3 Solid External Phase

The appropriate boundary condition for this case is given by Eq. (3-9) and the solution to the coupled partial differential equations was only recently obtained by Gandek (1986). Since no external mass-transfer coefficient is involved, the dimensionless group γ does not enter. Instead, a new dimensionless group β is introduced,

$$\beta = K(D_e/D_p)^{1/2} \qquad (3\text{-}28)$$

Then,

$$M_\tau = \frac{\alpha}{1+\alpha} - 2 \sum_{n=1}^{\infty} \frac{\tan^2\phi_n \exp(-\phi_n^2\tau)}{\phi_n^2[1+\alpha+(1+\alpha/\beta^2)\tan^2\phi_n]} \tag{3-29}$$

with ϕ_n determined by

$$\tan(\phi_n) + \beta\tan(\alpha\phi_n/\beta) = 0 \tag{3-30}$$

If the solid external phase volume is very large compared to the polymer film volume and K is not exceedingly small, then the dimensionless group α [Eq. (3-12)] becomes a large number. In such cases, it is mathematically more convenient to employ Eq. (3-22) as the boundary condition i.e., $\alpha \rightarrow \infty$. This approach leads to:

$$M_\tau = [2\beta/(\beta+1)](\tau/\pi)^{1/2}\{1-[2\beta/(1+\beta)] \sum_{n=1}^{\infty} [(1-\beta)/(1+\beta)]^{n-1} \times$$

$$[\exp(-n^2/\tau) - (n^2\pi/\tau)^{1/2}\mathrm{erfc}(n/\tau^{1/2})]\} \tag{3-31}$$

Note that, in Eq. (3-31), α does not enter as a variable.

3.4.4 Summary

Six relations have been presented to compute the fraction of additive lost as a function of time. Four of the equations apply for a fluid external phase and two for a solid external phase. The differences between the equations applicable to fluid or solid external phases relate to limiting cases when it may be assumed that some variable is sufficiently large such that one (or more) of the rate steps is of negligible importance. We summarize these equations, the input variables required, and the limiting constraints in Table 4.

For an external fluid phase, Eq. (3-17) represents the general case and, if desired, could be used for all external fluid phase situations. Eq. (3-20) is a simplification for those situations where the external fluid phase is so large that the bulk additive concentration is essentially zero or for situations where the additive is very soluble in the fluid. Mass transfer effects are considered though. In Eq. (3-26), finite external phase volumes or limited solubilities exist, but there is no limit to the mass transfer coefficient. Eq. (3-26), thus is also a simplification but does address solubility limitations. Finally, Eq. (3-23) allows one to specify a worst case scenario with a large external volume or no solubility limitation in the fluid and with a large (→ ∞) mass transfer coefficient.

For a solid external phase, Eq. (3-29) provides a solution for the general case while, with Eq. (3-31), one is not concerned with solubility limitations due either to a large value of V_e/A or because the additive solubility in the solid is very high.

TABLE 4. MIGRATION MODEL EQUATIONS

External Phase	Eq. No.	Input Variables Required*	External Volume Large and/or No Solubility Limitations in the Fluid	Mass Transfer Coefficient Large
Fluid	3-17	$K,k,V_e/A$	No	No
	3-20	K,k	Yes	No
	3-23	-	Yes	Yes
	3-26	$K,V_e/A$	No	Yes
Solid	3-29	$K,D_e,V_e/A$	No	NA**
	3-31	K,D_e	Yes	NA

* In all cases L, t, and D_p are required.

** NA = not applicable

The various models require different amounts of input data. Eqs. (3-17) and (3-29) require the most information while the limiting cases require less due to the relaxation of some constraints.

In Figure 1 we present an algorithm of the logic used in the computer program described in Section 6 to direct a user to the various model equations. At the start, one is required to define the physical scenario by specifying the time for migration, the film thickness (L), and whether the extraction is one- or two-sided extraction. Further, the diffusion coefficient of the additive in the polymer (D_p) must be given or estimated.

The initial concentration of the migrant is not required at this point since the equations yield the fraction of the additive that has migrated. If one desires the absolute flux of migrant, Eq. (3-16) would be used and the total mass of migrant lost per unit area would be the product of the fraction lost (M_τ) the initial migrant concentration ($C_{p,o}$) and the polymer thickness (L).

If the external phase is a fluid, the user must provide the mass transfer coefficient (k) or state that it is very large (e.g., to develop a worst-case scenario). When k is large, one must then provide the solubility of the additive in the fluid phase or state that it is unlimited. If the latter, Eq. (3-23) is employed to calculate the migration. If there is a finite solubility, but a very large quantity of external phase, again Eq. (3-23) is used. Both these situations will produce a worst-case estimate of the migration. However, if there is a finite solubility and a limited quantity of external phase, then the solubility of the additive in both the fluid and polymer must be specified to calculate the partition coefficient (K), and Eq. (3-26) is used to estimate the fractional migration.

Should the user elect to provide a mass transfer coefficient, solubilities of the additive in the fluid and the polymer are also necessary. Then, depending upon whether one states the external phase is unlimited (or the solubility of the additive in this phase is large) or limited, Eq. (3-20) or Eq. (3-17), respectively, is used to determine migration.

In the case of a solid external phase, specification of the solubilities of the additive in both phases must be given as well as the diffusion coefficient of the additive in the solid external phase. Depending upon the choice of an unlimited or limited external phase, Eq. (3-31) or Eq. (3-29) is employed in the computations.

3.5 Significance of the Dimensionless Groups

3.5.1 $\tau = D_p t/L^2$

This group provides a convenient method to non-dimensionalize the time for a given physical situation. For example, a thicker film would require longer times to attain the same value of τ.

3.5.2 $\alpha = KV_e/AL$

This group relates primarily to situations where the external phase becomes saturated with additive and migration ceases even though M_τ, the fraction migrated, is still less than unity. To illustrate this relationship, consider a case in which equilibrium between the two phases is attained when the additive concentration in the polymer has dropped from a

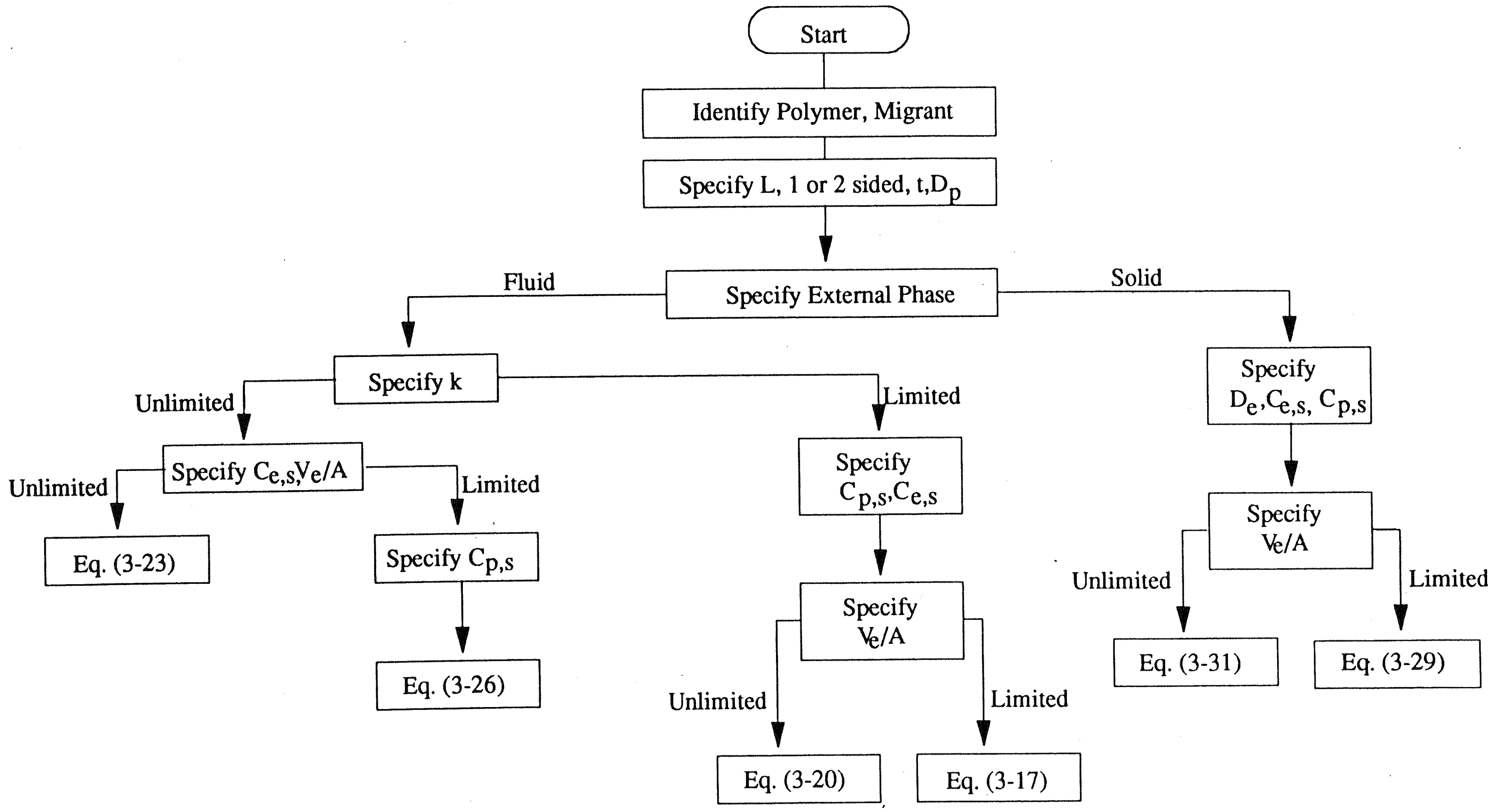

Figure 1. Flow Chart for Migration Model Equation Selection

starting value of $C_{p,o}$ to C_p*. Also, the concentration of the additive in the external phase has increased from zero to a new value C_e*. (Note that since an equilibrium state is assumed, neither C_p* nor C_e* are functions of position or time.) During the actual migration,

$$\text{Mass lost from the polymer} = AL(C_{p,o} - C_p^*) \tag{3-32}$$

This relationship would hold for both one- or two-sided migration because, in the former, L is the true film thickness and A the one-sided area whereas in the latter, L is only one-half the true film thickness but A now represents a two-sided area.

The mass lost from the polymer must appear in the external phase, i.e.,

$$\text{Mass in the external phase} = V_e(C_e^* - 0) \tag{3-33}$$

Since, at equilibrium,

$$K = C_e^*/C_p^* \tag{3-34}$$

then, equating Eqs. (3-32) and (3-33) and using Eq. (3-34),

$$AL(C_{p,o} - C_p^*) = V_eC_e^* \tag{3-35}$$

$$ALC_{p,o} - ALC_p^* = V_eC_e^* = V_eKC_p^* \tag{3-36}$$

$$C_p^*/C_{p,o} = AL/(AL + KV_e) = 1/[1 + (KV_e/AL)] = 1/(1+\alpha) \tag{3-37}$$

Since M_τ*, the fraction migrated at this equilibrium, can be defined as

$$M_\tau^* = (C_{p,o} - C_p^*)/C_{p,o} \tag{3-38}$$

then

$$M_\tau^* = \alpha/(1+\alpha) \tag{3-39}$$

Referring to the models in Section 3.4, we note that, in the equations which assume limited external volumes or solubility limitations [Eqs. (3-17), (3-26), and (3-29)], there is a leading term of $\alpha/(1+\alpha)$ in the expressions for M_τ. Therefore, as τ becomes large (e.g., long times), M_τ is constant and equal to $\alpha/(1+\alpha)$. The physical significance is that the external phase is saturated with additive and all migration ceases.

If $\alpha >> 1$, migration can occur to deplete essentially all the additive from the polymer film, but for $\alpha << 1$, the maximum fractional migration is $\approx \alpha$. For $\alpha = 1$, 50% of the additive would migrate.

3.5.3 $\gamma = kKL/D_p$

The dimensionless group γ provides some perspective about the magnitude of the resistance to transfer across the external phase boundary layer relative to the diffusional resistance within the polymer. Values of $\gamma > 100$ indicate that the boundary layer resistance is negligible and only the diffusional resistance within the polymer film is important. In such a case, the use of Eq. (3-23) or Eq. (3-26) would be acceptable. (See Table 4.) Values of γ less than about 1 would indicate that the resistance to transfer across the boundary layer far exceeds the diffusional resistance in the polymer film and Eq. (3-17) or Eq. (3-20) must be used.

3.5.4 $\beta = K(D_e/D_p)^{1/2}$

β is a measure of the relative resistances to diffusion in the solid external phase and in the polymer. If $\beta > 10$, diffusional resistances in the polymer greatly exceed those in the solid external phase. Conversely, if $\beta < 0.1$, then the diffusional resistance has shifted to the solid external phase. Note that, while D_e and D_p are important in defining β, the partition coefficient is also a key parameter. Small partition coefficients lead to a greater importance of external phase diffusion.

3.6 Illustrative Examples

3.6.1 Fluid External Phase

In Figure 2, we have graphed the results of applying Eq. (3-23) or Eq. (3-26). For these two cases, the mass transfer coefficient is assumed to be very large so that diffusional resistances within the polymer film greatly exceed any resistance across the boundary layer. When there is also no saturation limitation in the external fluid phase, $\alpha \rightarrow \infty$ and Eq. (3-23) applies. For α less than about 10, Eq. (3-26) must be used. Here, at large values of τ, the fractional migration levels out to a value of $\alpha/(1+\alpha)$ as the polymer film and external fluid phase approach saturation equilibrium. With large values of α, the fractional migration is proportional to the square root of τ (or time) up to a point where about 50-60% of the additive has been lost.

If a finite mass transfer coefficient is employed, the fractional migration as a function of τ is shown in Figure 3 for different values of γ but at a constant $\alpha = 0.1$. At small values of γ, essentially all resistance to migration resides in the boundary layer transfer. When $\gamma > 100$, the important resistance is the diffusion within the polymer. In Figure 3, the curve for $\gamma \rightarrow \infty$ is identical to the $\alpha = 0.1$ curve in Figure 2 that was drawn for an unlimited mass transfer coefficient. For $\alpha = 0.1$, a partition equilibrium is established at large values of τ (long times) with $M_\tau \rightarrow \alpha/(1+\alpha) = 0.1/1.1 = 0.091$.

3.6.2 Solid External Phase

We illustrate some results for the solid external phase models in Figure 4. The maximum migration occurs when $\alpha = \beta = \infty$ which is a special case of Eq. (3-31) with no saturation limitations. For α values smaller than about 10, Eq. (3-29) applies and, again, there is a partition equilibrium of $\alpha/(1+\alpha)$. Increasing β leads to more migration; this increase can result with systems having a large K, a large D_e, or when D_p is small relative to D_e.

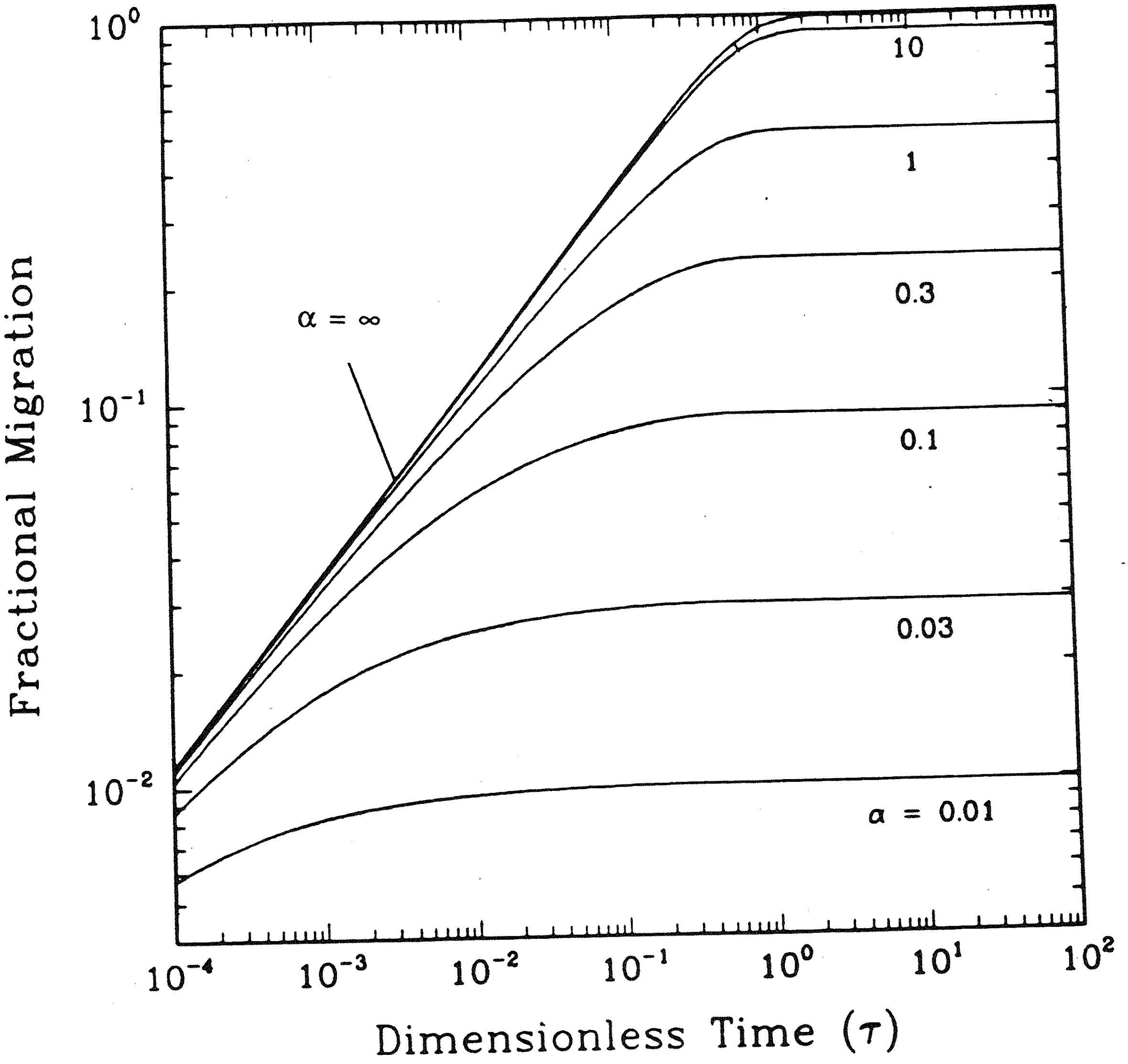

FIGURE 2. Migration Estimates for the Fluid External Phase Cases Where the Mass Transfer Coefficient is Unlimited. Eq. (3-23) Applies When $\alpha \rightarrow \infty$, All Other Curves from Eq. (3-26). (Gandek, 1986.)

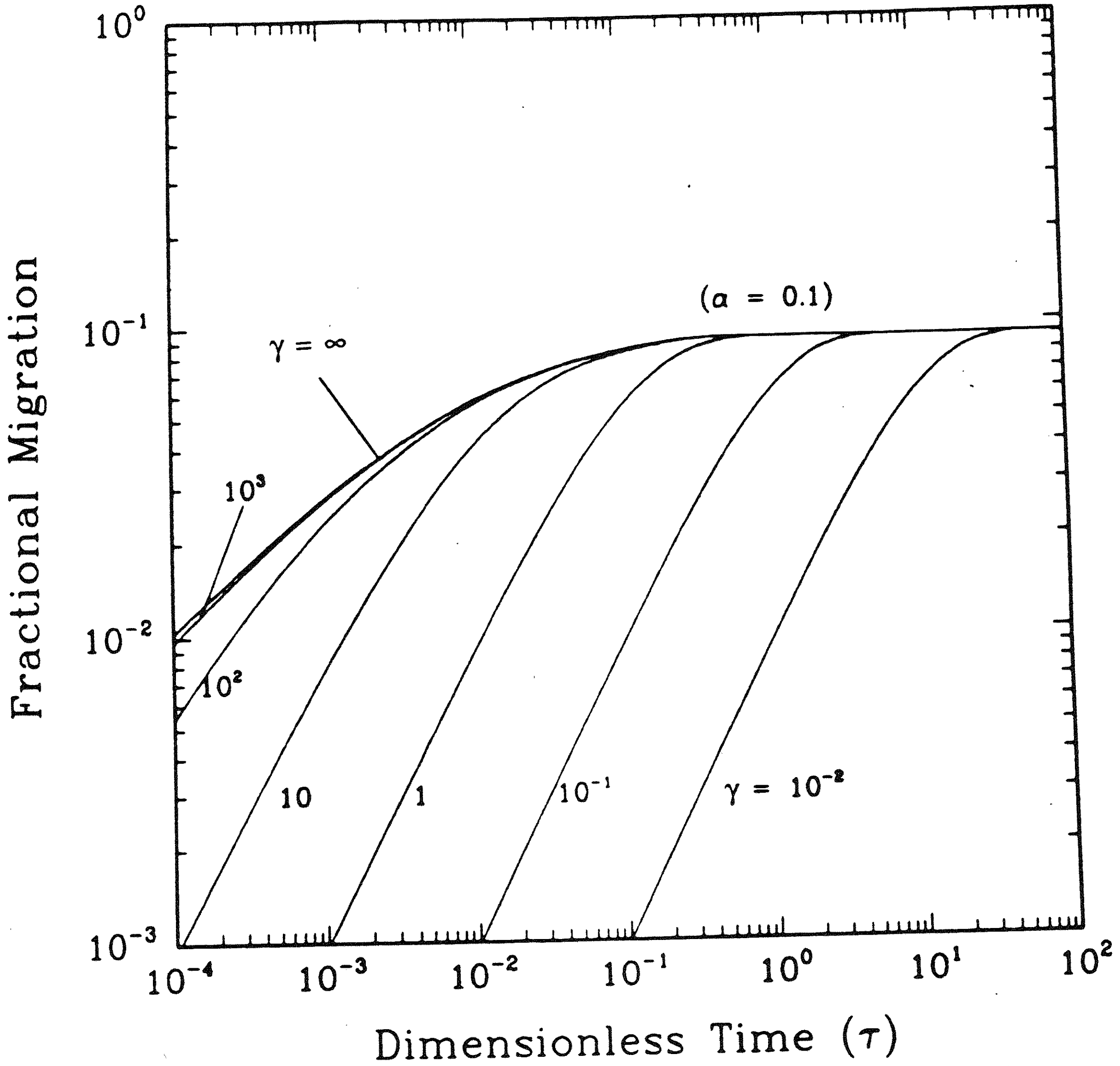

FIGURE 3. Migration Estimates for the Fluid External Phase Cases with a Finite Mass Transfer Coefficient, and $\alpha = 0.1$ (Gandek, 1986).

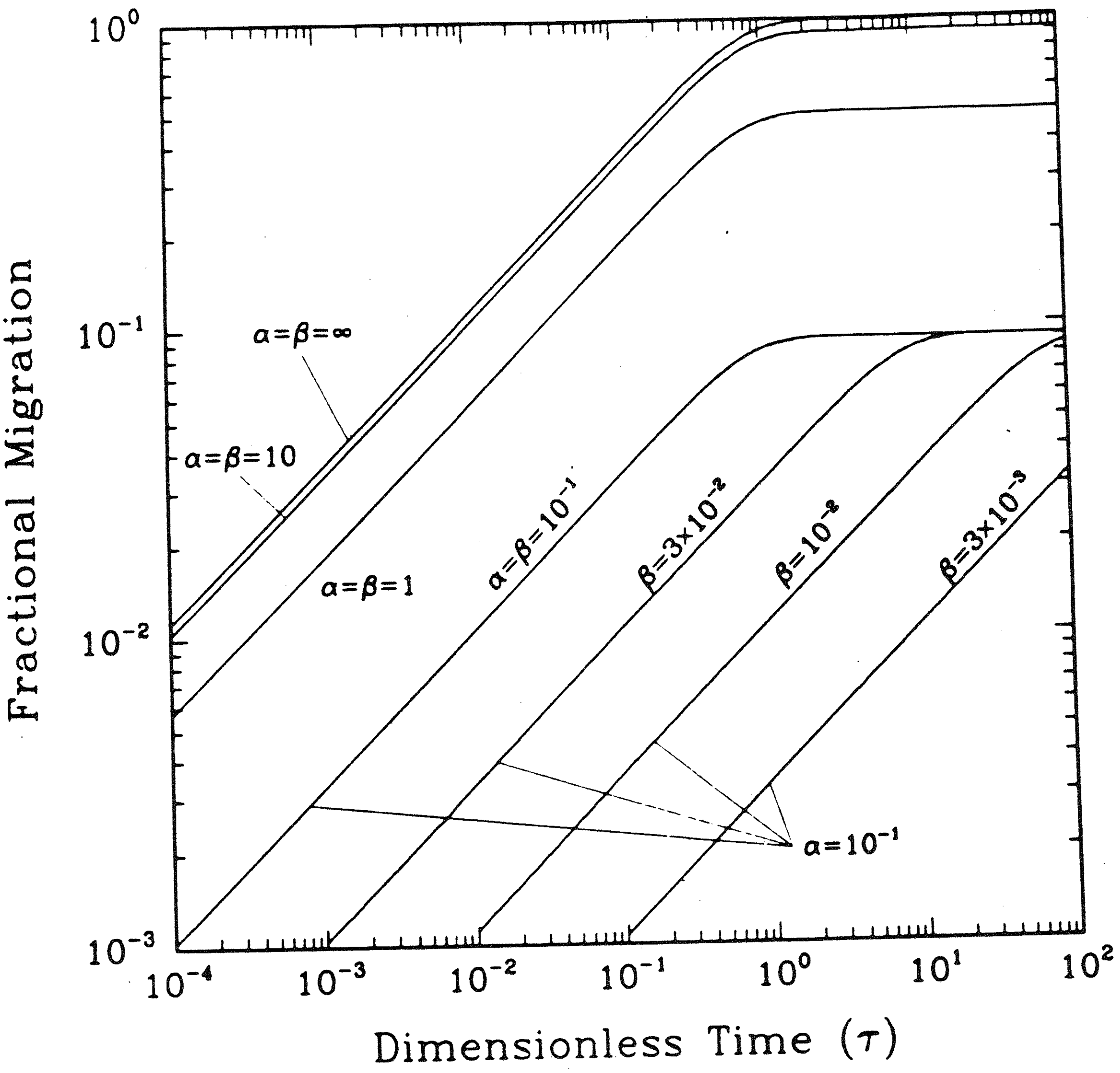

FIGURE 4. Migration Estimates for the Solid External Phase Cases (Gandek, 1986).

4. ESTIMATION OF VARIABLES

4.1 Introduction

The models developed in Section 3 provide equations to predict additive migration from polymeric materials under a variety of conditions. In order to use these models, input data are required. In all cases, the initial concentration of the additive in the polymer, the polymer thickness, the time, and the diffusion coefficient of the additive in the polymer are required. Also, a specification of whether the additive is removed from one or both faces of the polymer is necessary. Values of the initial additive concentration and polymer thickness are usually available or can be approximated within a fairly narrow range based on the application of the polymeric material. Values for the additive diffusion coefficient in the polymer, however, are generally not known nor readily available. Consequently, they must be estimated.

In some instances, other input data are required. These inputs include the partition coefficient (the ratio of the equilibrium solubility of the additive in the external phase to that in the polymer), the external phase mass-transfer coefficient, or, if the external phase is a solid or a stagnant liquid, the diffusion coefficient of the additive in this phase.

Section 4 addresses the estimation of these input data. Estimation techniques are provided for the variables listed in Table 5.

4.2 Diffusion Coefficients of Additives in Polymers (D_p)

The diffusion coefficient of an additive in a polymeric material is a function of the segmental mobility of the polymer molecules and the size and shape of the additive. Over the past 30-40 years, researchers have attempted to correlate the diffusion coefficient with a variety of properties of the polymer and additive. These correlations range from simple to quite complex, although a higher degree of correlation is not necessarily associated with the more complex methods. Herein, we suggest a simple approach which enables the estimation of D_p at 25°C knowing only the molecular weight of the migrant and the general type of polymer involved.

In Figure 5, experimentally determined diffusion coefficients for six common polymers are plotted versus diffusant molecular weight on log-log coordinates. Values used to generate Figure 5 were taken principally from Grun (1949), Flynn (1982), and Park (1950, 1951). The degree of correlation is remarkably good. As expected from theory, the largest diffusion coefficients are associated with the most flexible materials, silicone and natural rubbers, and the smallest diffusant molecules. Diffusion coefficients for the more flexible materials are less a function of molecular weight (or size) than those for the stiffer polymers [e.g., polyvinyl chloride (PVC) and polystyrene (PS)]. Over a similar range of molecular weights, D_p for the flexible materials covers 3 to 5 orders of magnitude while for D_p PVC ranges over 10 orders of magnitude. Note, however, that it appears that at high molecular weights, D_p drops precipitously in even the flexible polymers.

Correlation equations based on the curves in Figure 5 have been develoepd for each of the six polymers and are used in the computer program described in Section 6. Thus, by identifying the polymer of interest and inputing a value for the molecular weight of the

TABLE 5. VARIABLES FOR WHICH ESTIMATION TECHNIQUES ARE PROVIDED

Variable	Units	Section
Diffusion Coefficient in Polymer	cm^2/s	4.2
Diffusion Coefficient in External Phase		
• Air	cm^2/s	4.3.1
• Water	cm^2/s	4.3.2
• Other	cm^2/s	4.3.3
Partition Coefficient		
• Additive Solubility in Polymer	g/cm^3	4.4.1
• Additive Solubility in External Phase		
- Air	g/cm^3	4.4.2.1
- Water	g/cm^3	4.4.2.2
Mass Transfer Coefficients		
• Water	cm/s	4.5.1
• Air	cm/s	4.5.2

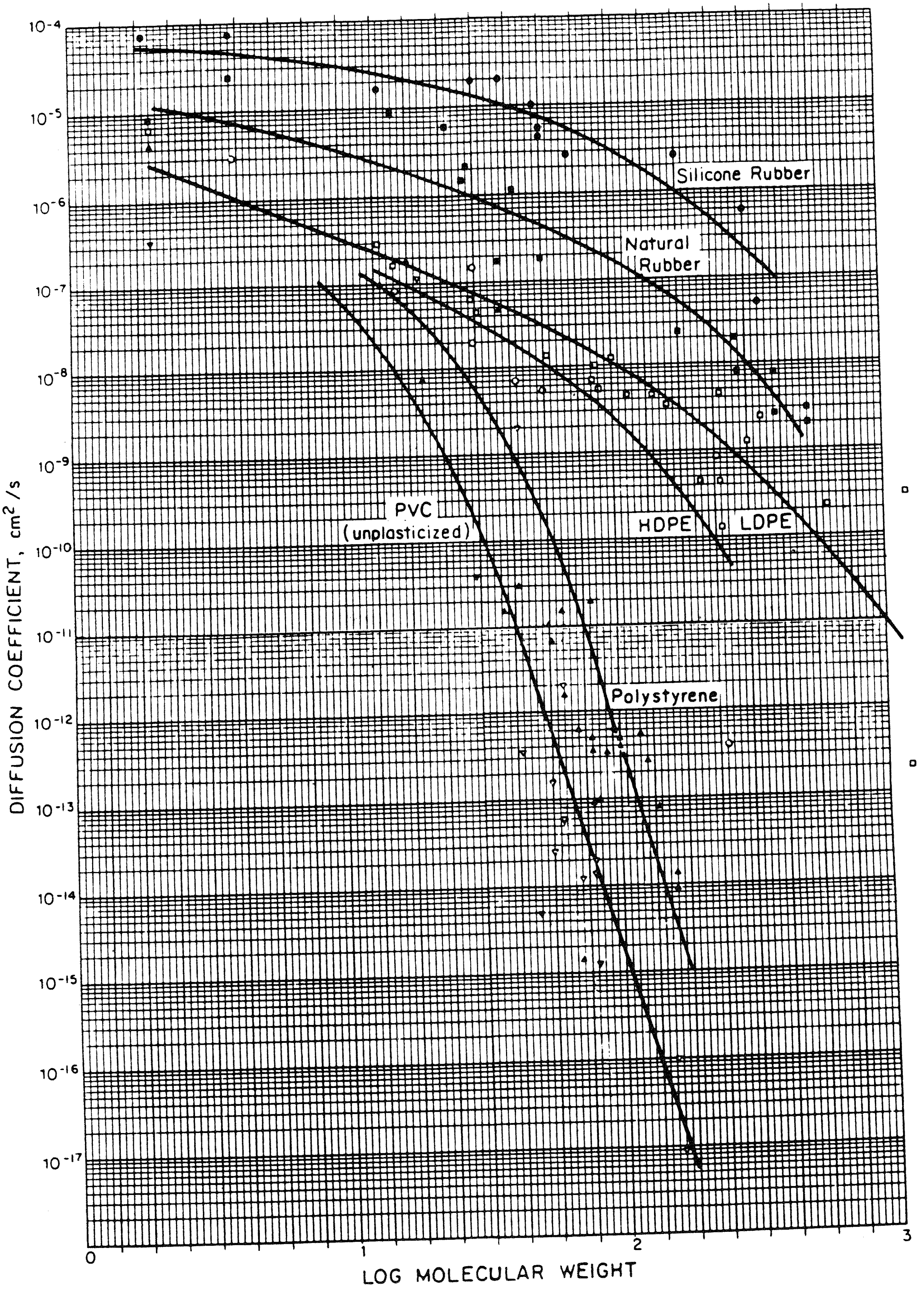

FIGURE 5. Diffusion Coefficients in Six Polymers as a Function of Molecular Weight of Diffusant, T = 25°C.

additive, a value for D_p can be estimated. D_p estimation equations are provided for silicone rubber, natural rubber, LDPE, HDPE, polystyrene and unplasticized polyvinyl chloride.

Most polymers do not have as extensive a compilation of D_p values as those shown in Figure 5. Consequently, estimation of a diffusion coefficient for these other polymers is more difficult and will be less exact. One approach for approximating D_p in a polymer not included in Figure 5 is to compare the diffusion coefficients of a common chemical through the polymer of interest with that for the polymers in Figure 5. Nitrogen, oxygen, and carbon dioxide permeation have been measured through a wide variety of polymers and are useful as "common chemicals." A listing of diffusion coefficients for these gases in polymers is given in Table 6.

As an example, suppose one was interested in estimating the diffusion coefficient of a chemical in Nylon 12 and only polystyrene data were available for this chemical. Using the technique noted above with carbon dioxide as the common chemical, we find from Table 6,

$$\frac{\text{diffusion coefficient (Nylon 12)}}{\text{diffusion coefficient (polystyrene)}} = \frac{0.02}{0.06}$$

This simple technique may lead to large errors, and somewhat different estimates can be obtained by changing the common chemical.

Another approach for estimating D_p for a polymer not addressed in Figure 5 is to assign the polymer to a polymer group or class that represents a relatively narrow range of diffusion coefficients. As a first step to such an approach, we reviewed the permeation and migration literature and compiled a list of diffusion coefficients for a wide variety of polymers and migrants. From this compilation, we categorized the polymers into four groups:

- rubbers,
- polyolefins I (mostly amorphous plastics above their glass transition temperatures),
- polyolefins II (mostly crystalline plastics above their glass transition temperature), and
- glassy polymers below their glass transition temperature.

Ranges were established for the diffusion coefficients in each polymer group. These ranges are shown in Figure 6 which is identical to Figure 5 except that, for clarity, the grid has been simplified and the datum points removed. To facilitate the use of Figure 6, polymers representative of each group are identified in Table 7, in which they are arranged in order of decreasing diffusion coefficient within their respective groups. For example, if one were interested in isotactic polypropylene with a high degree of crystallinity ($\approx$ 60 to 65%), then, from Table 7, this polymer is found near the bottom of the polyolefin II region. If the molecular weight of the migrant were, for example, 178 (log 178 = 2.25), the estimated value of the diffusion coefficient of this migrant would be approximately 3×10^{-11} cm^2/s at 25°C.

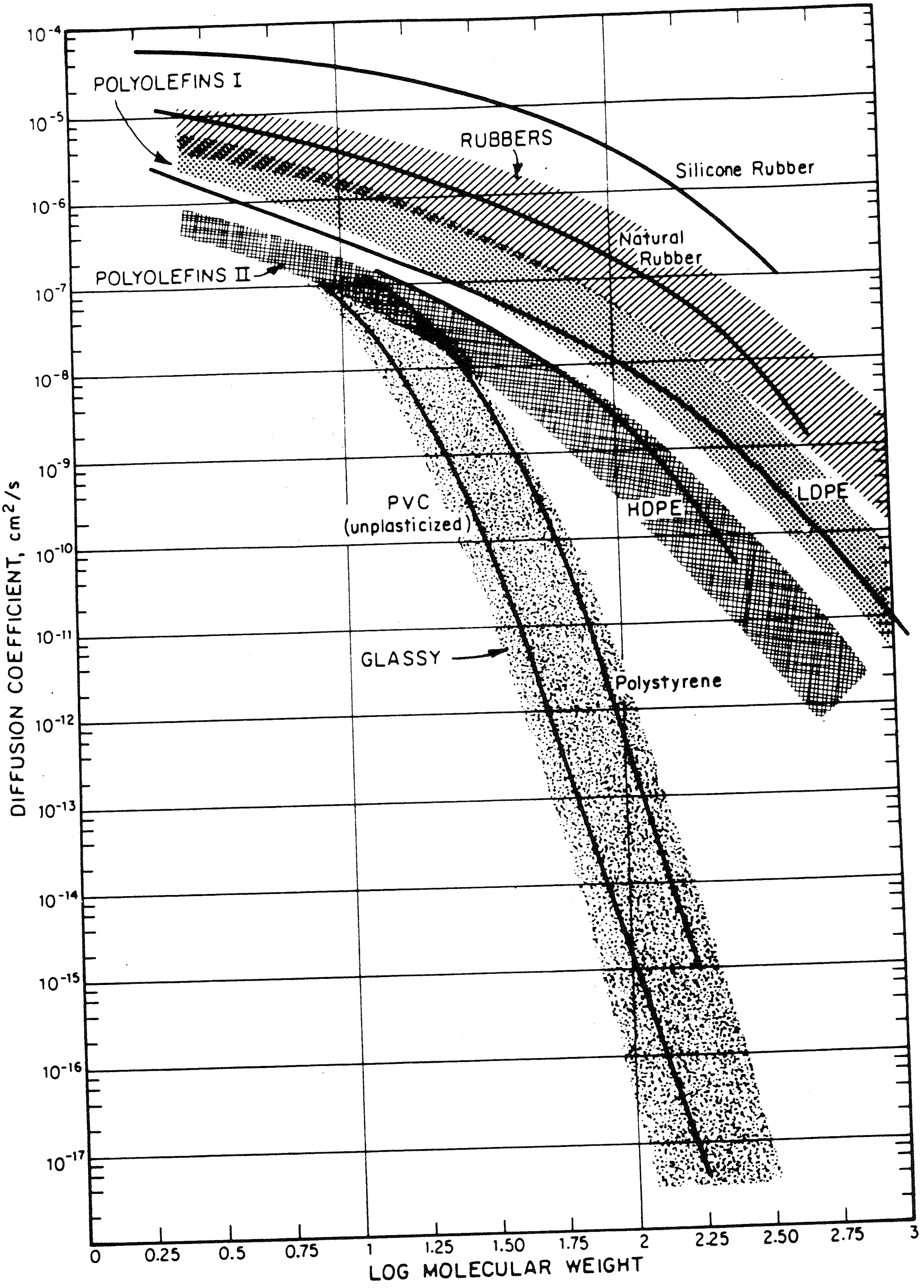

FIGURE 6. Diffusion Coefficients for Four Polymer Groups Described in Table 7, T = 25°C.

TABLE 6. DIFFUSION COEFFICIENTS FOR SELECTED POLYMERS AT 25°C

	$D_p \times 10^6$ (cm^2/s)		
Polymer	Nitrogen	Oxygen	Carbon Dioxide
Poly(1,3-butadiene)	1.1	1.5	1
Poly(butadiene-co-acrylonitrile)80/20	0.5	0.8	0.42
Poly(butadiene-co-acrylonitrile)61/39	0.06	1.4	0.04
Poly(butadiene-co-styrene)92/8	1		
Poly(carbonate) (Lexan)	0.2	0.02	0.005
Poly(chloroprene) (Neoprene)	0.3	0.4	0.3
Poly(dimethylbutadiene) (Methyl rubber)	0.08	0.14	0.06
Poly(dimethylsiloxane) (Silicone rubber)	16	21	
Poly(ethylene) (Density 0.91)	0.3	0.4	0.4
Poly(ethylene) (Density 0.96)	0.09	0.17	0.12
Poly(ethylene-co-propylene)40/60	0.7		
Poly(ethylene terephthalate)	0.001	0.003	0.0006
Poly(ethyl methacrylate)	0.02	0.1	0.03
Nitrocellulose	0.01	0.1	0.02
Nylon 66			0.0008
Nylon 12			0.02
Poly(isoprene) (Natural rubber)	1.2	1.7	1.3
Poly(isoprene-co-acrylonitrile)74/26	0.05	0.09	0.03
Poly(isoprene-co-methylacrylonitrile)74/26	0.1	0.2	0.09
Poly(isobutene-co-isoprene)98/2 (Butyl rubber)	0.05	0.08	0.06
Poly(oxy-2,6-dimethyl-1,4-phenylene)			0.06
Poly(oxymethylene)			0.01
Poly(propylene)			0.08
Poly(styrene)		0.1	0.06
Poly(tetrafluoroethylene) (Teflon)	0.09	0.15	0.09
Poly(tetrafluoroethylene-co-hexafluoroprene) (Teflon FEP)	0.09	0.18	0.1
Poly(vinyl acetate)		0.06	
Poly(vinyl butyral)	0.6		
Poly(vinyl chloride) (Crystalline)	0.004	0.012	0.002
Poly(vinyldene fluoride-co-hexafluoropropylene) (Viton A)	0.03	0.08	0.03

(Yasuda and Stannett, 1975; Bixler and Sweeting, 1971)

TABLE 7. RANK ORDERING OF POLYMER GROUPS FROM HIGH TO LOW DIFFUSION COEFFICIENTS (SEE FIGURE 6)

I. RUBBERS (AND SIMILAR MATERIALS)

Polybutadiene
Epichlorohydrin-ethylene oxide*
Natural
Styrene-butadiene copolymer
Neoprene
Nitrile

II. POLYOLEFINS-I (AND SIMILAR MATERIALS)

Poly(ethylene-co-propylene)
Polyurethane
Hydrogenated butadiene
Poly(4-methyl pentene-1)
Ethylene-Vinyl Acetate (up to 40% VA)
LDPE
Polychlorotrifluoroethylene
Isotactic polypropylene (30-40% crystallinity)

III. POLYOLEFINS-II (AND SIMILAR MATERIALS)

Butyl rubber
HDPE
Polyisobutylene
Plasticized PVC*
Teflon
Isotactic polypropylene (60-65% crystallinity)
Acrylonitrile-Butadiene-Styrene (ABS)*

IV. GLASSY POLYMERS

Polymethyl methylacrylate (PMMA)
Polystyrene
Polyacrylonitrile
Polyvinyl chloride (unplasticized)
Polyamides
Polyethylene terephthalate

---

* Very few data are available to indicate position.

Figure 6 should only be used to determine order of magnitude values of the diffusion coefficient. Furthermore, the polymers listed in Table 7 form only a small subset of the polymeric materials commercially available. A polymer not addressed in Table 7 may be classified by comparing its properties with those of the polymers in each of the groups. Key properties would be glass transition temperature, density, and coefficient of thermal expansion.

When using the above approaches to estimate diffusion coefficients for use in the models developed in Section 3, one must note the limitations imposed by two basic assumptions of the models:

- D_p is independent of migrant concentration
- D_p is not influenced by the phase external to the polymer

The first assumption is likely to hold for migrants initially present at less than 1% concentration or for the initial period of migration for concentrations above this level. The second assumption will hold for virtually all cases with air as the external phase, and for most cases with water as the external phase unless the polymer absorbs water. When the external phase readily penetrates the polymer, however, it is likely to swell the polymer and increase D_p. Oils and solvents can penetrate many polymers. It is generally true that the effect from any given level of penetration will be relatively greater for polymers having lower initial values of D_p. For example, a two-percent weight change due to solvent penetration is likely to produce a much greater change in the D_p of a glassy polymer than in the D_p of a rubber.

4.3 Diffusion Coefficients of Additives in the External Phase (D_e)

4.3.1 Air (D_a)

At 25°C, diffusion coefficients of both inorganic and organic molecules in air typically range from 0.04 to 0.23 cm²/s. A representative listing for organic molecules is shown in Table 8. In general, these diffusion coefficients are only weakly dependent on temperature; for example only a 6% reduction is expected upon lowering the temperature from 25°C to 15°C.

Several methods for estimating diffusion coefficients are available and are reviewed in handbooks of chemical property estimation techniques. See Chapter 11 of Reid, Prausnitz and Poling (1987) and Chapter 17 in Lyman, Reehl and Rosenblatt (1982). The former recommends the method of Fuller and co-workers (1965, 1966, 1969).

$$D_a = 0.00143T^{1.75}/\{PM_r^{1/2}[V_a^{1/3}+V_m^{1/3}]^2\} \qquad (4\text{-}1)$$

V_a and V_m are the characteristic or molar volumes of air and the migrant, respectively. For air, V_a = 19.7 cm³/mol, V_m is computed by an additive group procedure from the migrant chemical structure using the atomic values shown in Table 9.

$$M_r = 2M_aM_m/(M_a+M_m) \qquad (4\text{-}2)$$

TABLE 8. DIFFUSION COEFFICIENTS FOR SELECTED ORGANIC CHEMICALS IN AIR

(Values of the diffuson coefficient, D_a, are for 25°C and 1 atm.)

Chemical	Molecular Weight	D_a (cm^2/sec)	Source
Hexane	86.17	0.0732	1
Benzene	78.11	0.0932	1
Toluene	92,13	0.0849	1
Benzyl acohol	108.13	0.0712	1
Chlorobenzene	112.56	0.0747	1
Nitrobenzene	123.11	0.0721	1
Benzyl chloride	126.58	0.0713	1
o-Chlorotoluene	126.58	0.0688	1
m-Chlorotoluene	126.58	0.0645	1
p-Chlorotoluene	126.58	0.0621	1
Diethyl phthalate	222.23	0.0497	1
Dibutyl phthalate	278.34	0.0421	1
Diisooctyl phthalate	390.56	0.0377	1
Chloroform	119.39	0.0888	1
Carbon tetrachloride	153.84	0.0828	1
1,1-Dichloroethane	98.97	0.0919	1
1,2-Dichloroethane	98.97	0.0907	1
1,1-Dichloroethylene	96.95	0.1144	2
Vinyl chloride	62.50	0.1225	2
1,1,1-Trichloroethane	133.42	0.0794	1
1,1,2-Trichloroethane	133.42	0.0792	1
1,1,2,2-Tetrachloroethane	167.86	0.0722	1
Trichloroethylene	131.40	0.0875	1
Tetrachloroethylene	165.85	0.0797	1
Pentachloroethane	202.31	0.0673	1
Hexachlorobenzene	284.80	0.12	3

1. Lugg, 1968.

2. Barr, Watts, 1972.

3. Farmer, Yang and Letey, 1980. (It should be noted that the value reported by Farmer et al., was derived from data on soil volatilization rates of HCB.)

TABLE 9. ATOMIC CONTRIBUTIONS TO ESTIMATE V_m IN EQ. (4-1) (Fuller et. al., 1965, 1966, 1969)

Atom	Contribution
C	15.9
H	2.31
O	6.11
N	4.54
F	14.7
Cl	21.0
Br	29.8
I	22.9
Corrections	
Aromatic or heterocycylic ring	-18.3

where M_a = 29 g/mol and M_m is the molecular weight of the migrant. P is the pressure in bars and equals unity at atmospheric pressure. With the temperature in kelvins, D_a is calculated in units of cm²/s.

As an example, suppose one were interested in estimating D_a for allyl chloride vapor in air at 25°C and atmospheric pressure. From Table 9,

$$V_m = 3(C) + 5(H) + 1(Cl) = (3)(15.9) + (5)(2.31) + (1)(21) = 80.25 \text{ cm}^3/\text{mol}$$

With M_m = 76.5, then

$$M_r = (2)(29)(76.5)/(29+76.5) = 42 \text{ g/mol}$$

With P = 1 bar and T = 298 K, using Eq. (4-1),

$$D_a = (0.00143)(298)^{1.75}/\{(1)(42)^{1/2}[(19.7)^{1/3}+(80.25)^{1/3}]^2\} = 0.096 \text{ cm}^2/\text{s}$$

Lugg (1968) measured D_a for allyl chloride to be 0.098 cm²/s.

In general, the error in D_a associated with Fuller's method ranges from 5 to 15%.

4.3.2 Water (D_w)

At 25°C, the diffusion coefficients for both inorganic and organic molecules in water typically range from 0.4×10^{-5} to 5×10^{-5} cm²/s. Similar to those for air, the diffusion coefficients for water are not strong functions of temperature but, nevertheless, appear to follow an Arrhenius relationship (Reid, et al. 1987). A listing of diffusion coefficients for solutes in water is presented in Table 10.

For organic compounds diffusing in water up to about 30°C, the Wilke-Chang relation (Reid, et al. 1987) may be written as

$$D_w = (5.1 \times 10^{-7})T/V_m^{0.6} \tag{4-3}$$

with T in kelvins. V_m is a characteristic volume of the migrant which is close to the molar volume (cm³/mol) at the boiling point at atmospheric pressure. V_m may also be estimated from the atomic contributions in Table 11. As an example, suppose one wants to estimate D_w for ethylbenzene at 20°C (293 K). Using Table 11,

$$\begin{aligned} V_m &= 8(C) + 10(H) + 3(\text{double bond}) + \text{ring} = (8)(7) + (10)(7) + (3)(7) - 7 \\ &= 140 \text{ cm}^3/\text{mol} \end{aligned}$$

Then

$$D_w = (5.1\times10^{-7})(293)/(140)^{0.6} = 7.7\times10^{-6} \text{ cm}^2/\text{s}$$

It has also been suggested that, similar to polymers, diffusion coefficients for water may be simply related to the molecular weight of the diffusant (Höber, 1945). In Figure 7, diffusion coefficient data given by Höber are plotted as a function of molecular

TABLE 10. DIFFUSION COEFFICIENTS IN AQUEOUS SOLUTIONS AT INFINITE DILUTION

(Reid *et*. *al*., 1978)

Chemical	T, (°C)	$D_w \times 10^5$ (cm^2/s)
Hydrogen	25	4.8
Oxygen	25	2.41
	29.6	3.49
Nitrogen	29.6	3.47
Nitrous oxide	25	2.67
Carbon dioxide	25	2.00
Ammonia	12	1.64
Methane	2	0.85
	20	1.49
	60	3.55
n-Butane	4	0.50
	20	0.89
	60	2.51
Propylene	25	1.44
Methylcyclopentane	2	0.48
	10	0.59
	20	0.85
	60	1.92
Benzene	2	0.58
	10	0.75
	20	1.02
Ethylbenzene	2	0.44
	10	0.61
	20	0.81
	60	1.95
Methyl alcohol	15	1.26
Ethyl alcohol	10	0.84
	15	1.00
	25	1.24
n-Propyl alcohol	15	0.87
Isoamyl alcohol	15	0.69
Allyl alcohol	15	0.90
Benzyl alcohol	20	0.82
Ethylene glycol	20	1.04
	25	1.16
	40	1.71
	55	2.26
	70	2.75
Glycerol	15	0.72
Acetic acid	20	1.19
Benzoic acid	25	1.21
Ethyl acetate	20	1.00
Urea	20	1.20
	25	1.38
Diethylamine	20	0.97
Acetonitrile	15	1.26
Aniline	20	0.92
Pyridine	15	0.58
Vinyl chloride	25	1.34
	50	2.42
	75	3.67

TABLE 11. ATOMIC CONTRIBUTIONS TO ESTIMATE V_m IN EQ. (4-2)

Atom	Contribution
C	7
H	7
O	7
N	7
Br	31.5
Cl	24.5
F	10.5
I	38.5
S	21
Ring*	-7
Double bonds between carbon atoms	7
Triple bonds between carbon atoms	14

* 3, 4, 5, or 6 membered; also include for naphthalene or anthracene.

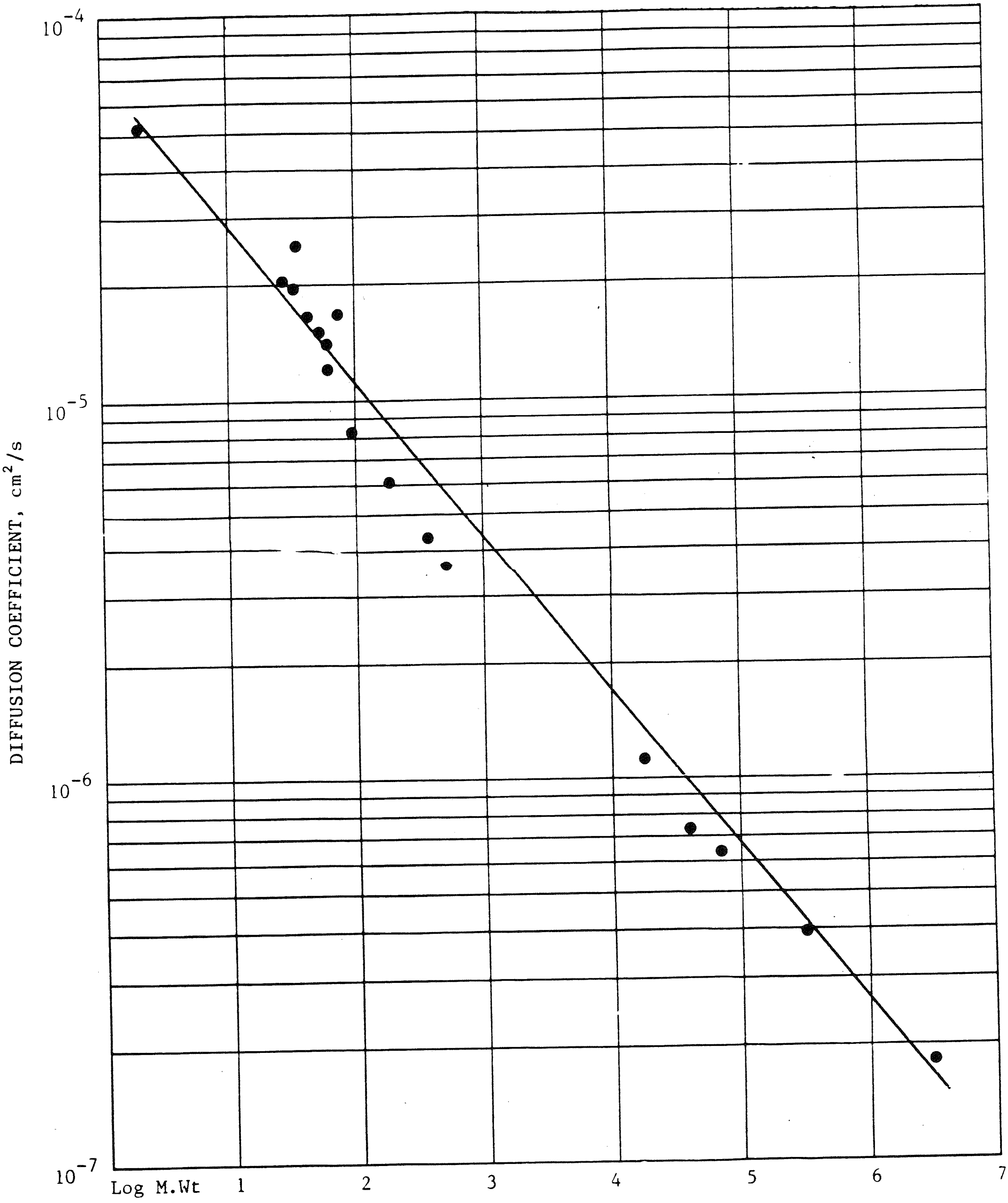

FIGURE 7. Diffusion Coefficients for Organic and Inorganic Chemicals in Water at 20°C (Höber, 1945).

weight on log-log coordinates. The correlation is reasonable and may be adequate for an initial estimate of D_w. The equation of the line in Figure 7 is

$$D_w = 7.4\times10^{-5}M^{-0.41} \tag{4-4}$$

Eq. (4-4) is the equation provided in the computer model described in Section 6 to estimate D_w when necessary.

4.3.3 Other Materials

The range of external phases obviously extends far beyond air and water. Migrant diffusion coefficients in other materials can be approximated by logical processes in which the external phase in question is compared to air, water, and solids as represented by the polymers in Figure 6. For example, diffusion coefficients for skin would probably be less than those for water but greater than those for low density polyethylene and perhaps greater than those for natural rubber. Recognizing that the result may be incorrect by as much as a half order of magnitude, one could estimate D_e for skin by using the silicone rubber curve.

Diffusion coefficients for soils would be highly dependent on the moisture content of the soil. For a dry sand, essentially all diffusion would occur through the air between the sand particles. Thus D_e would be similar to that of air. It may be also necessary to adjust migration to account for the polymer surface area occluded by the sand and the tortuous path for diffusion within the sand. For wet soils, D_e may be approximated using the values for water; again adjustments for occluded surface area and tortuosity may be required particularly for soils such as clay.

4.4 Partition Coefficient (K)

4.4.1 Solubility of Additive in the Polymer ($C_{p,s}$)

$C_{p,s}$ and $C_{e,s}$ are, respectively, the saturation concentration of the migrant in the polymer and the saturation concentration of the migrant in the external phase. With these parameters, K, the partition coefficient, can be calculated.

$$K = C_{e,s}/C_{p,s} \tag{4-5}$$

K is often required in migration calculations. Unfortunately $C_{p,s}$ is known only for a very few materials. For many rubbery polymers or elastomers, Goydan et al. (1989) present an estimation procedure for $C_{p,s}$. The technique, while complicated, has been coded for computer application. The FORTRAN program resides on personal computers within the Chemical Engineering Branch of the EPA Office of Toxic Substances. If this method is inapplicable, and no independent value of $C_{p,s}$ is available, one may use the initial concentration of the additive in the polymer ($C_{p,o}$) as an initial guess for $C_{p,s}$. This approach usually leads to an estimated value for K that is greater than the true K since additives are usually present at concentrations far below their solubility limits. In this sense, such a choice leads to a "worst case" situation since migration increases with K. Exceptions to this generalization are additives that are present at concentrations above their limit of saturation and are actually designed to migrate to the surface (i.e., bloom). In this case, migration could be at rates greater than those predicted using the assumption of $C_{p,s}$

equal to $C_{p,o}$. The migration of the bloom occurs by <u>dissolution</u> in the external phase rather than by diffusion processes. Dissolution is not addressed by the models presented herein.

4.4.2 Solubility of Additives in the External Phase ($C_{e,s}$)

4.4.2.1 Air (C_a)

The "solubility" of a chemical in air, C_a, is the same as its saturated vapor concentration at a specified temperature. The ideal gas law provides a sufficiently accurate basis for the calculation of this parameter if measured values are not available.

$$C_a = (1.3 \times 10^{-4})P_vM/(RT) \tag{4-6}$$

where

C_a = "solubility" in air, g/cm^3
P_v = vapor pressure of chemical (torr)
M = molecular weight of chemical, g/mol
R = gas constant = 8.314 J/mol K
T = temperature, kelvins

The multiplier (1.3×10^{-4}) in Eq. (4-6) leads to the units of g/cm^3 for C_a.

For example, to estimate the value of C_a for trimethylphosphate (140.1 g/mol) at 25°C where the vapor pressure is 3.80 mm Hg = 3.80 torr,

$$C_a = (1.3 \times 10^{-4})(3.80)(140.1)/[(8.314)(298)] = 2.79\times10^{-5} \text{ g/cm}^3$$

The key chemical-specific input for the calculation of C_a is the vapor pressure of the chemical (P_v). If a measured value of this property is not available, it may be estimated by the methods described by Grain (1982). The computerized chemical property estimation system CHEMEST (Lyman, <u>et</u> <u>al</u>., 1982) contains estimation methods for vapor pressures that are slightly more accurate than those covered by Grain. The inputs for the estimation methods in the cited works are a boiling point and, for solids only, a melting point. If necessary, both of these inputs can be estimated.

4.4.2.2 Water (C_w)

Estimation methods for the solubility of chemicals in water, C_w, have been reviewed by Lyman (1982), and the recommended methods have been incorporated into the computerized chemical property estimation system CHEMEST (Lyman, <u>et</u> <u>al</u>., 1982). In general, the best approach is to estimate C_w from the octanol-water partition coefficient K_{ow}, which itself can be estimated from the chemical structure. This approach involves relatively simple calculations and can often provide estimates within a factor of 2 of the true value. This technique provides estimates of C_w only at a temperature of 25°C.

At present, it is recommended that the following regression equation be used to predict C_w:

$$\log C_w = \log M - 1.123 \log K_{ow} - 0.0099 T_m - 2.067 \qquad (4\text{-}7)$$

where

C_w = water solubility at 25°C, g/cm^3
K_{ow} = octanol-water partition coefficient
T_m = melting point, °C, for liquids use 25°C
M = molecular weight of chemical, g/mol

This equation is recommended by Yalkowsky (1982) and is based upon the studies of Yalkowsky, et al. (1983) and Valvani, et al. (1981). When used for neutral organic chemicals, Eq. (4-7) is expected to have an average method error of about a factor of 2; this presumes that accurate values of K_{ow} and T_m are available.

When using Eq. (4-7), if the predicted value of C_w is greater than about 0.1 g/cm^3, the chemical should be assumed to be infinitely soluble in water.

4.5 Mass Transfer Coefficients (k) for a Fluid External Phase

In a migration process where the external phase is a fluid (vapor or liquid), consideration must be given to the possibility that mass transfer resistances in the external phase may influence the migration process. Techniques for estimating values of the mass transfer coefficient are empirical and highly dependent on the geometry of the physical situation and the flow rate of the fluid. Mass transfer coefficients for migration to water and air are addressed in this section.

4.5.1 Migration to Water

4.5.1.1 Flat Polymer Surfaces

Polymers in contact with water may be of various shapes and sizes. However, some geometry must be assumed to allow an estimation of the mass transfer coefficient. We have chosen to express the exposed area of the polymer in terms of an equivalent flat sheet of area A with a characteristic length l in the direction of the bulk water flow. It will also be assumed that, in the direction l, there is an average characteristic fluid velocity v.

In order to estimate the mass transfer coefficient, it is first necessary to determine whether the water flow over the polymer surface is laminar or turbulent. This is typically done by calculation of the length Reynolds number:

$$\text{Length Reynolds number} = Re_l = lv/\nu \qquad (4\text{-}8)$$

where

l = the characteristic length in the direction of flow, cm
v = characteristic water velocity, cm/s
ν = kinematic viscosity of water, cm^2/s, and is defined as the dynamic viscosity divided by the density of water. At room temperature $\nu \approx 0.01$ cm^2/s.

Laminar and turbulent flow regimes are delineated as

$Re_l < 10^6$: laminar
$Re_l > 10^6$: turbulent

The mass transfer coefficients in each regime may be estimated as proposed by Skelland (1974):

Laminar

$$k = C_L(D_w/l)(Re_l)^{1/2}(Sc)^{1/3} \tag{4-9}$$

Turbulent

$$k = C_T(D_w/l)(Re_l)^{0.8}(Sc)^{1/3} \tag{4-10}$$

where

k = mass transfer coefficient, cm/s

C_L = constant ≈ 0.664

C_T = constant ≈ 0.037

D_w = diffusion coefficient of the migrant in water, cm^2/s

Sc = Schmidt number = ν/D_w

and l and Re_l are as defined in Eq. (4-8).

D_w may be found in published tables such as Table 10 or estimated from Eq. (4-3) or Eq. (4-4). In most cases Eq. (4-4) may be used as a good approximation for D_w when calculating k. With it and setting $\nu = 0.01$, then

Laminar

$$k = 2.5\times10^{-3}(v/l)^{1/2}/M^{0.27} \tag{4-11}$$

Turbulent

$$k = 5.6\times10^{-4}(v^{0.8}/l^{0.2})/M^{0.27} \tag{4-12}$$

There is a weak dependence of k on the molecular weight M. If $M = 200$, $M^{0.27} = 4.2$ while if $M = 500$, $M^{0.27} = 5.4$. For simplicity, $M^{0.27}$ may be defined as a constant equal to 4.8. The final working equations then reduce to

Laminar

$$k = 5.2\times10^{-4}(v/l)^{1/2} \tag{4-13}$$

Turbulent

$$k = 1.2\times10^{-4}(v^{0.8}/l^{0.2}) \tag{4-14}$$

with the transition from laminar to turbulent flow at $Re_l \approx 10^6$. Although this transition point from the laminar to the turbulent regime is routinely used, some turbulence may be present within the laminar domain. We recommend, therefore, only the use of the turbulent correlation for simple, approximate estimations of k for water flowing over flat polymer surfaces. Eq. (4-14) is plotted in Figure 8 to illustrate the dependence of k on both the water velocity and l. Unless the water flow is very low (< 10 cm/s), this figure yields reasonable values of k.

For the special case where the water is essentially stagnant, there is no good correlation for the estimation of the mass transfer coefficient. Small eddies or instabilities can lead to transient variations in k. If no such eddies are present, the stagnant water might be modelled as a "solid" external phase and any transfer of additive would be by diffusion into the water.

4.5.1.2 Polymer Pipes

If water is flowing inside a polymer pipe and migrant from the pipe wall is transferred to the water, the mass transfer coefficient may be estimated by (Skelland, 1974):

$$k = 0.023(D_w/d)(Re)^{0.8}(Sc)^{1/3} \tag{4-15}$$

In this case

$$Re = dv/\nu \tag{4-16}$$

With Sc defined under Eq. (4-10), d is the pipe diameter (cm), v the water velocity (cm/s), D_w the diffusion coefficient of the migrant in water (cm²/s), and ν the kinematic viscosity of water (cm²/s). Inserting these definitions,

$$k = 0.023 D_w^{2/3} v^{0.8}/d^{0.2}\nu^{(0.8-0.33)} \tag{4-17}$$

With ν about 0.01 cm²/s and using Eq. (4-4) for D_w,

$$k = 3.5\times10^{-4} v^{0.8}/(d^{0.2}M^{0.27}) \tag{4-18}$$

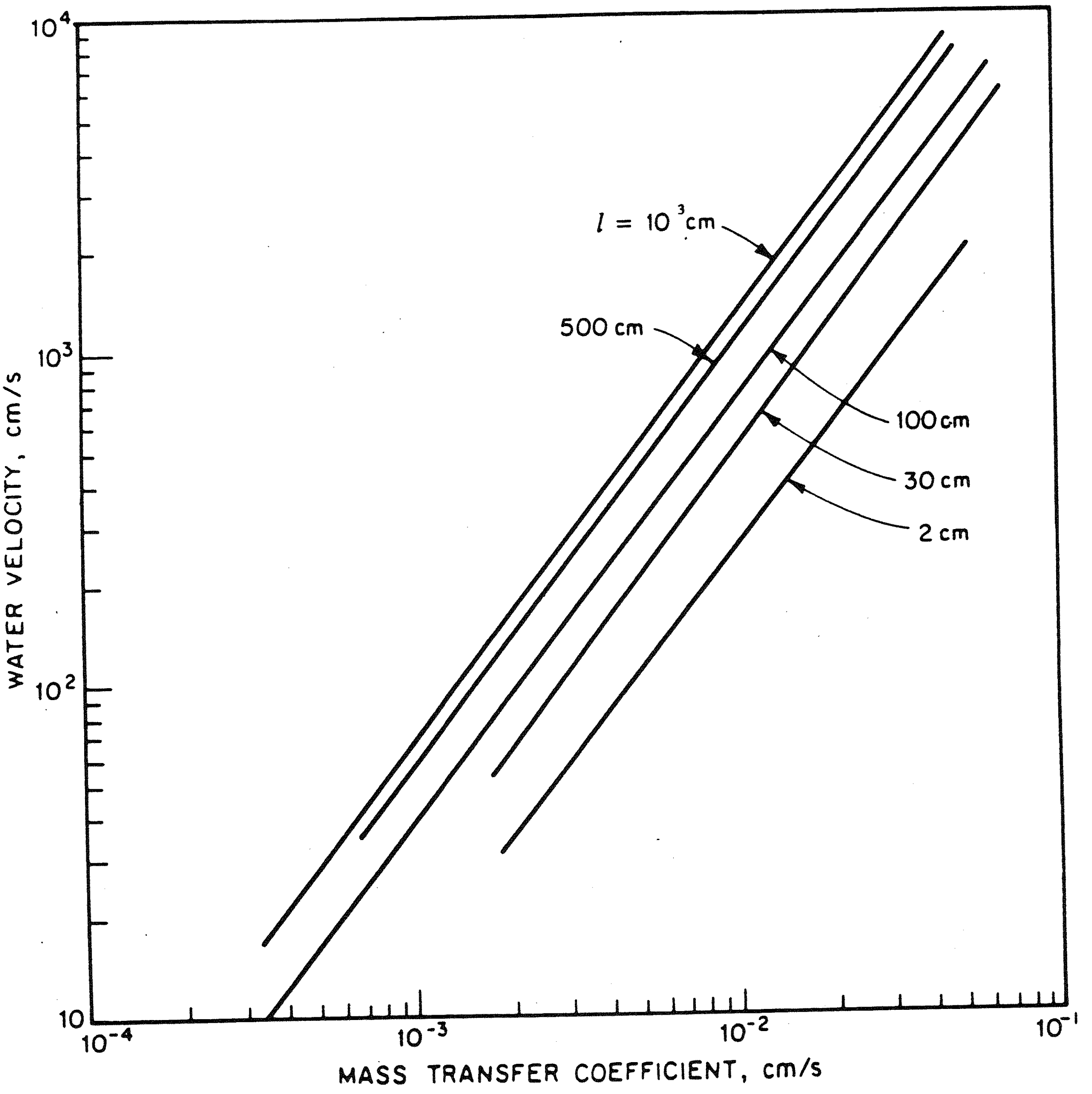

FIGURE 8. Estimation of Mass Transfer Coefficient for Water Flowing Over Flat Polymer Surfaces.

Assuming, as before, $M^{0.27} \approx 4.8$

$$k = 7.2\times10^{-5}v^{0.8}/d^{0.2} \tag{4-19}$$

with k in cm/s. The form of Eq. (4-19) is very similar to that of Eq. (4-14). Eq. (4-19) should only be applied when Re > 2000 as, otherwise, laminar not turbulent flow would exist. In essentially all applications, water flow in pipes occurs in the turbulent regime.

4.5.2 Migration to Indoor Air

The following discussion addresses polymers that are in some form of closed environment; not in the outside air. We note, however, that the presentation in Section 4.5.2.1 is applicable to polymers in both environments. The shape and orientation of the polymer surfaces are important as is the motion of air within the environment. In general, there are three different causes for air circulation:

1. Bulk flow due to open windows, forced air circulation by fans, or wind.
2. Density driven convective flows on vertical polymer surfaces due to the molecular weight difference between the migrant and air.
3. Thermally driven convection currents due to buoyancy effects.

We consider each of these circulation flows separately although all three may be present simultaneously. In general, we conclude that, for indoor air, thermally driven convection currents usually dominate and establish the degree of air turbulence that determines the mass transfer coefficient.

4.5.2.1 Bulk Air Over Horizontal Polymer Surface

The polymer surface is modelled as a flat, horizontal plate of area A with a characteristic length *l* in the direction of the bulk air flow. In essentially all cases of interest, the flow is laminar and Eq. (4-9) is applicable. The kinematic viscosity of air is 0.16 cm²/s at 25°C at atmospheric pressure. Thus, in a form comparable to Eq. (4-13),

$$k = 0.90D_a^{2/3}(v/l)^{1/2} \tag{4-20}$$

where D_a is the diffusion coefficient of the migrant in air (cm²/s), v is the air velocity (cm/s), and *l* is measured in the direction of v (cm). k is the mass transfer coefficient (cm/s). Values of D_a may be estimated by the method suggested in Section 4.3.1. For cases where the migrant is primarily composed of carbon and hydrogen and where the migrant molecular weight, M, is much larger than the molecular weight of air, the diffusion coefficient at 20 to 30°C and atmospheric pressure can be approximated as

$$D_a \approx 3.3/(2.5 + M^{1/3})^2 \text{ in cm}^2\text{/s} \tag{4-21}$$

For example, if the migrant were the antioxidant butylated hydroxytoluene (BHT), M = 220 and, with Eq. (4-21), $D_a \approx 0.045$ cm²/s. For Irganox 1010, a proprietary antioxidant with M = 1176, $D_a \approx 0.02$ cm²/s. While such values are only approximate, they are satisfactory for use in determining k with Eq. (4-20), which becomes, with the substitution of D_a from Eq. (4-21),

$$k \approx 2/[(2.5 + M^{1/3})^{4/3}(l/v)^{1/2}] \tag{4-22}$$

To employ Eq. (4-22), let us assume the migrant was BHT ($M = 220$) and the ratio (l/v) was 3600 s. Then

$$k \approx 2/\{[2.5+(220)^{1/3}]^{4/3}(3600)^{1/2}\} \approx 1.9\times10^{-3} \text{ cm/s}$$

To facilitate the estimation of k for horizontal surfaces, Eq. (4-22) is shown plotted in Figure 9 as a function of (l/v) and migrant molecular weight.

4.5.2.2 Vertical Polymer Surfaces

In this case, we assume a vertical polymer surface of average height H (cm) from which an additive is migrating. Because the mass density of the migrant-air mixture near a vertical surface exceeds the average mass density of air in the bulk, a natural circulation flow is initiated down the surface. For a laminar flow situation (Skelland, 1974),

$$k = (4D_a/3H)C_v f(Sc)Gr^{1/4} \tag{4-23}$$

where

C_v = constant ≈ 0.50

$$f(Sc) = Sc^{1/2}/(0.952+Sc)^{1/4} \tag{4-24}$$

Sc = Schmidt number defined under Eq. (4-10)

$$Gr = \text{Grashof number} = (gH^3/\nu^2)[(\rho_o-\rho_\infty)/\rho_\infty] \tag{4-25}$$

g = acceleration due to gravity = 980 cm/s^2

ν = kinematic viscosity of air = 0.16 cm^2/s at 25°C and 1 bar

ρ_∞ = mass density of the bulk air

ρ_o = mass density of the migrant-air mixture at the surface

If we set

$$\rho_\infty = PM_a/RT \tag{4-26}$$

$$\rho_o = (P_vM/RT) + (P-P_v)M_a/RT \tag{4-27}$$

where M and M_a are the molecular weights of the migrant and air and P_v is the partial pressure of the migrant in the air-migrant mixture at the surface. (P_v would equal the migrant vapor pressure if the polymer were saturated with migrant.) Then, with Eqs. (4-26) and (4-27),

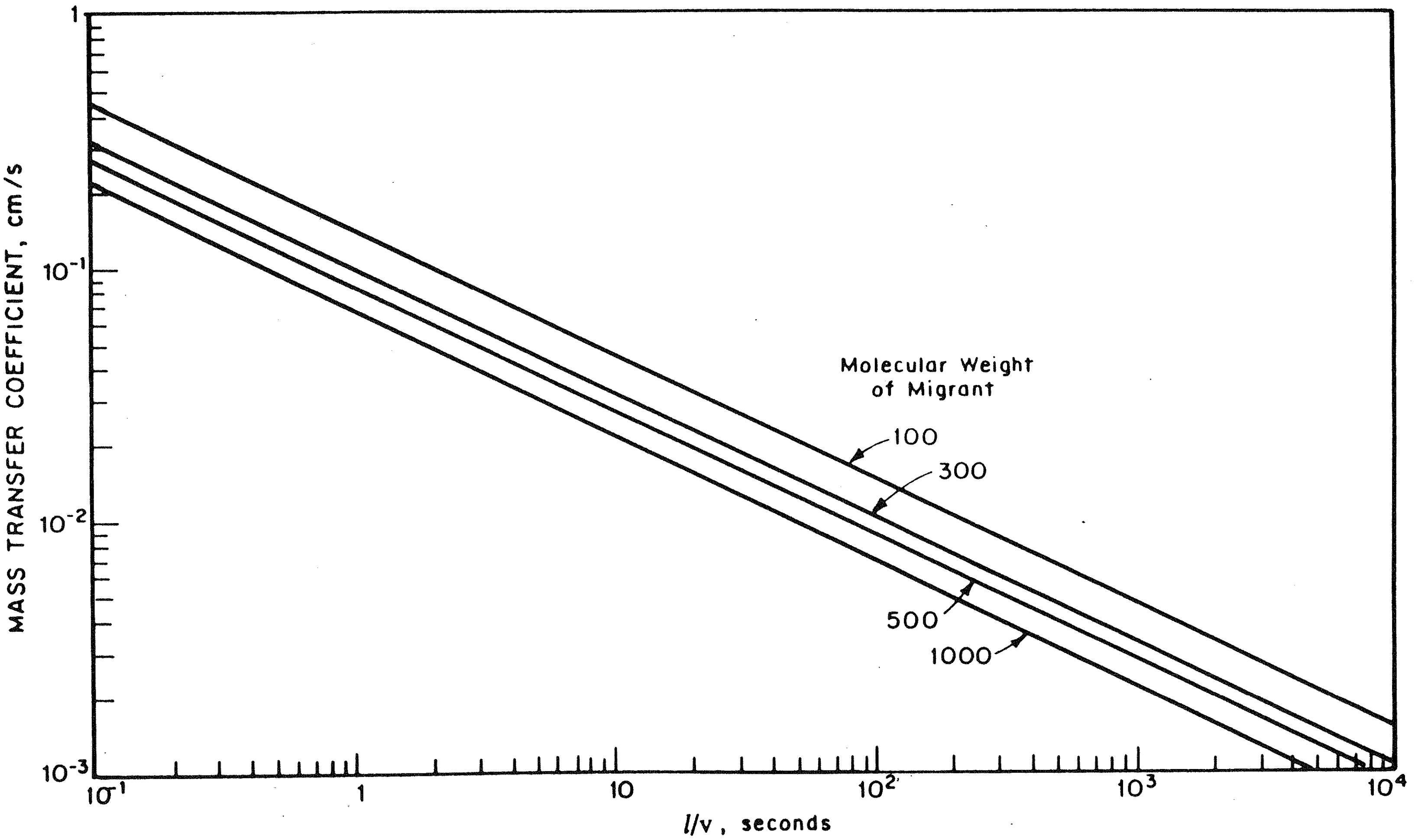

FIGURE 9. Estimated Mass Transfer Coefficients for Migrants Into Air Due To Bulk Flow (300K, 1 Bar, Laminar Flow).

$$(\rho_o-\rho_\infty)/\rho_\infty = (P_v/P)[(M-M_a)/M_a] \tag{4-28}$$

Substituting Eq. (4-28) into Eq. (4-23) with $\nu = 0.16$ cm^2/s,

$$k = 3.7(P_v/P)^{1/4}(Z/H^{1/4}) \tag{4-29}$$

where

$$Z = D_a^{1/2}\{[(M_a-M)/M_a][1/(0.952+0.16/D_a)]\}^{1/4} \tag{4-30}$$

From Eq. (4-21), we can approximate D_a as a function of M so that Z then depends only on the migrant molecular weight. Also, if one computes Z for various values of M, Z is found only to range from 0.23 for low values of M ($\approx$ 100) to 0.20 for M $\approx$ 1000. Assuming a mean value of Z = 0.22, then Eq. (4-29) simplifies to

$$k = [0.41(P_v/P)/H]^{1/4} \tag{4-31}$$

where H is in cm and k in cm/s.

As an example, suppose we were interested in the mass transfer of the antioxidant BHT from a vertical polymer surface to air. At 25°C, P_v for BHT $\approx$ 0.76 torr. This vapor pressure will be used since the actual BHT partial pressure over the polymer is unknown. (The use of this vapor pressure represents the greatest driving force for migration, i.e., it is a worst case.) The height of the vertical surface, H, is 3 m or 300 cm. With P = atmospheric pressure = 760 torr,

$$k = [0.41(0.76/760)/300]^{1/4} = 0.034 \text{ cm/s}$$

In Figure 10, the mass transfer coefficient is shown for various values of (P_v/P) and H.

4.5.2.3 Thermally Driven Convection

A large body of data has been developed by the American Society of Heating, Refrigeration, and Air Conditioning Engineers (ASHRAE, 1980) to estimate heat transfer coefficients in closed environments where there exist temperature gradients due to heating or cooling surfaces. Typical natural convection heat transfer coefficients, h, range from about 1 to 8 W/m^{2}K.

Using the analogy between heat and mass transfer processes and noting that for air, the Lewis number (the ratio of the Prandtl to the Schmitt number) is essentially unity, then the Sherwood number equals the Nusselt number:

$$\mathrm{Sh} = kl/D_a \tag{4-32}$$
$$\mathrm{Nu} = hl/\lambda \tag{4-33}$$

thus

$$k = (D_a/\lambda)h \tag{4-34}$$

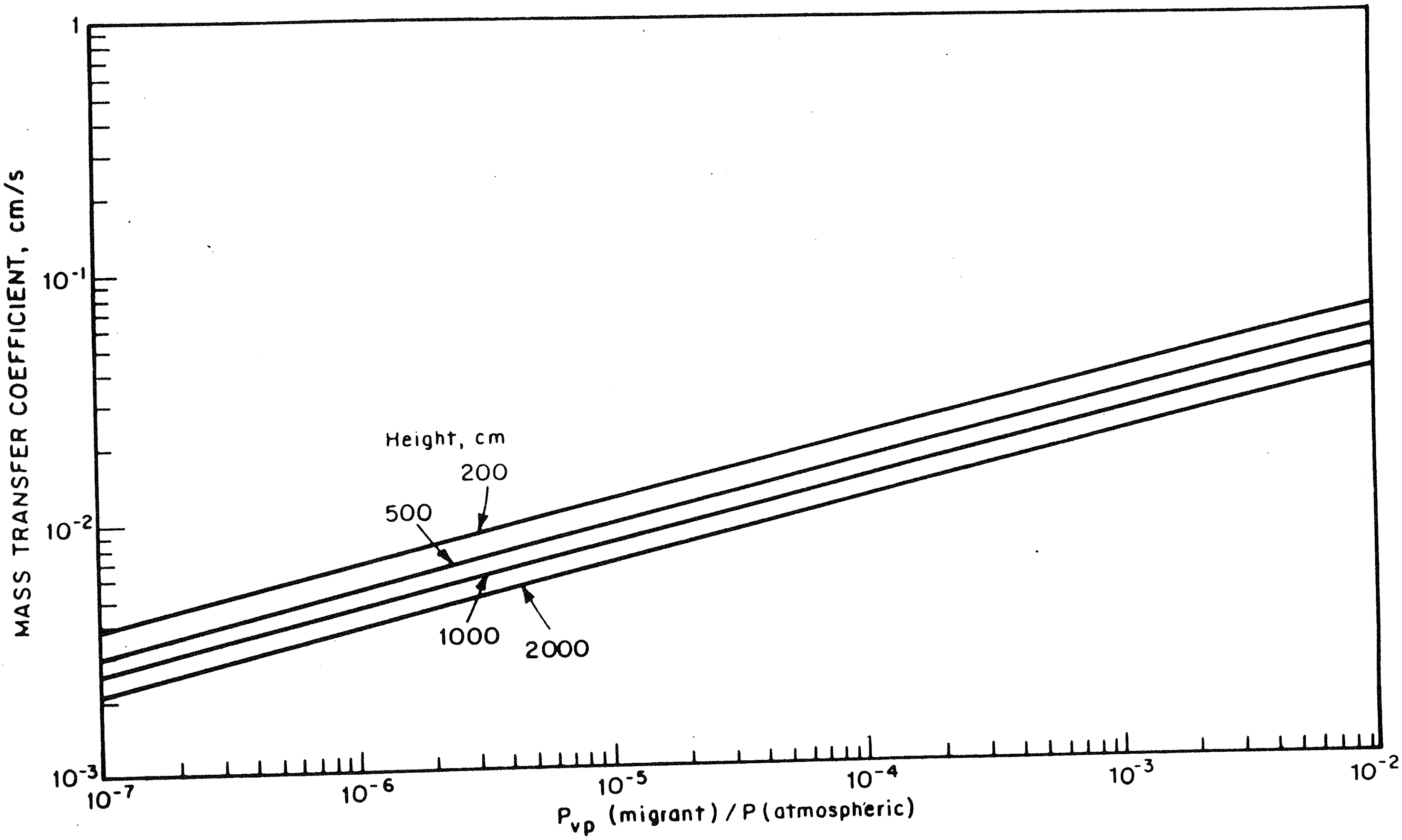

FIGURE 10. Estimated Mass Transfer Coefficients for Migrants In Air On Vertical Surfaces (300K, 1 Bar, Laminar Flow).

Here, Sh is the Sherwood number, Nu the Nusselt number, k the mass transfer coefficient, h the convective heat-transfer coefficient, D_a the diffusion coefficient of the migrant in air, λ the thermal conductivity of air and l some characteristic length. λ is about 0.026 W/mK for air near ambient conditions. Thus, using an average value of $h \approx 3.4$ W/m^{2}K, Eq. (4-34) becomes

$$k = D_a(3.4/0.026)(1/100) = 1.3\ D_a \qquad (4\text{-}35)$$

with k in cm/s. The factor of 100 in Eq. (4-35) was inserted to convert meters to centimeters. D_a may be estimated from Eq. (4-21) in terms of the migrant molecular weight M or calculated as described in Section 4.3.1. Then, for example, with M = 220, $D_a \approx 0.045$ cm^2/s and $k \approx 0.059$ cm/s. Increasing M to 1000, $D_a \approx 0.021$ cm^2/s and $k \approx 0.027$ cm/s.

4.5.2.4 Discussion

Of the three air movement mechanisms likely to be present in enclosed spaces, the largest mass-transfer coefficient is usually found when considering thermally-driven convection. Since the largest k is the most important, Eq. (4-35) is usually only necessary to estimate k. In cases where it is known that no thermal convective currents are important, however, k may be estimated from the bulk-flow model (Section 4.5.2.1) or the vertical convective model (Section 4.5.2.2). For example, the bulk-flow model would be more appropriate outdoors.

5. EXAMPLE MIGRATION CALCULATIONS

Examples are provided to illustrate the use of the migration equations described in Section 3 and the techniques to estimate the input variables described in Section 4. In most cases, these example calculations were performed using the computer program described in Section 6.

5.1 Worst Case Examples

Often one is interested in "worst case" scenarios to initially estimate additive migration because, if the results from such cases are acceptable, more complicated estimations are unnecessary. Several "worst case" examples illustrate the procedures and results.

5.1.1 Background

There is a large TV console in a room of a house. The dimensions of the room are 3 by 3 by 2.1 m (10 by 10 by 7 feet) and the volume is 19 m^3 (700 feet). This console is made of a plastic that is believed to be ABS (acrylonitrile-butadiene-styrene copolymer). The migrant is styrene (molecular weight = 104) at an initial concentration of 450 ppm. The cabinet is 2 mm thick and migration only occurs from the outside surfaces. The exposed surface area (neglecting the base) is 9,000 cm^2. We are interested in finding the loss of the styrene as a function of time to the room air.

First obtain a value for the diffusion coefficient of styrene in the ABS plastic. ABS is not one of the six polymers for which the computer program includes a subroutine for estimation of D_p. Thus, D_p must be estimated by classifying ABS into one of the four generic polymer classes and using Figure 6 to estimate a value for D_p. From Table 7, ABS is ranked at the low end of the Polyolefins II class and with log(104) = 2.0, $D_p \approx 3 \times 10^{-10}$ cm^2/s from Figure 6.

Thus, the required input data are:

- $D_p = 3 \times 10^{-10}$ cm^2/s
- $L = 0.2$ cm
- One-sided migration

5.1.2 Initial Considerations

Neglecting any consideration of rates, one can readily obtain the total migration of the styrene through a simple calculation given a value for the initial concentration, $C_{p,o}$.

$$
\begin{aligned}
\text{Total Migration} &= (\text{area})(L)(C_{p,o}) \\
&= (9{,}000\ \text{cm}^2)(0.2\ \text{cm})(450 \times 10^{-6}\ \text{g/cm}^3) \\
&= 0.81\ \text{g styrene}
\end{aligned}
$$

This value could be employed to obtain a <u>maximum</u> possible concentration of styrene in the room air. At 25°C, there are $(19)(10^5)/(8.314)(298) = 77$ moles of air in the room, calculated using the ideal gas law. If 0.81 g (0.0081 moles) of styrene were added, the styrene concentration would be $(0.0081/77) \times 10^6 = 105$ ppm (by volume). If this maximum possible concentration were high relative to exposure risk, one would proceed to consider migration rates over time using the computer model for more realistic estimates of the styrene concentrations in the air.

5.1.3 Estimations of Migration

5.1.3.1 No Partitioning, No External Mass Transfer Resistance

In this case, we assume that there is no partitioning between the styrene in the ABS and the room air and, in addition, there is no external mass transfer resistance for styrene leaving the TV console and entering the air. Thus, the solubility of the styrene in air is unlimited as is the external phase mass transfer coefficient. With reference to the computer program, partitioning and mass transfer options are not selected and, consequently, the computer program proceeds to Eq. (3-23).

Suppose we choose times equal to one day, one week, one month, and one year after installation of the console at which to estimate the fraction migrated, M_τ. Then with $D_p = 3 \times 10^{-10}$ cm²/s and $L = 0.2$ cm,

Time	$\tau = D_p t/L^2$	Fraction Migrated, Eq. (3-23)
1 day	6.5×10^{-4}	0.03
1 week	4.5×10^{-3}	0.08
1 month	0.020	0.16
1 year	0.24	0.55

This worst case situation indicates that about 8% of the styrene is lost within a week and some 50% within a year. We next illustrate some simple perturbations in the problem.

5.1.3.2 Two-Sided Loss

Suppose one assumes that styrene can be lost from both sides of the console (i.e., the styrene leaving the interior face would exit to the room through vents in the console). Then, in the problem formulation, two-sided loss would be specified and the "L" term in Eq. (3-23) becomes one-half the true thickness, 0.2/2 = 0.1 cm. After one day, then $\tau = (3 \times 10^{-10})(8.64 \times 10^4)/(0.1)^2 = 2.6 \times 10^{-3}$, four times larger than in the one-sided case. With Eq. (3-23), the fraction migrated is then estimated as 0.06 after one day which, for this particular example, is twice that for the one-sided situation.

Should one be interested in converting the fraction migrated estimate to the mass of styrene lost in the two cases, Eq. (3-16) is used with the initial concentration, effective thicknesses, and areas.

Duration: 1 day

	One-Sided	Two-sided
Fraction Migrated	0.03	0.06
Mass Lost/Area, $(M_\tau C_{p,o} L)$ g/cm^2	$(0.03)(450 \times 10^{-6})(0.2)$ $= 3.0 \times 10^{-6}$	$(0.06)(450 \times 10^{-6})(0.1)$ $= 3.0 \times 10^{-6}$
Area for Loss, cm^2	9,000	(2)(9,000)
Total Styrene Loss, g	0.03	0.06

Note that all migration estimates by the computer program are provided as the fraction migrated, M_τ. These values can be readily converted to a mass/area or total mass migrated using the initial concentration, the polymer thickness, and the polymer surface area.

5.1.3.3 Air Flow Through Room

Instead of having a constant closed air reservoir in the room, suppose there was air flow in and out equivalent to 5 room volume changes per day. Then one could compute the average styrene concentration for any given day by computing the total lost at the end of the day and subtracting the loss at the start of the day and dividing by the total air moved through the room during the day. Obviously, the average concentration would be highest on the first day and decrease thereafter. Such concentration calculations, however, are not included as part of the computer model. The user should refer to other volumes in this series for guidance.

5.1.3.4 Diffusion Coefficient Variation

The estimate of 3×10^{-10} cm^2/s as the diffusion coefficient for styrene in the ABS TV cabinet was, at best, approximate. Suppose one perturbed this estimate an order of magnitude in either direction, i.e., consider $D_p = 3 \times 10^{-9}$ cm^2/s and $D_p = 3 \times 10^{-11}$ cm^2/s. Let the time be 1 day and assume one-sided migration with $L = 0.2$ cm:

Duration: 1 day

D_p	$\tau = D_p t/L^2$	Fraction Migrated Eq. (3-23)
3×10^{-9} cm^2/s	6.5×10^{-3}	0.09
3×10^{-10} cm^2/s	6.5×10^{-4}	0.03
3×10^{-11} cm^2/s	6.5×10^{-5}	0.01

In the case for the highest estimate of D_p, 9% of the styrene is lost in the first day whereas for the lowest estimate only 1% was lost.

5.2 Partition Limited Examples

In some instances, the migration of an additive from a polymer decreases in rate and eventually stops as the concentration of the additive increases in the external phase until it is in equilibrium with the additive in the polymer. Such partitioning effects are normally important only when the volume of the external phase is small and the solubility of the additive in it is low. We consider such a case here but allow the external mass transfer resistance to be unlimited.

5.2.1 Background

A 5-liter polypropylene (isotactic) bag is to be produced that will contain potable water. The wall thickness is about 10 mils (0.025 cm) and the area = 1,400 cm^2. The polypropylene contains an antioxidant (molecular weight is 250) that is initially present at a level of 1,200 ppm. The density of the polypropylene is close to 1 g/cm^3.

5.2.2 Initial Considerations

A worst case analysis as illustrated in Section 5.1 would indicate that the total antioxidant present is:

$$(\text{area})(L)(C_{p,o}) = (1{,}400)(0.025)(1{,}200 \times 10^{-6}) = 0.042 \text{ g}$$

If this amount of the antioxidant were to enter the 5 liters of water, a concentration of about 8.4 ppm would result. However, this value is above the saturation concentration (6 ppm) of the antioxidant in water. Thus, partitioning must be considered.

To use the computer program, an estimate of the diffusion coefficient of the antioxidant in the isotactic polypropylene is required. Again, this polymer is not one of the six for which an estimation equation is provided in the computer model. From Table 7, we find that this polymer is listed near the bottom of the class Polyolefins II. So, with a molecular weight of the antioxidant of 250 from Figure 6, $D_p \approx 5 \times 10^{-11}$ cm^2/s. The migration is one-sided with $L = 0.025$ cm. We have no data concerning the solubility of the antioxidant in the polymer. As suggested in Section 4, we could assume the value was the same as $C_{p,o}$ (1,200 ppm) although this value is probably low.

5.2.3 Estimation of Migration

The necessary input data for the case of partitioning but no external mass transfer resistance are shown below for the example under consideration.

- $D_p = 5 \times 10^{-11}$ cm^2/s
- $L = 0.025$ cm
- One-sided exposure
- Solubility in polypropylene, $C_{s,p} \approx C_{p,o} \approx 1{,}200$ ppm (1.2×10^{-3} g/cm^3)

- Solubility in water, $C_{s,e} \approx 6$ ppm (6×10^{-6} g/cm^3)
- Volume of external phase, $V_e = 5{,}000$ cm^3
- Area for migration, $A = 1{,}400$ cm^2

Eq. (3-26) is employed and, here,

$$K = C_{e,s}\ (\text{water})/C_{p,s}\ (\text{polypropylene}) = 6/1{,}200 = 0.005$$

$$\alpha = V_e\ K/AL = (5{,}000)(0.005)/[(1{,}400)(0.025)] = 0.71$$

The value of α (= 0.7) is significant because, by Eq. (3-39), the maximum fraction migrated is $\alpha/(1 + \alpha) = 0.42$ before a partition equilibrium is achieved. This migration would correspond to that after long times and would give a concentration of about

$$M_\tau C_{p,o} AL/V_e = (0.42)(1200 \times 10^{-6})(1400)(0.025)(10^6)/(5000) = 3.5 \text{ ppm}$$

To estimate the effect of time on the fraction migrated, with Eq. (3-26) we find

Time	$\tau = D_p t/L^2$	Fraction Migrated Eq. (3-26)
1 day	6.9×10^{-3}	0.08
1 week	4.8×10^{-2}	0.19
1 month	0.21	0.32
3 months	0.62	0.40
1 year	2.5	0.42

Therefore, if the water is held in the bag for only one day, approximately 8% of the antioxidant would migrate and the expected concentration would be less than 1 ppm. After a week, the concentration would be ≈ 2 ppm while if the water is stored for more than three months, the antioxidant attains a partition equilibrium between the water and polymer with a concentration of ≈ 3.5 ppm in the water. If the bag were used for multiple fillings and drainings, however, the antioxidant level in the polypropylene available for migration would soon drop to a low value.

5.3 Mass Transfer Examples

5.3.1 Background

This example concerns the loss of a plasticizer DEHP (di-2-ethylhexyl phthalate) from PVC (polyvinyl chloride) tubing into water. The PVC is fabricated into a tube about 2 cm in inner diameter, d, with a wall thickness of L = 0.1 cm. The tubing length is about 23 m (75 feet). The initial loading of the DEHP is 50 phr (parts per hundred resin) or 0.33 weight fraction. Since the density of PVC (without plasticizer) is approximately 1.4 g/cm^3 and the density of DEHP is approximately 1 g/cm^3, the initial density of the plasticized PVC tube is

$$\text{plasticized PVC density} = (50 + 100)/[50 + (100/1.4)] = 1.24 \text{ g/cm}^3$$

Also, the initial concentration of the DEHP in the PVC tubing is

$$C_{p,o} = \text{phr}/[\text{phr} + (100/1.4)]$$

$$= 50/[50 + (100/1.4)] = 0.41 \text{ g/cm}^3.$$

The diffusion coefficient of DEHP within plasticized PVC is not well-documented. Quackenbos (1954) reported values obtained by a variety of techniques over a temperature range from 20°C to 90°C. We will consider two temperatures, 20°C and 80°C and, from his data for a loading of 47 phr,

$$D_{20} = 3.5 \times 10^{-12} \text{ cm}^2/\text{s}$$

$$D_{80} = 3 \times 10^{-10} \text{ cm}^2/\text{s}$$

The solubility of DEHP in water is not well known. A review of the literature indicates an average value of about 1 ppm or 1×10^{-6} g/cm³. For this example, this value of $C_{e,s}$ is assumed to be temperature independent. For $C_{p,s}$ the solubility of DEHP in PVC, we know the value is greater than 50 phr or 0.41 g/cm³, but since we do not have a definitive value, we will use the initial concentration of 0.41 g/cm³. Thus, the estimated partition coefficient is

$$K = 10^{-6}/0.41 \approx 2.4 \times 10^{-6}$$

As water is inside the tubing, migration is one-sided.

With these estimates of parameters, let us next consider some examples.

5.3.2 Stagnant Water

The maximum transfer of DEHP from the PVC tube to stagnant water in the tube would occur with a fractional loss at the partition equilibrium given by Eq. (3-39)

$$M_\tau = \alpha/(1 + \alpha)$$

where $\alpha = KV_e/LA$. (V_e/A) is the external phase volume per surface area of transfer. For a length of tubing = Z,

$$V_e = (\pi d^2/4)(Z)$$
$$A = (\pi d)(Z)$$
$$(V_e/A) = (d/4) = 0.5 \text{ cm}^3/\text{cm}^2$$

and, with $K \approx 2.4 \times 10^{-6}$ and $L = 0.1$ cm,

$$\alpha = (2.4 \times 10^{-6})(0.5)/0.1 = 1.22 \times 10^{-5}.$$

With Eq. (3-39), the fraction of DEHP in the tubing which would migrate to stagnant water at equilibrium is 1.22×10^{-5}.

Thus, the mass of DEHP lost from the tubing of length Z = 2300 cm is

$$M_\tau C_{p,o} LA = (1.2 \times 10^{-5})(0.41)(0.1)[(0.2)(\pi \times 2)(2300)] = 0.007 \text{ g}$$

The volume of water in length Z = 2300 cm is

$$V_e = (\pi d^2/4)(Z) = (\pi \times 2^2/4)(2300) = 7226 \text{ cm}^3$$

so the equilibrium concentration in the stagnant water is

$$0.007/7226 = 9.8 \times 10^{-7} \text{ g/cm}^3 = 0.98 \text{ ppm}$$

To obtain an estimate for the times involved to reach the partition equilibrium, we could first estimate the "shortest" time by envisioning that the "stagnant" fluid was recirculated at a high rate of flow through the tubing. Thus, the external mass transfer coefficient is unlimited and one could use Eq. (3-26) with the following input parameters:

- $D_p = 3.5 \times 10^{-12}$ cm²/s at 20°C
- L = 0.1 cm (wall thickness)
- One-sided migration
- Solubility in PVC, $C_{s,p} \approx C_{p,o} \approx 0.41$ g/cm³
- Solubility in water, $C_{s,\ell} \approx 1$ ppm (1×10^{-6} g/cm³)
- $V_e = 7226$ cm³
- A = 14451 cm²

For this example, $K = 2.4 \times 10^{-6}$ and $\alpha = 1.22 \times 10^{-5}$ and the computer program gives the following estimates of the fraction migrated over time using Eq. (3-26).

Time	$\tau = D_p t/L^2$	Fraction Migrated (Eq. 3-26)
0.5 hours	6.3×10^{-7}	1.20×10^{-5}
1 hour	1.3×10^{-6}	1.21×10^{-5}
1 day	3.0×10^{-5}	1.22×10^{-5}

As the results show, the partition equilibrium is reached in almost one hour. Because of the partitioning limitations only a very small fraction of the DEHP initially present in the tubing is estimated to migrate. The partition limitation is driven mainly by the low value for K (i.e., the solubility of DEHP in water relative to that in the PVC).

5.3.3 Flowing Water

Next we consider the situation in which fresh water flows through the tubing at such a high rate that the external mass transfer coefficient is very large and there is no partitioning of DEHP in the water. In this "worst case" (maximum DEHP loss), Eq. (3-23) is operative. The same input parameters are used except in this case we will treat two temperatures, 20°C and 80°C with $D_{20} = 3.5 \times 10^{-12}$ cm²/s and $D_{80} = 3.0 \times 10^{-10}$ cm²/s. In these cases,

	Fraction Migrated Eq. (3-23)	
Time	T = 20°C	T = 80°C
1 day	0.006	0.06
1 week	0.016	0.15
1 month	0.034	0.32
1 year	0.12	0.92

Since a very high flow rate of water was assumed, the DEHP concentration in the outlet flow would be negligible, but, clearly, at 80°C, large losses are estimated at long times. Such losses actually invalidate the procedure since the diffusion coefficient decreases as the plasticizer concentration drops. When encountering situations where large losses are predicted and D_p is a strong function of concentration, the simple equations given in this report are not valid.

5.3.4 External Mass Transfer Resistance But No Partitioning

In this case, we assume that there is a low external mass transfer coefficient but that there is a sufficiently high volume to minimize partitioning. That is, we still set $\alpha \rightarrow \infty$, but we must now consider the dimensionless group $\gamma = KkL/D_p$.

Mass transfer from walls of plastic tubes to water was considered in Section 4.5.1.2 and Eq. (4-19) developed. However, to illustrate the procedure, let us first return to the basic relation [Eq. (4-15)] to estimate k, and compare results with values from the simplified equation [Eq. (4-19)].

To employ Eq. (4-15), we require some physical constants.

- kinematic viscosity of water
  $\nu = 0.01$ cm²/s at 20°C
  $\nu = 0.0036$ cm²/s at 80°C
- diffusion coefficient of DEHP in water
  We employed Eq. (4-3) with V_m determined from Table 11. Since there are 24 carbon atoms, 4 oxygen atoms, 38 hydrogen atoms, one ring, and three double bonds in DEHP,

$$V_m = (24)(7) + (4)(7) + (38)(7) + (1)(-7) + (3)(7) = 476 \text{ cm}^3/\text{mole}$$

and

$$D_w = (5.1 \times 10^{-7})(T)/(476)^{0.6}$$

$$D_w\ (20°C) = 3.7 \times 10^{-6}\ cm^2/s$$

$$D_w\ (80°C) = 4.4 \times 10^{-6}\ cm^2/s$$

- Schmidt number = ν/D_w

  $(Sc)_{20} = 2700$

  $(Sc)_{80} = 820$

Then, with d = 2.0 cm and the basic relation Eq. (4-15),

$$k_{20} = 4.1 \times 10^{-5}\ v^{0.8}\ (cm/s)$$

$$k_{80} = 7.4 \times 10^{-5}\ v^{0.8}\ (cm/s)$$

with v, the water velocity, in cm/s.

If we had employed the simplified Eq. (4-19), we would have obtained, for both temperatures,

$$k = 6.3 \times 10^{-5}\ v^{0.8}\ (cm/s)$$

Thus, one can see that temperature is not an important variable in estimating mass transfer coefficients and the simplified Eq. (4-19) will provide reasonable accuracy. For this example, we will select a velocity of 10 cm/s and, thus, the estimated value for k is 1.2×10^{-5} cm/s at both temperatures.

The dimensionless group $\gamma = KkL/D_p$ can then be estimated since $K \approx 2.4 \times 10^{-6}$, $k = 1.2 \times 10^{-5}$ cm/s, L = 0.1 cm and $D_p = 3.5 \times 10^{-12}$ cm²/s at 20°C and 3.0×10^{-10} cm²/s at 80°C.

$$\gamma_{20} = 0.82$$

$$\gamma_{80} = 0.01$$

The fraction migrated is then found from Eq. (3-20) for conditions with external phase mass transfer resistances but no solubility limitations.

Time	Fraction Migrated Eq. (3-20) T = 20°C	Fraction Migrated Eq. (3-20) T = 80°C
1 day	2.5×10^{-5}	2.5×10^{-5}
1 week	1.7×10^{-4}	1.7×10^{-4}
1 month	7.3×10^{-4}	7.4×10^{-4}
1 year	8.5×10^{-3}	9.0×10^{-3}

In this example, the mass transfer resistance in the external phase is controlling the migration process. Thus, there are only small differences in the amount migrated estimates at the two temperatures even though D_p varied by two orders of magnitude over this temperature range. These results, in comparison with the results reported for the no mass transfer/no partitioning case in Section 5.3.3, illustrate that the mass transfer resistance in the PVC-water boundary layer reduces the amount of DEHP estimated to migrate into the water flowing through the PVC tubing. However, these amounts migrated are higher than those estimated when partitioning alone was considered.

5.3.5 External Mass Transfer Resistance With Partitioning

In a real case, with a long plastic tube, it is possible to attain a situation where there are no partitioning effects near the inlet, but, due to accumulation of migrant during flow, the plastic tube walls downstream "see" water with a sufficiently high concentration of additive to cause partitioning. The models developed in this report do not address such a case with variable conditions in the external phase during the migration process. However, to illustrate the applicability of Eq. (3-17) which allows for both external mass transfer, as well as partitioning, we assume that the water in the plastic tubing is recirculated sufficiently fast so that there is an "average" additive concentration in the water independent of position.

For this example, we will use the conditions and parameters specified earlier for DEHP migration from PVC tubing into water at 20°C:

- $D_p = 3.5 \times 10^{-12}$ cm²/s at 20°C
- $L = 0.1$ cm
- $d = 2.0$ cm
- One-sided migration
- Solubility in PVC, $C_{s,p} \approx C_{p,o} \approx 0.41$ g/cm³
- Solubility in water, $C_{s,e} \approx 1.0 \times 10^{-6}$ g/cm³
- $V_e = 7226$ cm³
- $A = 14451$ cm²
- $v = 10$ cm/s

- $k = 1.2 \times 10^{-5}$ cm/s

With these values,

$K = 2.4 \times 10^{-6}$

$\alpha = 1.22 \times 10^{-5}$

$\gamma = 0.82$

The fraction migrated estimates as a function of time at 20°C are:

Time	$\tau = D_p t/L^2$	Fraction Migrated (Eq. 3-27)
1 hour	1.3×10^{-6}	1.0×10^{-6}
1 day	3.0×10^{-5}	1.1×10^{-5}
1 week	2.1×10^{-4}	1.22×10^{-5}
1 month	9.1×10^{-4}	1.22×10^{-5}

In this example, a partition equilibrium is reached after approximately one week. In comparison, when partitioning but no mass transfer was considered in Section 5.3.2, the equilibrium was reached in about one hour. Thus, the combined effects of mass transfer and partitioning increase the time required to reach the partition equilibrium.

6. COMPUTER PROGRAM

AMEM (Arthur D. Little Migration Estimation Model) is a computer program that facilitates the rapid estimation of the fraction of the additive originally in a polymer sheet that will migrate under the various conditions defined in Section 3. AMEM incorporates many of the physical property estimation techniques presented in Section 4. AMEM was coded in FORTRAN for operation on IBM-AT personal computers and compatibles. The program should be run on a personal computer with a math coprocessor. The FORTRAN code and operational flowchart are provided in Appendix A. The program and floppy diskette on which it was delivered should be considered integral parts of this report.

With AMEM, one can estimate migration to both fluid and solid external phases. The program is designed to enable its user to first estimate the maximum rate of migration from the polymer with the minimum set of inputs. If this fraction migrated is below a "trigger" level, then the user need proceed no further. If the fraction migrated is above the trigger level or if the user wants to explore other scenarios, then additional inputs are required of the user. Because of coprocessor limitations regarding the convergence of some infinite series terms near zero, the smallest fraction migrated value predicted by AMEM under worst case conditions is 1×10^{-4} fraction migrated. For fluid external phases, estimates are made for the worst-case scenario in which migration is not hindered by partitioning or mass transfer resistances in the external phase [Eq. (3-23)], for scenarios that consider partitioning effects [Eq. (3-26)], and for scenarios that consider mass transfer [Eq. (3-20)], and for scenarios that consider both partitioning and mass transfer limitations [Eq. (3-17)]. For solid external phases, the computer program estimates migration for the worst case scenario (Eq. (3-23)] and for scenarios with and without partitioning limitations [Eq. (3-29) and (3-31)].

AMEM contains subroutines to estimating values for the diffusion coefficient of the additive in the polymer, air, and water; for the partition coefficient; and for the external phase mass transfer coefficient. The equations and techniques used in these subroutines are designated in the appropriate paragraphs of Section 4. The FORTRAN code for these routines is given in Appendix A.

AMEM's user interface was developed to facilitate data input selections. The user is queried for the required input data through a series of information screens and selection menus. Table 12 summarizes the input data requirements for the various migration scenarios and equations. The program calculates the fraction migrated for the conditions specified. The output screen repeats the key inputs as well as presents the results of the calculations. The user may execute "Print Screen" or print the appropriate Eq*.LIS file to document the results. The user may then re-run the program changing either one or more of the data inputs, or terminate the session.

Appendix B provides a limited validation of AMEM in which the AMEM predictions are compared with migration data from the technical literature for 13 example cases.

TABLE 12. SUMMARY OF COMPUTER PROGRAM INPUT REQUIREMENTS

Input Variable	Section*
POLYMER	Scenario Specific
Thickness, cm	
Exposure to External Phase, one or both sides	
EXTERNAL PHASE	Scenario Specific
Air, Water, or Solid	
TIME	Scenario Specific
Period over which migration occurs, hrs	
DIFFUSION COEFFICIENT OF MIGRANT IN POLYMER, cm^2/s	4.2
Estimated by program if unknown using:	
Migrant Molecular Weight, g/mole	
Polymer Type, select from menu:	
Silicone Rubber	
Natural Rubber	
LDPE	
HDPE	
Polystyrene	
Polyvinyl Chloride (unplasticized)	
PARTITIONING EFFECTS (Air or Water External Phase)	4.4
To consider, input:	
Volume of External Phase, m^3	
Surface Area of Polymer, cm^2	
Partition Coefficient - to calculate input:	
Saturation Concentration of Migrant in Polymer, g/cm^3	4.4.1
If unknown use Initial Concentration, g/cm^3	

(continued)

TABLE 12. (continued)

Input Variable	Section*
PARTITIONING EFFECTS (Air or Water External Phase) (continued)	
Saturation Concentration of Migrant in External Phase, g/cm^3	4.4.2
To estimate input:	
for AIR: Migrant Vapor Pressure, torr	4.4.2.1
for WATER: Migrant Melt Temp., °C Migrant Octanol/Water Partition Coefficient	4.4.2.2
MASS TRANSFER EFFECTS (Air or Water External Phase)	
To consider, input:	
Mass Transfer Coefficient, cm/s	4.5
for AIR: Air Flow Velocity, cm/s Polymer Position - Horizontal or Vertical Polymer Location - Indoors or Outdoors	4.5.2
for WATER: Water Flow Velocity, cm/s Polymer Plate Surface Length or Pipe Diameter, cm	4.5.1
Partition Coefficient - see above	
SOLID EXTERNAL PHASE	
To consider, input:	
Diffusion Coefficient in External Phase, cm^2/s	4.3.3 (4.2)

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* Section of report that describes the input variable and documents the procedures used to estimate it in the computer program.

7. NOMENCLATURE

This section provides definitions of the symbols and equation variables used throughout the text. When applicable, the variable name used in the AMEM program code provided in Appendix A is listed in parenthesis.

A	Surface area of polymer exposed to external phase, cm^2; (SAP)
C_a	Solubility of migrant in air, g/cm^3; (CSATA)
C_e	Concentration of migrant in external phase, g/cm^3
$C_{e,s}$	Solubility of migrant in external phase, g/cm^3; (CSATE)
C_p	Concentration of additive in polymer, g/cm^3
$C_{p,o}$	Initial concentration of additive in polymer, g/cm^3; (CINIT)
$C_{p,s}$	Solubility of aditive in polymer, g/cm^3; (CSATP)
C_w	Solubility of migrant in water, g/cm^3; (CSATW)
d	Diameter of pipe, cm; (DPIPE)
D_a	Diffusion coefficient of migrant in air, cm^2/s; (DAIR)
D_e	Diffusion coefficient of migrant in external phase, cm^2/s; (DEXT)
D_p	Diffusion coefficient of migrant in polymer, cm_2/s; (DP)
D_w	Diffusion coefficient of migrant in water, cm^2/s; (DMIG)
g	Acceleration due to gravity, 980 cm/s^2
h	Convective heat transfer coefficient
H	Height of vertical polymer surface over which air is flowing, cm; (HEIGHT)
k	Mass transfer coefficient, cm/s; (RK)
K	Partition coefficient; ratio of additive concentration in external phase to additive concentration in polymer at equilibrium; (PC)
K_{ow}	Octanol-water partition coefficient; (XKOWM)
l	Characteristic length of polymer in direction of external phase flow, cm; (RSURFA or RSURFW)
L	Thickness of polymer in cases of one-sided exposure to external phase; half-thickness of polymer in cases of two-sided exposure to external phase, cm; (XLEN)
M	Molecular weight, g/mol
M_a	Molecular weight of air, 29 g/mol
M_m	Molecular weight of migrant, g/mol; (XMW)
M_τ	Fraction migrated; (FRMIG)

P	Pressure, atm
P_v	Vapor pressure of migrant, torr; (VPMT)
R	Gas constant
t	Time, seconds; (TSEC)
T	Temperature, degrees kelvin
T_m	Melting temperature of migrant, °C; (TMM)
v	Bulk velocity of external phase, cm/s; (AIRVEL or WATVEL)
V	Molar volume, cm^3/mol
V_a	Molar volume of air, 19.7 cm^3/mol
V_e	External phase volume; (VEP)
V_m	Molar volume of migrant, cm^3/mol
V_p	Polymer volume
δ	Boundary layer thickness, cm
ν	Kinematic viscosity, cm^2/s
ρ	Density, g/cm^3
λ	Thermal conductivity of air

DIMENSIONLESS GROUPS

α	$(V_e/A)(K/L)$; (ALPHA)
β	$K(D_e/D_p)^{0.5}$; (BETA)
τ	$D_p t/L^2$; (TAU)
γ	kKL/D_p; (GAMMA)
Gr	Grashof number, $(gH^3/\nu^2)[(\rho_o-\rho_\infty)/\rho_\infty]$
Nu	Nusselt number, $\eta l/\lambda$
R_e	Reynolds number, dv/ν
Re_l	Length Reynolds number, vl/ν
Sc	Schmidt number, ν/D_e
Sh	Sherwood number, kl/D_e

8. REFERENCES

Arthur D. Little, Inc. 1983. "Migration of BHT and Irganox 1010 from Low Density Polyethylene". Summary Report on FDA Contract 223-77-2360 (1983).

ASHRAE Handbook and Product Directory. 1980. American Society of Heating, Refrigeration and Air-Conditioning Engineers, Inc., New York. Chapter 21.

Ayres, J.L., J.C. Osborne, H.B. Hopfenberg, and W.J. Koros. 1983. "Effect of Variable Storage Times on the Calculation of Diffusion Coefficients Characterizing Small Molecule Migration in Polymers". Ind. Eng. Chem. Prod. Res. Dev. Vol. (22):86-89.

Barr, R.F. and H. Watts. 1972. "Diffusion of Some Organic and Inorganic Compounds in Air". J. Chem. Eng. Data. Vol. (17):45-46.

Barrens, A.R. and H.B. Hopfenberg. 1982. "Diffusion of Organic Vapors at Low Concentrations in Glassy PVC, Polystyrene, and PMMA". J. Membrane Sci. Vol. (10):283-30.

Bixler, H.J. and O.J. Sweeting. 1971. "Barrier Properties of Polymer Films". The Science and Technology of Polymer Films, Vol. II". Sweeting (ed), Wiley & Sons, NY.

Crank, J.. 1975. The Mathematics of Diffusion. Clarendon Press, Oxford.

Crank, J. and G.S. Park. 1975. Diffusion in Polymers. Academic Press, NY.

Eckert, E.R.G. and R.M. Drake. 1972. Analysis of Heat and Mass Transfer. McGraw-Hill, New York.

Farmer, W.J., M.S. Yang and J. Letey. 1980. "Land Disposal of Hexachlorobenzene Wastes--Controlling Vapor Movement in Soil". U.S. Environmental Protection Agency Report No. EPA-600/2-80-119.

Flynn, J.H.. 1982. "A Collection of Kinetic Data for the Diffusion of Organic Compounds in Polyolefins". Polymer. Vol. (23):1325-1344.

Fuller, E.N. and J.C. Giddings. 1965. "A Comparison of Methods for Predicting Gaseous Diffusion Coefficients". J. Gas Chromatogr. Vol. (3):222-7.

Fuller, E.N., K. Ensley, and J.C. Giddings. 1969. "Diffusion of Halogenated Hydrocarbons in Helium". J. Phys. Chem. Vol. (73):3679-3685.

Fuller, E.N., P.D. Schettler, and J.C. Giddings. 1966. "A New Method for Prediction of Binary Gas-Phase Diffusion Coefficients". Ind. Eng. Chem. Vol. (58)(5):18-27.

Gandek, T.P. 1986. "Migration of Phenolic Antioxidants From Polyolefins to Aqueous Media with Application to Indirect Food Additive Migration". Ph.D. Thesis. Mass. Inst. of Tech. Cambridge, MA. .

Goydan, R., R.C. Reid, and H.-S. Tseng. 1989. "Estimation of the Solubilities of Organic Compounds in Polymers by Group Contribution Methods". Ind. Eng. Chem. Res. Vol. (28):445-454.

Grain, C.F. 1982. "Vapor Pressure". Handbook of Chemical Property Estimation Methods. W. Lyman, W. Reehl, and D. Rosenblatt (eds), McGraw-Hill Book Co., NY.

Grun, F. 1949. "Measurements of Diffusion in Rubber". Rubber Chem. and Technol. Vol. (22):316-319.

Hatton, T.A., A.S. Chiang, P.T. Noble, and E.N. Lightfoot. 1979. "Transient Diffusional Interactions Between Solid Bodies and Isolated Fluids". Chem. Eng. Sci. Vol. (34):1339-1344.

Hatton, T.A. 1985. "On the Calorimeter Problem for Finite Cylinders and Rectangular Prisms". Chem. Eng. Sci. Vol. (40):167-170.

Hayduk, W. and H. Laude. 1974. "Prediction of Diffusion Coefficients for Nonelectrolytes in Dilute Aqueous Solutions". AICHE J. Vol. (20):611-615.

Höber, R. 1945. Physical Chemistry of Cells and Tissues. Blakiston Company, PA (1945).

Lugg, G.A. 1968. "Diffusion Coefficients of Some Organic and Other Vapors in Air". Anal. Chem. Vol. (40):1072-1077.

Lyman, W.J., R.G. Potts and G.C. Magil. 1982. User's Guide [to] CHEMEST, prepared for the U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, and the U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Dedrick, Frederick, MD.

Lyman, W.J. 1982. "Solubility in Water" in Handbook of Chemical Property Estimation Methods, W. Lyman, W. Reehl and D. Rosenblatt (eds), McGraw-Hill Book Co., NY.

Lyman, W.J., W. Reehl, and D. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill Book Co., NY.

Nah, S.H. and A.G. Thomas. 1980. "Migration and Blooming of Waxes to the Surface of Rubber Vulcanizates". J. Poly. Sci.: Poly Phys. Ed. Vol. (18):511-521.

Park, G.S. 1950. "The Diffusion of Some Halo-methanes in Polystyrene". Trans. Faraday Soc. Vol. (46):684-697.

Park G.S. 1951. "The Diffusion of Some Organic Substances in Polystyrene". Trans. Faraday Soc. Vol. (47):1007-1013.

Quackenbos, H.M. 1954. "Plasticizers in Vinyl Chloride Resins, Migration of Plasticizer". Ind. Eng. Chem. Vol. (46):1335-1344.

Reid, R.C., J.M. Prausnitz, and B.E. Poling. 1987. The Properties of Gases and Liquids. McGraw-Hill Book Co., NY. 4th edition.

Reid, R.C., J.M. Prausnitz, and T.K. Sherwood. 1977. The Properties of Gases and Liquids. McGraw-Hill Book Co., NY.

Reid, R.C., K.R. Sidman, A.D. Schwope, and D.E. Till. 1980. "Loss of Adjuvants from Polymer Films to Foods or Food Simulants. Effect of the External Phase". I&EC Prod. Res. and Dev. Vol. (19):580-587.

Rodriquez, F. 1982. Principles of Polymer Systems. McGraw-Hill Book Co., NY. 2nd edition.

Seymour, R.B. and C.E. Carraher. 1981. Polymer Chemistry. Marcel Dekker, NY.

Skelland, A.H.P. 1974. Diffusional Mass Transfer. Wiley and Sons, NY.

Smith, L.E., I.C. Sanchez, S.S. Chang, and F.L. McCrackin. 1979. "Models for the Migration of Paraffinic Additives in Polyethylene". National Bureau of Standards, NBSIR 79-1598, pp 4-11.

Till, D.E., R.C. Reid, P.S. Schwartz, K.R. Sidman, J.R. Valentine, and R.H. Whelan. 1982. "Plasticizer Migration from Polyvinyl Chloride Film to Solvents and Foods". Fd. Chem. Toxic. Vol. (20):95-104.

Till, D.E., D.J. Ehntholt, A.D. Schwope, K.R. Sidman, R.H. Whelan, and R.C. Reid. 1983. "A Study of Indirect Food Additive Migration". Final Report on FDA Contract Number 223-77-2360.

Valvani, S.C., S.H. Yalkowsky and T.J. Roseman. 1981. "Solubility and Partitioning. IV. Aqueous Solubility and Octanol-Water Partition Coefficients of Liquid Non-electrolytes". J. Pharm. Sci. Vol. (70):502-507.

Yalkowsky, S.H. 1982. (University of Arizona, Tuscon, AZ). Personal communication to W. Lyman of Arthur D. Little, Inc.

Yalkowsky, S.H., S.C. Valvani, and D. Mackay. 1983. "Estimation of the Aqueous Solubility of Some Aromatic Compounds". Residue Rev. Vol. (85):43-45.

Yasuda, H. and V. Stannett. 1975. "Permeability Coefficients". Chap. III.9 in Polymer Handbook, 2nd Ed. Bandrup and Immergut (eds), Wiley and Sons, NY.

APPENDIX A

FORTRAN Code for AMEM
Arthur D. Little Migration Estimation Model Computer Program

This appendix provides a listing of the FORTRAN code for the AMEM computer program, a brief description of the functions and subroutines used, a definition list for the program variables, and a program flowchart with example AMEM input/output screens.

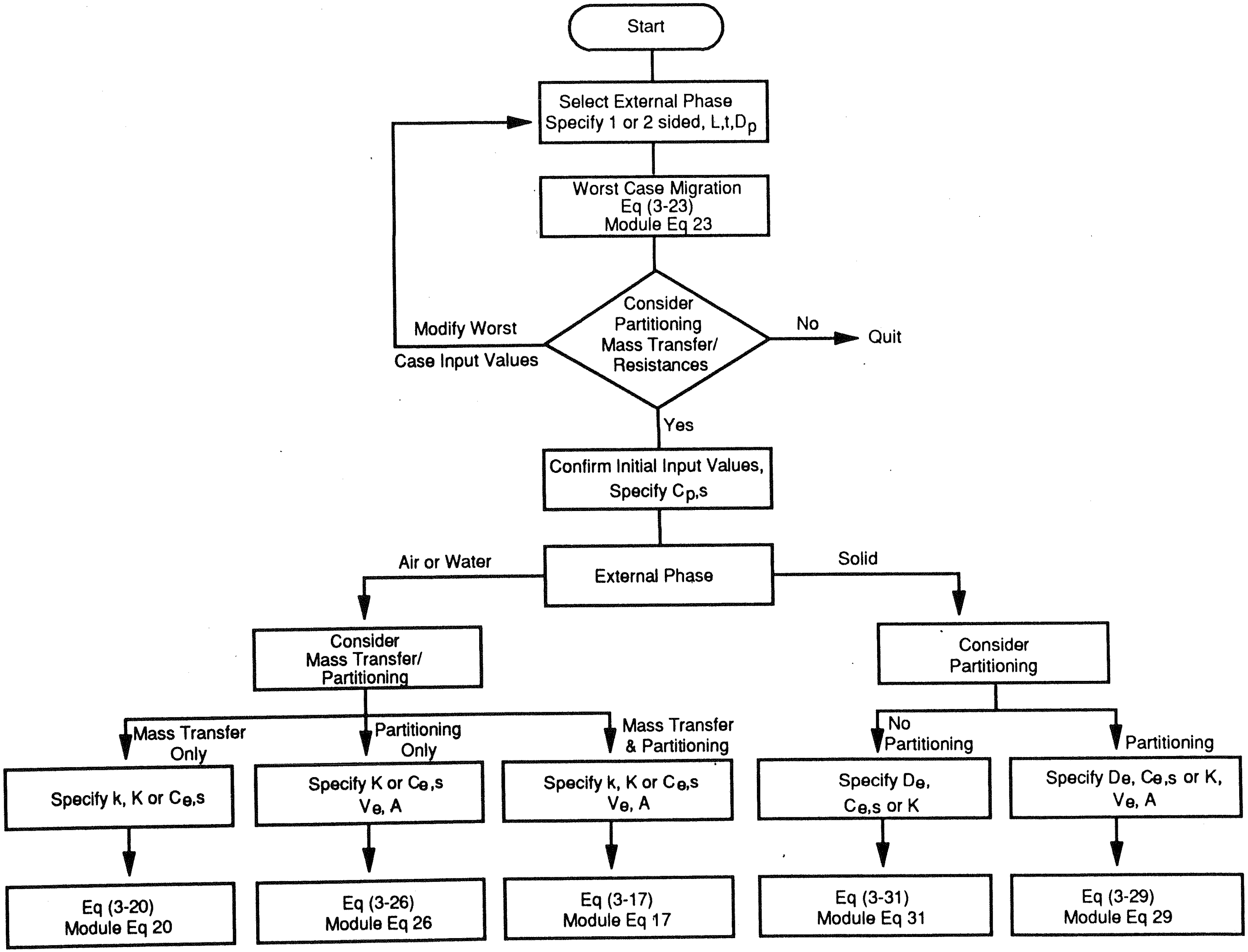

Figure A-1. Flowchart for AMEM Migration Estimation Computer Program

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DEFINITION OF VARIABLES USED IN PROGRAM AMEM 0990

****

Variable	Description	Units
AIRVEL	Velocity of air as the external phase, as it moves across the polymer surface.	cm/s
ALPHA	Non-dimensional variable calculated as the product of the partition coefficient and the external phase volume, divided by the exposed surface area and polymer length.	
BETA	Non-dimensional variable defined as the product of the partition coefficient and the square root of the ratio of the migrant-external phase diffusion coefficient and the migrant-polymer diffusion coefficient.	
CINIT	Initial concentration of migrant in polymer	g/cm3
CSATA	Saturation concentration of migrant in air	g/cm3
CSATE	Saturation concentration of migrant in external phase	g/cm3
CSATP	Saturation concentration of migrant in polymer	g/cm3
CSATW	Saturation concentration of migrant in water	g/cm3
DAIR	Diffusion coefficient of migrant in air, calculated as a function of the migrant molecular weight.	cm2/s
DEXT	Diffusion coefficient of migrant in external phase	cm2/s
DMIG	Diffusion coefficient of migrant in water, calculated as a function of the migrant molecular weight.	cm2/s
DP	Diffusion coefficient of migrant in polymer, which can be user-specified or calculated as a function of the migrant molecular weight.	cm2/s
DPIPE	Diameter of polymer pipe through which water flows	cm
FRMIG	Fraction of migrant that diffuses into external phase	-
GAMMA	Non-dimensional variable that is calculated as the product of the mass transfer coefficient, partition coefficient, and polymer length, all divided by the polymer diffusion coefficient.	

HEIGHT	Average height of vertical polymer surface from which a migrant is migrating.	cm
IPOLY	Index to specify one of six polymer types, as follows: 01= Silicone rubber 02= Natural rubber 03= Low-density polyethylene 04= High-density polyethylene 05= Polystyrene 06= Unplasticized Polyvinylchloride	-
IR	Integer variable that routes program to read from input file	
IRWAT	Integer variable that is set equal to 1 for water flowing through polymer pipe, and 2 for water flowing over a polymer plate	
IW	Integer variable that routes program to write to output file	
JEXT	Variable used in the solid-solid diffusion case that defines the type of external polymer phase. See variable IPOLY for 01-06 polymer type definitions.	
KHORZ	Integer variable to define polymer position in air: 1=Horizontal, 2=Vertical	
NEXT	Integer variable to define external phase type: 01=Air, 02=Water	
NMAX	: Maximum Iteration Counter (1000) in series convergence routines within Equation 23 and Equation 31 modules.	
NPLC	Polymer location in air (1=Indoors; 2=Outdoors)	
NRTBFFMAX	: Maximum Iteration Counter (1000) in series convergence routine within Equation 17 module.	
NRTBFIMAX	: Maximum Iteration Counter (1000) in series convergence routine within Equation 20 module.	
NRTDFFMAX	: Maximum Iteration Counter (1000) in series convergence routine within Equation 29 module.	
NRTMFFMAX	: Maximum Iteration Counter (1000) in series convergence routine within Equation 26 module.	
NSIDE	Integer variable to define number of polymer sides involved in diffusion: 01=One-sided, 02=Two-sided	
PC	Partition coefficient,a non-dimensional variable defined as the ratio of the saturation concentration of the migrant in the external phase to the saturation concentration of the migrant in the polymer. This variable can be user-specified or estimated by the program.	

RK	Mass transfer coefficient can be specified by the user or computed within the program as a function of the polymer position(horizontal,vertical),location (indoors,outdoors), characteristic length(or diameter), the type of external phase(water,air), and the external phase flow velocity.	cm/s
RSURFA	Surface length of polymer exposed to air	cm
RSURFW	Plate length of polymer exposed to water	cm
SAP	Surface area of polymer exposed to external phase	cm2
TAU	Non-dimensional variable defined as the product of the diffusion coefficient of the migrant in the polymer and time divided by the polymer thickness squared.	-
THRS	Exposure time input by user	hrs
TITLE	One-line alphanumeric variable to define scenario	
TMM	Migrant melt temperature for calculation of saturation concentration of migrant in water	deg C
TSEC	Exposure time (units converted hrs->sec)	sec
VEP	Volume of external phase as input by user	m3
VEPCC	Volume of external phase (units converted m3->cm3)	cm3
VPM	Migrant vapor pressure (units converted torr->atm)	atm
VPMT	Migrant vapor pressure as input by user to estimate saturation concentration in air	torr
WATVEL	Velocity of water as the external phase, as it moves across the polymer surface (min. value 10cm/s)	cm/s
XKOWM	Migrant octanol-water partition coefficient for calculation of saturation concentration in water	-
XL	Total polymer film thickness	cm
XLEN	Polymer film thickness redefined, based on number of sides exposed to external phase for diffusion	cm
XMW	Molecular weight of migrant	g/g-mol

```
****************************************************************************
        FUNCTION SUBROUTINES IN PROGRAM AMEM          0990
     REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
****************************************************************************
1. DOMBFF:
       Domain BFF:  Finite polymer in contact with a finite fluid external
       phase. Boundary layer resistance.  Returns fractional migration assuming
       the migrant is initially uniformly distributed in the polymer and
       the initial external phase concentration is zero.
       Requires subprogram ROOTBFF

       Note that TAU   = Dpt/L2
                 R     = kKL/Dp
                 ALPHA = KV/AL

2. ROOTBFF:
       Finds roots of the equation
         Tan(BN) = R*BN/(BN2-N)
       or
         Cot(BN) = (BN2-N)/(R*BN)
       where
         I  = number of desired root
         R  = kKL/Dp
         ALPHA = KV/AL
         N  = R/ALPHA

3. DOMBFI
       Domain BFI:  Finite polymer in contact with an infinite fluid
       external phase. Boundary layer resistance.  Returns fractional
       migration assuming the fluid phase concentration is initially zero
       and the migrant is uniformly distributed in the polymer.
       Requires subprogram ROOTBFI
       Note that R   = kKL/Dp
                 Tau = Dpt/L2

4. ROOTBFI
       Returns roots of the equation
         tan(GN) = R/GN       or       cot(GN) = GN/R
       where R is a constant

5. DOMMFI
       Domain MFI: Finite polymer in contact with an infinite, well-stirred
       fluid external phase.  Returns fractional migration assuming the
       initial migrant concentration in the fluid external phase is zero and
       the polymer distribution is uniform.

       Note that TAU = Dpt/L2

6. DOMMFF
       Domain MFF:  Finite polymer in contact with a finite, well-stirred
```

fluid external phase. Returns fractional migration, assuming that the migrant concentration in the fluid external phase is initially zero, and the distribution in the polymer is uniform.
Requires the subprogram ROOTMFF.

Note that TAU = Dpt/L2
ALPHA = KV/AL

7. ROOTMFF

Finds roots of the equation Tan (BN) + ALPHA*BN = 0
Requires argument ALPHA = KV/AL and N = root #

8. DOMDFF

Domain DFF: Finite polymer in contact with a finite solid external phase. Returns fractional migration assuming the migrant concentration in the solid external phase is initially zero and initial concentration in the polymer is uniform.
Requires subprogram ROOTDFF

Note that TAU = Dpt/L2
BETA = Ksqrt(De/Dp)
DOMDFF(TAU,ALPHA,BETA)

In order to avoid problems with the rootfinding routine, ROOTDFF, ALPHA is perturbed slightly. The potential problems occur when round figures are used for BETA and ALPHA, when either are simply related multiples or are common factors of a larger number, because then asymptotes of the two tangent functions (in the characteristic eqn.) can coincide.
If alpha > beta it is faster to calculate migration by letting alpha and beta equal their reciprocals and tau = tau times the square of beta/alpha. The value of migration thus calculated is multiplied by the true value of alpha to give migration for the original case.

9. ROOTDFF

Finds Nth root of the equation
tan (LN) + BETA*tan(ALPHA*LN/BETA) = 0
given the parameters ALPHA and BETA. The root for N=0 is 0.

N = root number; root 0 = 0
N1 = N + 1, used for calcaulation of asymptotes
EPS1 = desired accuracy of root
EPS2 = part of interval away from asymptote where the search begins
EPS3 = EPS2*BETA/ALPHA if BETA < ALPHA
= EPS2 if BETA > ALPHA
ETA = 1/(1 + BETA/ALPHA)
BOA = BETA/ALPHA
BAB = BOA if BETA < ALPHA
= 1/BOA if BETA > ALPHA
ETA = ETA if ALPHA < BETA
= 1/(1+ALPHA/BETA) if ALPHA > BETA

To trace program execution for diagnostic purposes, set IDIAG = 1 by passing a negative value of N to ROOTDFF

When roots cannot be determined (message indicates such), the returned root will be negative.

The two asymptotes bound the desired root. To find the root, we start at the right and use Newton's method to 'walk down the curve' to the root. If an inflection point is encountered, we start from the other direction. If the root is within EPS3 of an asymptote, an alternate form of the residual is used.

Note that TAU = Dpt/L2
ALPHA = KV/AL
BETA = Ksqrt(De/Dp)

10. DOMDFI

Domain DFI: Finite polymer in contact with a semi-infinite solid external phase. Returns fractional migration assuming the external phase concentration is initially zero and the migrant is uniformly distributed in the polymer.
Requires the subprograms ERFCA, SHANK

Note that TAU = Dpt/L2
ALPHA = KV/AL
BETA = Ksqrt(De/Dp)

11. ERFCA

Function ERFCA(Z) calculates the complementary error function of the real, positive argument Z. The result is accurate to about 8 significant figures at worst.
Requires function SHANK.

12. SHANK

Function SHANK uses Shanks transform to accelerate convergence of a series.
S is a vector (length 25) containing N consecutive terms of the series. S is destroyed during the calculation.

```
C    PROGRAM NAME: EQ17                    KM DILWALI 0990

C  THIS PROGRAM MODULE SERVES AS THE I/O SHELL TO
C  COMPUTE THE FRACTION OF ADDITIVE MIGRATION
C  ASSUMING THE FOLLOWING CONDITIONS:  (BFF)
C  - BOUNDARY LAYER RESISTANCE EFFECTS CONSIDERED
C  - POLYMER PHASE THICKNESS MUST BE CONSIDERED FINITE
C  - EXTRACTANT PHASE FINITE;I.E. PARTITIONING EFFECTS CONSIDERED
C  INPUT REQUIREMENTS:
C        IPOLY : 01-06 POLYMER TYPE                             -
C          01= SILICONE RUBBER    04=HDPE
C          02= NATURAL  RUBBER    05=POLYSTYRENE
C          03= LDPE               06=PVC(UNPLASTICIZED)
C        XMW   : MOLECULAR WEIGHT OF MIGRANT                   G/MOL
C        DP    : DIFFUSION COEFF. OF ADDITIVE IN POLYMER       CM2/S
C        THRS  : TIME                                          HRS
C        XL    : POLYMER FILM THICKNESS                        CM
C        NSIDE : 01=ONE-SIDED , 02=TWO-SIDED DIFFUSION          -
C        CINIT : INIT MIGRANT CONCN IN POLYMER                G/CM3
C                (ONLY REQUIRED IF CSATP IS UNKNOWN)
C      > NEXT  : EXT PHASE TYPE 01=AIR, 02=H2O , 03=SOLID
C        VEP   : VOL OF EXT PHASE       ,M3
C        SAP   : EXPOSED SURFACE AREA  ,CM2
C        PC    : PARTITION COEFF; 0 IF UNKNOWN
C        CSATP : SAT CONCN OF MIGR IN POLYMER OR 0.,G/CM3
C        CSATA : SAT CONCN OF MIGR IN AIR     OR 0.,G/CM3
C        CSATW : SAT CONCN OF MIGR IN H2O     OR 0.,G/CM3
C        CSATE : SAT CONCN OF MIGR IN SOLID (N/A)    G/CM3
C      > VPMT  : MIGR VAPOR PRESSURE,TORR FOR CSATA,RK CALCS
C        TMM   : MIGR MELT TEMP DEG C     FOR CSATW CALC
C        XKOWM : MIGR OCT-H2O PART COEFF FOR CSATW CALC
C        RK    : MASS TRANSFER COEFF CM/S; 0. IF UNKNOWN
C        KHORZ : AIR: POLYMER POSITION 1=HORIZONTAL, 2=VERTICAL
C        NPLC  : AIR: POLYMER LOCN 1=INDOORS, 2=OUTDOORS
C        RSURFA: AIR: SURFACE LENGTH ,CM
C        AIRVEL: AIR: AIRFLOW VELOCITY, CM/S
C        HEIGHT: AIR: SURFACE HEIGHT FOR VERTICAL POSITION, CM
C        WATVEL: H2O: WATER FLOW VELOCITY , CM/S
C        IRWAT : H2O: 01=FLOW THRU PIPE; 02=FLOW OVER PLATE
C        RSURFW: H2O: FOR IRWAT=2,PLATE LENGTH, CM
C        DPIPE : H2O: FOR IRWAT=1,PIPE  DIAMETER, CM
C********************
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/PARAM3/B3(1000),NRTBFF,A3LAST,R3LAST,NRTBFFMAX
      TAU = 0.0
      ALPHA = 0.0
      GAMMA = 0.0
      NRTBFFMAX = 1000
C********************
      COMMON/IO/IR,IW
```

```
      CHARACTER*2 TITLE(36)
      IR = 5
      IW = 6
      OPEN(IR,FILE='EQ17.INP')
      OPEN(IW,FILE='EQ17.LIS',STATUS='UNKNOWN')
C  READ INPUT DATA
      READ(IR,'(36A2)')TITLE
      READ(IR,'(I2)')IPOLY
      READ(IR,'(F10.2)')XMW
      READ(IR,'(F10.2)')DP
      READ(IR,'(F10.2)')THRS
      READ(IR,'(F10.2)')XL
      READ(IR,'(I2)')NSIDE
      READ(IR,'(F10.2)')CINIT
      READ(IR,'(I2)')NEXT
      READ(IR,'(F10.2)')VEP
      READ(IR,'(F10.2)')SAP
      READ(IR,'(F10.2)')PC
      READ(IR,'(F10.2)')CSATP
      READ(IR,'(F10.2)')CSATA
      READ(IR,'(F10.2)')CSATW
      READ(IR,'(F10.2)')VPMT
      READ(IR,'(F10.2)')TMM
      READ(IR,'(F10.2)')XKOWM
      READ(IR,'(F10.2)')RK
      READ(IR,'(I2)')KHORZ
      READ(IR,'(I2)')NPLC
      READ(IR,'(F10.2)')RSURFA
      READ(IR,'(F10.2)')AIRVEL
      READ(IR,'(F10.2)')HEIGHT
      READ(IR,'(F10.2)')WATVEL
      READ(IR,'(I2)')IRWAT
      READ(IR,'(F10.2)')RSURFW
      READ(IR,'(F10.2)')DPIPE
C  INITIALIZE
      IF(RK.NE.0..AND.WATVEL.EQ.0.)WATVEL=10.
      XLEN = XL
      IF(NSIDE.EQ.2)XLEN=XL/2.
      TSEC = THRS*3600.
C   ECHO INPUT
      WRITE(IW,201)TITLE
      WRITE(IW,210)
      IF(IPOLY.EQ.0)WRITE(IW,209)
      IF(IPOLY.EQ.1)WRITE(IW,211)
      IF(IPOLY.EQ.2)WRITE(IW,212)
      IF(IPOLY.EQ.3)WRITE(IW,213)
      IF(IPOLY.EQ.4)WRITE(IW,214)
      IF(IPOLY.EQ.5)WRITE(IW,215)
      IF(IPOLY.EQ.6)WRITE(IW,216)
      IF(XMW.NE.0.)WRITE(IW,220)XMW
      WRITE(IW,221)THRS,XL
      IF(DP.NE.0.)WRITE(IW,225)DP
      IF(NSIDE.EQ.1)WRITE(IW,230)
      IF(NSIDE.EQ.2)WRITE(IW,235)
      WRITE(IW,280)VEP
```

```
      WRITE(IW,290)SAP
      IF(NEXT.EQ.1)WRITE(IW,260)
      IF(NEXT.EQ.2)WRITE(IW,265)
      IF(PC.NE.0.)WRITE(IW,331)PC
        IF(PC.NE.0.)GO TO 15
      IF(CSATP.NE.0.)WRITE(IW,266)CSATP
      IF(CSATP.EQ.0.)WRITE(IW,267)CINIT
      IF(NEXT.EQ.1.AND.CSATA.NE.0.)WRITE(IW,268)CSATA
      IF(NEXT.EQ.2.AND.CSATW.NE.0.)WRITE(IW,269)CSATW
      IF(NEXT.EQ.1.AND.CSATA.EQ.0.)WRITE(IW,270)VPMT
      IF(NEXT.EQ.2.AND.CSATW.EQ.0.)WRITE(IW,275)TMM,XKOWM
15    IF(RK.NE.0.)WRITE(IW,330)RK
        IF(RK.NE.0.)GO TO 30
        IF(NEXT.EQ.2)GO TO 20
      IF(KHORZ.EQ.1)WRITE(IW,335)
      IF(KHORZ.EQ.2)WRITE(IW,340)
      IF(NPLC.EQ.1)WRITE(IW,345)
      IF(NPLC.EQ.2)WRITE(IW,350)
      WRITE(IW,355)AIRVEL
      IF(KHORZ.EQ.1)WRITE(IW,360)RSURFA
      IF(KHORZ.EQ.2)WRITE(IW,365)HEIGHT
      GO TO 30
20    WRITE(IW,370)WATVEL
      IF(IRWAT.EQ.1)WRITE(IW,375)
      IF(IRWAT.EQ.2)WRITE(IW,380)
      IF(IRWAT.EQ.1)WRITE(IW,390)DPIPE
      IF(IRWAT.EQ.2)WRITE(IW,360)RSURFW
30    CONTINUE
C   LIST OUTPUT
      WRITE(IW,310)
C   CALC DIFFUSION COEFF IN POLYMER (DP) IF NOT USER-SPECIFIED
      IF(IPOLY.EQ.0.AND.DP.EQ.0.)GO TO 900
      IF(DP.EQ.0.)CALL DPCALC(IPOLY,XMW,DP)
C   CALC PARTITION COEFF IF NOT USER-SPECIFIED
      VPM = VPMT/760.
      IF(PC.EQ.0.)CALL KCALC(NEXT,CSATP,CSATA,CSATW,CINIT,CSATE,
     1                        XMW,VPM,TMM,XKOWM,PC)
C   CALC MASS TRANSFER COEFF IF NOT USER-SPECIFIED
      IF((NEXT.EQ.2).AND.(WATVEL.LT.10.))GO TO 850
      IF(RK.EQ.0.)CALL RKCALC(NEXT,KHORZ,NPLC,AIRVEL,RSURFA,VPM,
     1 HEIGHT,WATVEL,IRWAT,RSURFW,DPIPE,XMW,RKO)
      IF(RK.EQ.0.)WRITE(IW,395)RKO
      IF(RK.EQ.0.)RK = RKO
C CALC NONDIMENSIONAL PARAMETERS
      TAU = DP*TSEC/XLEN/XLEN
      VEPCC = VEP*1.0E6
      ALPHA = PC*VEPCC/SAP/XLEN
      GAMMA = RK*PC*XLEN/DP
      WRITE(IW,320)TAU,ALPHA,GAMMA
      FRMIG = DOMBFF(TAU,ALPHA,GAMMA)
201   FORMAT(6X,36A2//)
210   FORMAT(6X,'** INPUT PARAMETERS **'/)
209   FORMAT(6X,'POLYMER CATEGORY:',T60,'  UNDEFINED       ')
211   FORMAT(6X,'POLYMER CATEGORY:',T60,'  SILICONE RUBBER ')
212   FORMAT(6X,'POLYMER CATEGORY:',T60,'  NATURAL  RUBBER ')
```

```
  213 FORMAT(6X,'POLYMER CATEGORY:',T60,'  LDPE              ')
  214 FORMAT(6X,'POLYMER CATEGORY:',T60,'  HDPE              ')
  215 FORMAT(6X,'POLYMER CATEGORY:',T60,'  POLYSTYRENE       ')
  216 FORMAT(6X,'POLYMER CATEGORY:',T60,'  PVC(UNPLASTICIZED)')
  220 FORMAT(6X,'MOLECULAR WEIGHT OF ADDITIVE   ',T60,1PE10.2)
  221 FORMAT(6X,'TIME  (HRS)       ',T60,1PE10.2/
     1       6X,'TOTAL POLYMER SHEET THICKNESS  (CM)',T60,1PE10.2)
  225 FORMAT(6X,'USER-SPECIFIED DIFFUSION COEFFICIENT(CM2/S)',
     1       T60,1PE10.2)
  230 FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  ONE-SIDED')
  235 FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  TWO-SIDED')
C
  260 FORMAT(6X,'EXTERNAL PHASE IS         ',T60,'  AIR')
  265 FORMAT(6X,'EXTERNAL PHASE IS         ',T60,'  WATER')
  266 FORMAT(6X,'SATURATION CONC. OF MIGRANT IN POLYMER (G/CM3)',
     1           T60,1PE10.2)
  267 FORMAT(6X,'LET SATUR. CONC. IN POLYMER = INIT CONC. (G/CM3)',
     1           T60,1PE10.2)
  268 FORMAT(6X,'SATURATION CONC. IN AIR (G/CM3)',T60,1PE10.2)
  269 FORMAT(6X,'SATURATION CONC. IN WATER (G/CM3)',T60,1PE10.2)
  270 FORMAT(6X,'MIGRANT VAPOR PRESSURE (TORR)  ',T60,1PE10.2)
  275 FORMAT(6X,'MIGRANT MELT TEMP (DEG C)',T60,1PE10.2/
     1       6X,'MIGRANT OCTANOL-WATER PART. COEF.',T60,1PE10.2)
  280 FORMAT(6X,'VOLUME OF EXTERNAL PHASE (M3)',T60,1PE10.2)
  290 FORMAT(6X,'SURFACE AREA OF POLYMER (CM2)',T60,1PE10.2)
C
  310 FORMAT(//6X,'** OUTPUT VALUES (MODULE: EQUATION 17) **'/)
  320 FORMAT(6X,'TAU                                ',T60,1PE10.2,/
     1       6X,'ALPHA                              ',T60,1PE10.2,/
     1       6X,'GAMMA                              ',T60,1PE10.2)
C
  330 FORMAT(6X,'USER-SPECIFIED MASS TRANSFER COEFFICIENT (CM/S)',
     1       T60,1PE10.2)
  331 FORMAT(6X,'USER-SPECIFIED PARTITION COEFFICIENT ',T60,1PE10.2)
  335 FORMAT(6X,'POLYMER POSITION',T60,'  HORIZONTAL')
  340 FORMAT(6X,'POLYMER POSITION',T60,'  VERTICAL  ')
  345 FORMAT(6X,'POLYMER LOCATION',T60,'  INDOORS   ')
  350 FORMAT(6X,'POLYMER LOCATION',T60,'  OUTDOORS  ')
  355 FORMAT(6X,'AIRFLOW VELOCITY(CM/S)',T60,1PE10.2)
  360 FORMAT(6X,'POLYMER PLATE SURFACE LENGTH (CM)',T60,1PE10.2)
  365 FORMAT(6X,'POLYMER PLATE HEIGHT (CM)',T60,1PE10.2)
  370 FORMAT(6X,'WATER FLOW VELOCITY (CM/S)',T60,1PE10.2)
  375 FORMAT(6X,'WATER FLOW IS   ',T60,'  THROUGH PIPE')
  380 FORMAT(6X,'WATER FLOW IS   ',T60,'  OVER PLATE  ')
  390 FORMAT(6X,'POLYMER PIPE DIAMETER (CM)',T60,1PE10.2)
  395 FORMAT(6X,'ESTD. MASS TRANSFER COEFFICIENT (CM/S)',T60,1PE10.2)
C
      GO TO 999
850   WRITE(IW,702)WATVEL
702   FORMAT(/6X,'THE WATER FLOW VELOCITY GIVEN IS ',1PE10.2,' CM/S',
     1 /6X,'WATER CAN BE CONSIDERED ESSENTIALLY STAGNANT AT VELOCITIES',
     2 /6X,'LESS THAN 10 CM/S. MODIFY INPUT TO EXECUTE PROGRAM.'
     3 /6X,'RECOMMENDATION: RE-DEFINE EXTERNAL PHASE AS "SOLID".')
      GO TO 999
 900  WRITE(IW,801)
```

```
  801  FORMAT(/6X,'PROGRAM STOP. INPUT ERROR. FOR A USER-SPECIFIED'
     1        /6X,'POLYMER CLASS, THE DIFFUSION COEFFICIENT OF    '
     2        /6X,'ADDITIVE IN POLYMER MUST BE A NON-ZERO VALUE.  ')
  999  STOP
       END
C        File DOMBFF
C      REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C        Domain BFF:  finite slab in contact with a finite bath.
C         Boundary layer resistance.  Returns fractional migration assuming
C         the solute is initially uniformly distributed in the solid and
C         the initial fluid concentration is zero.
C        Requires subprogram ROOTBFF
C        Note that TAU   = Dpt/L2
C                  R     = kKL/Dp
C                  ALPHA = KV/AL
         DOUBLE PRECISION FUNCTION DOMBFF(TAU,ALPHA,R)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/PARAM3/B(1000),NROOT,ALAST,RLAST,NRTBFFMAX
       COMMON/IO/IR,IW
      IF ((ALAST.NE.ALPHA).OR.(RLAST.NE.R)) NROOT=0
         EPS = 1.d-8
         IEPS = 0
         SUM = 1.d0
         I = -1
10       I = I + 1
         IF (I.EQ.NRTBFFMAX) GOTO 30
         IF (I.LT.NROOT) GOTO 20
           J = I+1
           B(J) = ROOTBFF(I,ALPHA,R)
           NROOT = J
20       BN = B(J)
         SIN1 = SIN(BN)
         COS1 = COS(BN)
         EN   = (R*COS1 - BN*SIN1)
         D1   = EN*EN*ALPHA/(R*R)
         D2   = 0.5d0
         IF (I.NE.0) D2 = SIN1*COS1/(2.d0*BN)
         DEN  = 0.5d0 + D1 + D2
         T1 = 1.d0
         IF (I.NE.0) T1 = SIN1/BN
         T2 = 0.d0
         T3 = -BN*BN*TAU
         IF (T3.GT.-120.d0) T2 = EXP(T3)
         TERM = T1*T1*T2/DEN
         SUM = SUM - TERM
         RAT = ABS(TERM/SUM)
         IF (RAT.LT.EPS) IEPS = IEPS + 1
         IF (IEPS.LT.3) GOTO 10
         GOTO 40
30       write(iw,101)
101      FORMAT(/6X,'NOTE: GIVEN THE ABOVE INPUT AND THE ESTIMATED'
     1   /6X,'TAU VALUE, MIGRATION IS VERY CLOSE TO ZERO {<1.0E-04}.'
     2   //6X,'RECOMMENDATION: INCREASE EXPOSURE TIME, INCREASE      '
     3   /6X,'MIGRANT-POLYMER DIFFUSION COEFFICIENT, OR REDUCE POLYMER'
     4   /6X,'THICKNESS, AND RE-RUN SCENARIO.'/)
```

```
40       DOMBFF = SUM
       WRITE(IW,100)DOMBFF
100    FORMAT(6X,'FRACTION MIGRATED                ',T60,1PE10.2)
         RETURN
         END
C        File ROOTBFF
C      REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C        Finds roots of the equation
C          Tan(BN) = R*BN/(BN2-N)
C        or
C          Cot(BN) = (BN2-N)/(R*BN)
C        where
C          I   = number of desired root
C          R   = kKL/Dp
C          ALPHA = KV/AL
C          N   = R/ALPHA
         DOUBLE PRECISION FUNCTION ROOTBFF(I,ALPHA,R)
      IMPLICIT REAL*8 (A-H,O-Z)
         REAL N
         IF (I.LE.0) GOTO 39
         EPS1 = 1.d-3
         EPS2 = 1.d-12
         RI    = FLOAT(I)
         PI    = 2.d0*ACOS(0.d0)
         RIPI = RI*PI
         N     = R/ALPHA
         SRN   = SQRT(N)
         REPS1= (PI/2.d0)-EPS1
         ISTEP= 0
         ITAN = 0
         FLAG = 1.d0
         CTR   =  (RI-0.5d0)*PI
         IF(RIPI.GT.SRN) FLAG = -1.d0
         BN    = CTR + FLAG*REPS1
10       BN2   = BN*BN
         IF(ITAN.EQ.1) GOTO 15
         COT1 = 1.d0/TAN(BN)
         CSC1 = 1.d0/SIN(BN)
         CSC2 = CSC1*CSC1
         RES   = COT1 + (N-BN2)/(R*BN)
         DR    =-CSC2 - (BN2+N)/(R*BN2)
         DDR   = 2.d0*CSC2*COT1 + 2.d0*N/(R*BN2*BN)
         GOTO 18
15       TAN1 = TAN(BN)
         SEC1 = 1.d0/COS(BN)
         SEC2 = SEC1*SEC1
         BN2N = BN2-N
         RES   = TAN1 - R*BN/BN2N
         DR    = SEC2 + R*(BN2+N)/(BN2N*BN2N)
         DDR   = 2.d0*SEC2*TAN1 - 2.d0*R*BN*(BN2+3.d0*N)/(BN2N*BN2N*BN2N)
18       BNN   = BN - (RES/DR)
         ISTEP= ISTEP + 1
         IF ((RES*FLAG.GT.0.).AND.(ISTEP.EQ.1)) GOTO 30
         IF (ABS(BNN-BN).LT.EPS2) GOTO 40
         IF ((FLAG*DDR).GT.0.d0) GOTO 20
```

```
      IF (ABS(BNN-CTR).GT.PI/2.d0)  GOTO 20
      BN    = BNN
      GOTO 10
C     Inflection point, start search from other asymptote
20    FLAG = -1.d0*FLAG
      BN    = CTR + FLAG*REPS1
      IF (ITAN.EQ.1) BN = CTR - FLAG*REPS1
      ISTEP = 0
      GOTO 10
C     Root within EPS1 of asymptote;  solve reciprocal (tan) equation
30    CTR   = RIPI
      IF (FLAG.LT.0.d0) CTR = CTR-PI
      REPS1= EPS1
      ITAN = 1
      BN    = CTR - FLAG*REPS1
      GOTO 10
39    BNN   = 0.d0
40    ROOTBFF = BNN
      RETURN
      END
```

```
C    PROGRAM NAME: EQ20               KM DILWALI 0990

C  THIS PROGRAM MODULE SERVES AS THE I/O SHELL TO
C  COMPUTE THE FRACTION OF ADDITIVE MIGRATION
C  ASSUMING THE FOLLOWING CONDITIONS:  (BFI)
C  - BOUNDARY LAYER RESISTANCE EFFECTS CONSIDERED
C  - POLYMER PHASE THICKNESS MUST BE CONSIDERED FINITE
C  - EXTRACTANT PHASE INFINITE;I.E. LIMITED PARTITIONING EFFECTS*
C * NOTE: PART COEFF. STILL REQD FOR CALCN OF NON-DIMNAL MASS
C        TRANSFER PARAMETER GAMMA. CAN BE USER-SPECD OR CALCD.
C  INPUT REQUIREMENTS:
C        IPOLY : 01-06 POLYMER TYPE                              -
C          01= SILICONE RUBBER   04=HDPE
C          02= NATURAL  RUBBER   05=POLYSTYRENE
C          03= LDPE              06=PVC(UNPLASTICIZED)
C        XMW    : MOLECULAR WEIGHT OF MIGRANT                   G/MOL
C        DP     : DIFFUSION COEFF. OF ADDITIVE IN POLYMER       CM2/S
C        THRS   : TIME                                          HRS
C        XL     : POLYMER FILM THICKNESS                        CM
C        NSIDE  : 01=ONE-SIDED , 02=TWO-SIDED DIFFUSION          -
C        CINIT  : INIT MIGRANT CONC. IN POLYMER G/CM3
C      > NEXT   : EXT PHASE TYPE 01=AIR, 02=H2O
C        PC     : PARTITION COEFF; 0 IF UNKNOWN
C        CSATP  : SAT CONC. OF MIGR IN POLYMER OR 0.,G/CM3
C        CSATA  : SAT CONC. OF MIGR IN AIR     OR 0.,G/CM3
C        CSATW  : SAT CONC. OF MIGR IN WATER   OR 0.,G/CM3
C        CSATE  : SAT CONC. OF MIGR IN SOLID(N/A)    G/CM3
C      > VPMT   : MIGR VAPOR PRESSURE, TORR FOR CSATA , RK CALCS
C        TMM    : MIGR MELT TEMP DEG C     FOR CSATW CALC
C        XKOWM  : MIGR OCT-H2O PART COEFF FOR CSATW CALC
C        RK     : MASS TRANSFER COEFF CM/S; 0. IF UNKNOWN
C        KHORZ  : AIR: POLYMER POSITION 1=HORIZONTAL, 2=VERTICAL
C        NPLC   : AIR: POLYMER LOCN 1=INDOORS, 2=OUTDOORS
C        RSURFA: AIR: SURFACE LENGTH ,CM
C        AIRVEL: AIR: AIRFLOW VELOCITY, CM/S
C        HEIGHT: AIR: SURFACE HEIGHT FOR VERTICAL POSITION, CM
C        WATVEL: H2O: WATER FLOW VELOCITY , CM/S
C        IRWAT  : H2O: 01=FLOW THRU PIPE; 02=FLOW OVER PLATE
C        RSURFW: H2O: FOR IRWAT=2,PLATE LENGTH, CM
C        DPIPE  : H2O: FOR IRWAT=1,PIPE  DIAMETER, CM
C*******************
      IMPLICIT REAL*8 (A-H,O-Z)
      TAU = 0.0
      GAMMA = 0.0
      NRTBFIMAX = 1000
C*******************
      COMMON/PARAM2/B(1000),NROOT,RLAST,NRTBFIMAX
      COMMON/IO/IR,IW
      CHARACTER*2 TITLE(36)
      IR = 5
```

```
      IW = 6
      OPEN(IR,FILE='EQ20.INP')
      OPEN(IW,FILE='EQ20.LIS',STATUS='UNKNOWN')
C   READ INPUT DATA
      READ(IR,'(36A2)')TITLE
      READ(IR,'(I2)')IPOLY
      READ(IR,'(F10.2)')XMW
      READ(IR,'(F10.2)')DP
      READ(IR,'(F10.2)')THRS
      READ(IR,'(F10.2)')XL
      READ(IR,'(I2)')NSIDE
      READ(IR,'(F10.2)')CSATP
      READ(IR,'(I2)')NEXT
      READ(IR,'(F10.2)')VEP
      READ(IR,'(F10.2)')SAP
      READ(IR,'(F10.2)')PC
      READ(IR,'(F10.2)')CINIT
      READ(IR,'(F10.2)')CSATA
      READ(IR,'(F10.2)')CSATW
      READ(IR,'(F10.2)')VPMT
      READ(IR,'(F10.2)')TMM
      READ(IR,'(F10.2)')XKOWM
      READ(IR,'(F10.2)')RK
      READ(IR,'(I2)')KHORZ
      READ(IR,'(I2)')NPLC
      READ(IR,'(F10.2)')RSURFA
      READ(IR,'(F10.2)')AIRVEL
      READ(IR,'(F10.2)')HEIGHT
      READ(IR,'(F10.2)')WATVEL
      READ(IR,'(I2)')IRWAT
      READ(IR,'(F10.2)')RSURFW
      READ(IR,'(F10.2)')DPIPE
C   INITIALIZE
      IF(RK.NE.0..AND.WATVEL.EQ.0.)WATVEL=10.
      XLEN = XL
      IF(NSIDE.EQ.2)XLEN=XL/2.
      TSEC = THRS*3600.
C    ECHO INPUT
      WRITE(IW,201)TITLE
      WRITE(IW,210)
      IF(IPOLY.EQ.1)WRITE(IW,211)
      IF(IPOLY.EQ.2)WRITE(IW,212)
      IF(IPOLY.EQ.3)WRITE(IW,213)
      IF(IPOLY.EQ.4)WRITE(IW,214)
      IF(IPOLY.EQ.5)WRITE(IW,215)
      IF(IPOLY.EQ.6)WRITE(IW,216)
      IF(XMW.NE.0.)WRITE(IW,220)XMW
      WRITE(IW,221)THRS,XL
      IF(DP.NE.0.)WRITE(IW,225)DP
      IF(NSIDE.EQ.1)WRITE(IW,230)
      IF(NSIDE.EQ.2)WRITE(IW,235)
      IF(NEXT.EQ.1)WRITE(IW,260)
      IF(NEXT.EQ.2)WRITE(IW,265)
      IF(PC.NE.0.)WRITE(IW,331)PC
        IF(PC.NE.0.)GO TO 15
```

```
      IF(CSATP.NE.0.)WRITE(IW,266)CSATP
      IF(CSATP.EQ.0.)WRITE(IW,267)CINIT
      IF(NEXT.EQ.1.AND.CSATA.NE.0.)WRITE(IW,268)CSATA
      IF(NEXT.EQ.2.AND.CSATW.NE.0.)WRITE(IW,269)CSATW
      IF(NEXT.EQ.1.AND.CSATA.EQ.0.)WRITE(IW,270)VPMT
      IF(NEXT.EQ.2.AND.CSATW.EQ.0.)WRITE(IW,275)TMM,XKOWM
 15   IF(RK.NE.0.)WRITE(IW,330)RK
        IF(RK.NE.0.)GO TO 30
        IF(NEXT.EQ.2)GO TO 20
      IF(KHORZ.EQ.1)WRITE(IW,335)
      IF(KHORZ.EQ.2)WRITE(IW,340)
      IF(NPLC.EQ.1)WRITE(IW,345)
      IF(NPLC.EQ.2)WRITE(IW,350)
      WRITE(IW,355)AIRVEL
      IF(KHORZ.EQ.1)WRITE(IW,360)RSURFA
      IF(KHORZ.EQ.2)WRITE(IW,365)HEIGHT
      GO TO 30
 20   WRITE(IW,370)WATVEL
      IF(IRWAT.EQ.1)WRITE(IW,375)
      IF(IRWAT.EQ.2)WRITE(IW,380)
      IF(IRWAT.EQ.1)WRITE(IW,390)DPIPE
      IF(IRWAT.EQ.2)WRITE(IW,360)RSURFW
 30   CONTINUE
C   LIST OUTPUT
      WRITE(IW,310)
C   CALC DIFFUSION COEFF IN POLYMER (DP) IF NOT USER-SPECIFIED
      IF(IPOLY.EQ.0.AND.DP.EQ.0.)GO TO 900
      IF(DP.EQ.0.)CALL DPCALC(IPOLY,XMW,DP)
C   CALC PARTITION COEFF IF NOT USER-SPECIFIED
      VPM = VPMT/760.
      IF(PC.EQ.0.)CALL KCALC(NEXT,CSATP,CSATA,CSATW,CINIT,CSATE,
     1                        XMW,VPM,TMM,XKOWM,PC)
C   CALC MASS TRANSFER COEFF IF NOT USER-SPECIFIED
      IF((NEXT.EQ.2).AND.(WATVEL.LT.10.))GO TO 850
      IF(RK.EQ.0.)CALL RKCALC(NEXT,KHORZ,NPLC,AIRVEL,RSURFA,VPM,
     1 HEIGHT,WATVEL,IRWAT,RSURFW,DPIPE,XMW,RKO)
      IF(RK.EQ.0.)WRITE(IW,395)RKO
      IF(RK.EQ.0.)RK = RKO
C CALC NONDIMENSIONAL PARAMETERS
      TAU = DP*TSEC/XLEN/XLEN
      GAMMA = RK*PC*XLEN/DP
      WRITE(IW,320)TAU,GAMMA
      FRMIG = DOMBFI(TAU,GAMMA)
 201  FORMAT(6X,36A2//)
 210  FORMAT(6X,'** INPUT PARAMETERS **'/)
 211  FORMAT(6X,'POLYMER CATEGORY:',T60,'  SILICONE RUBBER ')
 212  FORMAT(6X,'POLYMER CATEGORY:',T60,'  NATURAL  RUBBER ')
 213  FORMAT(6X,'POLYMER CATEGORY:',T60,'  LDPE            ')
 214  FORMAT(6X,'POLYMER CATEGORY:',T60,'  HDPE            ')
 215  FORMAT(6X,'POLYMER CATEGORY:',T60,'  POLYSTYRENE     ')
 216  FORMAT(6X,'POLYMER CATEGORY:',T60,'  PVC(UNPLASTICIZED)')
 220  FORMAT(6X,'MOLECULAR WEIGHT OF ADDITIVE   ',T60,1PE10.2)
 221  FORMAT(6X,'TIME  (HRS)      ',T60,1PE10.2/
     1        6X,'TOTAL POLYMER SHEET THICKNESS  (CM)',T60,1PE10.2)
 225  FORMAT(6X,'USER-SPECIFIED DIFFUSION COEFFICIENT(CM2/S)',
```

```
     1       T60,1PE10.2)
 230  FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  ONE-SIDED')
 235  FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  TWO-SIDED')
C
 260  FORMAT(6X,'EXTERNAL PHASE IS         ',T60,'  AIR')
 265  FORMAT(6X,'EXTERNAL PHASE IS         ',T60,'  WATER')
 266  FORMAT(6X,'SATURATION CONC. IN POLYMER (G/CM3)',T60,1PE10.2)
 267  FORMAT(6X,'LET SATUR. CONC. IN POLY = INIT CONC. (G/CM3)',
     1       T60,1PE10.2)
 268  FORMAT(6X,'SATURATION CONC. IN AIR     (G/CM3)',T60,1PE10.2)
 269  FORMAT(6X,'SATURATION CONC. IN WATER   (G/CM3)',T60,1PE10.2)
 270  FORMAT(6X,'MIGRANT VAPOR PRESSURE (TORR)  ',T60,1PE10.2)
 275  FORMAT(6X,'MIGRANT MELT TEMP (DEG C)',T60,1PE10.2/
     2       6X,'MIGRANT OCTANOL-WATER PART. COEFF.',T60,1PE10.2)
C
 310  FORMAT(//6X,'** OUTPUT VALUES (MODULE: EQUATION 20) **'/)
 320  FORMAT(6X,'TAU                                ',T60,1PE10.2,/
     1       6X,'GAMMA                              ',T60,1PE10.2)
 330  FORMAT(6X,'USER-SPECIFIED MASS TRANSFER COEFFICIENT (CM/S)',
     1       T60,1PE10.2)
 331  FORMAT(6X,'USER-SPECIFIED PARTITION COEFFICIENT ',T60,1PE10.2)
 335  FORMAT(6X,'POLYMER POSITION',T60,'  HORIZONTAL')
 340  FORMAT(6X,'POLYMER POSITION',T60,'  VERTICAL  ')
 345  FORMAT(6X,'POLYMER LOCATION',T60,'  INDOORS   ')
 350  FORMAT(6X,'POLYMER LOCATION',T60,'  OUTDOORS  ')
 355  FORMAT(6X,'AIRFLOW VELOCITY(CM/S)',T60,1PE10.2)
 360  FORMAT(6X,'POLYMER PLATE SURFACE LENGTH (CM)',T60,1PE10.2)
 365  FORMAT(6X,'POLYMER PLATE HEIGHT (CM)',T60,1PE10.2)
 370  FORMAT(6X,'WATER FLOW VELOCITY (CM/S)',T60,1PE10.2)
 375  FORMAT(6X,'WATER FLOW IS   ',T60,'  THROUGH PIPE')
 380  FORMAT(6X,'WATER FLOW IS   ',T60,'  OVER PLATE  ')
 390  FORMAT(6X,'POLYMER PIPE DIAMETER (CM)',T60,1PE10.2)
 395  FORMAT(6X,'ESTD. MASS TRANSFER COEFFICIENT (CM/S)',T60,1PE10.2)
C
      GO TO 999
850   WRITE(IW,702)WATVEL
702   FORMAT(/6X,'THE WATER FLOW VELOCITY GIVEN IS ',1PE10.2,' CM/S',
     1 /6X,'WATER CAN BE CONSIDERED ESSENTIALLY STAGNANT AT VELOCITIES',
     2 /6X,'LESS THAN 10 CM/S. MODIFY INPUT TO EXECUTE PROGRAM.'
     3 /6X,'RECOMMENDATION: RE-DEFINE EXTERNAL PHASE AS "SOLID".')
      GO TO 999
900   WRITE(IW,801)
801   FORMAT(/6X,'PROGRAM STOP. INPUT ERROR. FOR A USER-SPECIFIED'
     1      /6X,'POLYMER CLASS, THE DIFFUSION COEFFICIENT OF    '
     2      /6X,'ADDITIVE IN POLYMER MUST BE A NON-ZERO VALUE.  ')
 999  STOP
      END
C       File DOMBFI                                        0990
C     REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C       Domain BFI: finite slab in contact with an infinite bath.
C        Boundary layer resistance.  Returns fractional migration assuming
C        the fluid phase concentration is initially zero and the solute is
C        uniformly distributed in the slab.
C       Requires subprogram ROOTBFI
C       Note that R  = kKL/Dp
```

```
C                Tau = Dpt/L2
        DOUBLE PRECISION FUNCTION DOMBFI (TAU,R)
      IMPLICIT REAL*8 (A-H,O-Z)
        COMMON/PARAM2/B(1000),NROOT,RLAST,NRTBFIMAX
       COMMON/IO/IR,IW
      IF (RLAST.NE.R) NROOT=0
        R2 = R*R
        EPS1 = 1.d-8
        SUM = 1.d0
        N = 0
10      N = N + 1
        IF (N.EQ.NRTBFIMAX) GOTO 30
        IF (N.LE.NROOT) GOTO 20
          B(N) = ROOTBFI(N,R)
          NROOT = N
20      GN = B(N)
        GN2 = GN*GN
        E1 = 0.d0
        IF ((GN2*TAU).LT.120.) E1 = EXP(-GN2*TAU)
        TERM = 2.d0*R2*E1/(GN2*(GN2+R2+R))
        SUM = SUM - TERM
        IF (ABS(TERM/SUM).GT.EPS1) GOTO 10
        GOTO 40
30      write(iw,101)
101     FORMAT(/6X,'NOTE: GIVEN THE ABOVE INPUT AND THE ESTIMATED'
     1  /6X,'TAU VALUE, MIGRATION IS VERY CLOSE TO ZERO {<1.0E-04}.'
     2  //6X,'RECOMMENDATION: INCREASE EXPOSURE TIME, INCREASE     '
     3  /6X,'MIGRANT-POLYMER DIFFUSION COEFFICIENT, OR REDUCE POLYMER'
     4  /6X,'THICKNESS, AND RE-RUN SCENARIO.'/)
40      DOMBFI = SUM
      WRITE(IW,100)DOMBFI
100   FORMAT(6X,'FRACTION MIGRATED                 ',T60,1PE10.2)
        RETURN
        END
C       File ROOTBFI                                       0990
C     REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C       Returns roots of the equation
C         tan(GN) = R/GN       or       cot(GN) = GN/R
C       where R is a constant
        DOUBLE PRECISION FUNCTION ROOTBFI (N,R)
     IMPLICIT REAL*8 (A-H,O-Z)
        IF (N.LE.0) GOTO 29
        EPS1 = 1.d-3
        EPS2 = 1.d-12
        RN   = FLOAT(N)
        PI   = 2.d0*ACOS(0.d0)
        RNPI1= (RN-1.d0)*PI
        ISTEP= 0
        GN   = RNPI1 + EPS1
10      COT1 = 1.d0/TAN(GN)
        CSC1 = 1.d0/SIN(GN)
        CSC2 = CSC1*CSC1
        RES  = COT1 - GN/R
        DRES = -CSC2 - 1.d0/R
        GNN  = GN - (RES/DRES)
```

```
      ISTEP= ISTEP + 1
      IF ((GNN.LT.GN).AND.(ISTEP.EQ.1)) GOTO 20
      IF (ABS(GNN-GN).LT.EPS2) GOTO 30
      GN   = GNN
      GOTO 10
C     Root close to asymptote of cot; use tan form...
20    TAN1 = TAN(GN)
      SEC1 = 1.d0/COS(GN)
      SEC2 = SEC1*SEC1
      RES  = TAN1 - R/GN
      DRES = SEC2 + R/(GN*GN)
      GNN  = GN - (RES/DRES)
      IF (ABS(GNN-GN).LT.EPS2) GOTO 30
      GN   = GNN
      GOTO 20
29    GNN = 0.d0
30    ROOTBFI = GNN
      RETURN
      END
```

```
C    PROGRAM NAME: EQ23                  KM DILWALI 0990

C  THIS PROGRAM MODULE SERVES AS THE I/O SHELL TO
C  COMPUTE THE FRACTION OF ADDITIVE MIGRATION
C  ASSUMING THE FOLLOWING CONDITIONS:  (MFI)
C  - NO BOUNDARY LAYER RESISTANCE;I.E INFINITE WELL-STIRRED BATH
C  - POLYMER PHASE THICKNESS MUST BE CONSIDERED FINITE
C  - EXTRACTANT PHASE INFINITE;I.E. PARTITIONING EFFECTS NEGL.
C  INPUT REQUIREMENTS:
C        IPOLY : 00-06 POLYMER TYPE                               -
C          01= SILICONE RUBBER   04=HDPE
C          02= NATURAL  RUBBER   05=POLYSTYRENE
C          03= LDPE              06=PVC(UNPLASTICIZED)
C        XMW   : MOLECULAR WEIGHT OF MIGRANT                      G/MOL
C        DP    : DIFFUSION COEFF. OF ADDITIVE IN POLYMER          CM2/S
C        THRS  : TIME                                             HRS
C        XL    : POLYMER FILM THICKNESS                           CM
C        NSIDE : 01=ONE-SIDED , 02=TWO-SIDED DIFFUSION            -
      COMMON/IO/IR,IW
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*2 TITLE(36)
      IR = 5
      IW = 6
      OPEN(IR,FILE='EQ23.INP')
      OPEN(IW,FILE='EQ23.LIS',STATUS='UNKNOWN')
C  READ INPUT DATA
      READ(IR,'(36A2)')TITLE
      READ(IR,'(I2)')IPOLY
      READ(IR,'(F10.2)')XMW
      READ(IR,'(F10.2)')DP
      READ(IR,'(F10.2)')THRS
      READ(IR,'(F10.2)')XL
      READ(IR,'(I2)')NSIDE
C  INITIALIZE
      XLEN = XL
      IF(NSIDE.EQ.2)XLEN=XL/2.
      TSEC = THRS*3600.
C   ECHO INPUT
      WRITE(IW,201)TITLE
      WRITE(IW,210)
      IF(IPOLY.EQ.1)WRITE(IW,211)
      IF(IPOLY.EQ.2)WRITE(IW,212)
      IF(IPOLY.EQ.3)WRITE(IW,213)
      IF(IPOLY.EQ.4)WRITE(IW,214)
      IF(IPOLY.EQ.5)WRITE(IW,215)
      IF(IPOLY.EQ.6)WRITE(IW,216)
      IF(XMW.NE.0.)WRITE(IW,220)XMW
      WRITE(IW,221)THRS,XL
      IF(DP.NE.0.)WRITE(IW,225)DP
      IF(NSIDE.EQ.1)WRITE(IW,230)
```

```
      IF(NSIDE.EQ.2)WRITE(IW,235)
C   LIST OUTPUT
      WRITE(IW,310)
C CALC NONDIMENSIONAL PARAMETERS
      IF(IPOLY.EQ.0.AND.DP.EQ.0.)GO TO 900
      IF(DP.EQ.0.)CALL DPCALC(IPOLY,XMW,DP)
      TAU = DP*TSEC/XLEN/XLEN
      WRITE(IW,320)TAU
      FRMIG = DOMMFI(TAU)
 201  FORMAT(6X,36A2//)
 210  FORMAT(6X,'** INPUT PARAMETERS **'/)
 211  FORMAT(6X,'POLYMER CATEGORY:',T60,'  SILICONE RUBBER ')
 212  FORMAT(6X,'POLYMER CATEGORY:',T60,'  NATURAL  RUBBER ')
 213  FORMAT(6X,'POLYMER CATEGORY:',T60,'  LDPE            ')
 214  FORMAT(6X,'POLYMER CATEGORY:',T60,'  HDPE            ')
 215  FORMAT(6X,'POLYMER CATEGORY:',T60,'  POLYSTYRENE     ')
 216  FORMAT(6X,'POLYMER CATEGORY:',T60,'  PVC(UNPLASTICIZED)')
 220  FORMAT(6X,'MOLECULAR WEIGHT OF ADDITIVE   ',T60,1PE10.2)
 221  FORMAT(6X,'TIME  (HRS)      ',T60,1PE10.2/
     1       6X,'TOTAL POLYMER SHEET THICKNESS  (CM)',T60,1PE10.2)
 225  FORMAT(6X,'USER-SPECIFIED DIFFUSION COEFFICIENT (CM2/S)',
     1       T60,1PE10.2)
 230  FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  ONE-SIDED')
 235  FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  TWO-SIDED')
 310  FORMAT(//6X,'** OUTPUT VALUES (MODULE: EQUATION 23) **'/)
 320  FORMAT(6X,'TAU                         ',T60,1PE10.2)
      GO TO 999
 900  WRITE(IW,801)
 801  FORMAT(/6X,'PROGRAM STOP. INPUT ERROR. FOR A USER-SPECIFIED'
     1       /6X,'POLYMER CLASS, THE DIFFUSION COEFFICIENT OF    '
     2       /6X,'ADDITIVE IN POLYMER MUST BE A NON-ZERO VALUE.  ')
 999  STOP
      END
C       File DOMMFI                                       0990
C     REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C       Domain MFI: Finite slab in contact with an infinite, well-stirred
C        bath.  Returns fractional migration assuming the initial solute
C        concentration in the bath is zero and the slab distribution is
C        uniform.
C       Note that TAU = Dpt/L2
        DOUBLE PRECISION FUNCTION DOMMFI(TAU)
     IMPLICIT REAL*8 (A-H,O-Z)
        DOUBLE PRECISION QN
      COMMON/IO/IR,IW
        EPS = 1.0D-8
        PI = 3.1415926535898d0
        N = 0
        NMAX = 1000
        SUM = 1.d0
10      N = N + 1
        IF(N.GT.NMAX)GO TO 99
        RN = FLOAT(N)
C       QN = (2.d0*RN + 1.d0)*PI/2.d0
        QN = (2.d0*RN - 1.d0)*PI/2.d0
        QN2 = QN*QN
```

```
        TERM = 2.d0*EXP(-QN2*TAU)/QN2
        SUM = SUM - TERM
        RAT = ABS(TERM/SUM)
        IF (RAT.GT.EPS) GOTO 10
        DOMMFI = SUM
        WRITE(IW,100)DOMMFI
100     FORMAT(6X,'FRACTION MIGRATED     ',T60,1PE10.2)
        RETURN
 99     WRITE(IW,101)
        DOMMFI = SUM
        RETURN
101     FORMAT(/6X,'NOTE: GIVEN THE ABOVE INPUT AND THE ESTIMATED'
     1  /6X,'TAU VALUE, MIGRATION IS VERY CLOSE TO ZERO (<1.0E-04).'
     2  //6X,'RECOMMENDATION: INCREASE EXPOSURE TIME, INCREASE      '
     3  /6X,'MIGRANT-POLYMER DIFFUSION COEFFICIENT, OR REDUCE POLYMER'
     4  /6X,'THICKNESS, AND RE-RUN SCENARIO.'/)
        END
```

```
C    PROGRAM NAME: EQ26                KM DILWALI 0990

C  THIS PROGRAM MODULE SERVES AS THE I/O SHELL TO
C  COMPUTE THE FRACTION OF ADDITIVE MIGRATION
C  ASSUMING THE FOLLOWING CONDITIONS:  (MFF)
C  - NO BOUNDARY LAYER RESISTANCE;I.E INFINITE WELL-STIRRED BATH
C  - POLYMER PHASE THICKNESS MUST BE CONSIDERED FINITE
C  - EXTRACTANT PHASE FINITE;I.E. PARTITIONING EFFECTS CONSIDERED
C  INPUT REQUIREMENTS:
C        IPOLY : 01-06 POLYMER TYPE                               -
C          01= SILICONE RUBBER   04=HDPE
C          02= NATURAL  RUBBER   05=POLYSTYRENE
C          03= LDPE              06=PVC(UNPLASTICIZED)
C        XMW   : MOLECULAR WEIGHT OF MIGRANT                    G/MOL
C        DP    : DIFFUSION COEFF. OF ADDITIVE IN POLYMER  CM2/S
C        THRS  : TIME                                           HRS
C        XL    : POLYMER SHEET THICKNESS                        CM
C        NSIDE : 01=ONE-SIDED , 02=TWO-SIDED DIFFUSION          -
C        CINIT : INIT MIGRANT CONCN IN POLYMER                  G/CM3
C                (ONLY REQUIRED IF CSATP NOT AVAILABLE)
C        NEXT  : EXT PHASE TYPE 01=AIR, 02=H2O , 03=SOLID(N/A)
C        VEP   : VOL OF EXT PHASE      ,M3
C        SAP   : EXPOSED SURFACE AREA ,CM2
C        PC    : PARTITION COEFF; 0 IF UNKNOWN
C        CSATP : SAT CONCN OF MIGR IN POLYMER OR 0.,G/CM3
C        CSATA : SAT CONCN OF MIGR IN AIR     OR 0.,G/CM3
C        CSATW : SAT CONCN OF MIGR IN H2O     OR 0.,G/CM3
C        CSATE : SAT CONCN OF MIGR IN SOLID EXT PHASE (N/A),G/CM3
C        VPMT  : MIGR VAPOR PRESSURE,TORR FOR CSATA CALC
C        TMM   : MIGR MELT TEMP DEG C    FOR CSATW CALC
C        XKOWM : MIGR OCT-H2O PART COEFF FOR CSATW CALC
C********************
         IMPLICIT REAL*8 (A-H,O-Z)
         COMMON/PARAM4/B4(1000),NRTMFF,A4LAST,NRTMFFMAX
         TAU = 0.0
         ALPHA = 0.0
         NRTMFFMAX = 1000
C********************
      COMMON/IO/IR,IW
      CHARACTER*2 TITLE(36)
      IR = 5
      IW = 6
      OPEN(IR,FILE='EQ26.INP')
      OPEN(IW,FILE='EQ26.LIS',STATUS='UNKNOWN')
C  READ INPUT DATA
      READ(IR,'(36A2)')TITLE
      READ(IR,'(I2)')IPOLY
      READ(IR,'(F10.2)')XMW
      READ(IR,'(F10.2)')DP
      READ(IR,'(F10.2)')THRS
```

```
      READ(IR,'(F10.2)')XL
      READ(IR,'(I2)')NSIDE
      READ(IR,'(F10.2)')CINIT
      READ(IR,'(I2)')NEXT
      READ(IR,'(F10.2)')VEP
      READ(IR,'(F10.2)')SAP
      READ(IR,'(F10.2)')PC
      READ(IR,'(F10.2)')CSATP
      READ(IR,'(F10.2)')CSATA
      READ(IR,'(F10.2)')CSATW
      READ(IR,'(F10.2)')VPMT
      READ(IR,'(F10.2)')TMM
      READ(IR,'(F10.2)')XKOWM
C  INITIALIZE
      XLEN = XL
      IF(NSIDE.EQ.2)XLEN=XL/2.
      TSEC = THRS*3600.
C   ECHO INPUT
      WRITE(IW,201)TITLE
      WRITE(IW,210)
      IF(IPOLY.EQ.1)WRITE(IW,211)
      IF(IPOLY.EQ.2)WRITE(IW,212)
      IF(IPOLY.EQ.3)WRITE(IW,213)
      IF(IPOLY.EQ.4)WRITE(IW,214)
      IF(IPOLY.EQ.5)WRITE(IW,215)
      IF(IPOLY.EQ.6)WRITE(IW,216)
      IF(XMW.NE.0.)WRITE(IW,220)XMW
      WRITE(IW,221)THRS,XL
      IF(DP.NE.0.)WRITE(IW,225)DP
      IF(NSIDE.EQ.1)WRITE(IW,230)
      IF(NSIDE.EQ.2)WRITE(IW,235)
      WRITE(IW,280)VEP
      WRITE(IW,290)SAP
      IF(NEXT.EQ.1)WRITE(IW,260)
      IF(NEXT.EQ.2)WRITE(IW,265)
      IF(PC.NE.0.)WRITE(IW,331)PC
        IF(PC.NE.0.)GO TO 15
      IF(CSATP.NE.0.)WRITE(IW,266)CSATP
      IF(CSATP.EQ.0.)WRITE(IW,267)CINIT
      IF(NEXT.EQ.1.AND.CSATA.NE.0.)WRITE(IW,268)CSATA
      IF(NEXT.EQ.2.AND.CSATW.NE.0.)WRITE(IW,269)CSATW
      IF(NEXT.EQ.1.AND.CSATA.EQ.0.)WRITE(IW,270)VPMT
      IF(NEXT.EQ.2.AND.CSATW.EQ.0.)WRITE(IW,275)TMM,XKOWM
C   LIST OUTPUT
15    WRITE(IW,310)
C   CALC DIFFUSION COEFF IN POLYMER (DP) IF NOT USER-SPECIFIED
      IF(IPOLY.EQ.0.AND.DP.EQ.0.)GO TO 900
      IF(DP.EQ.0.)CALL DPCALC(IPOLY,XMW,DP)
C   CALC PARTITION COEFF IF NOT USER-SPECIFIED
      VPM = VPMT/760.
      IF(PC.EQ.0.)CALL KCALC(NEXT,CSATP,CSATA,CSATW,CINIT,CSATE,
     1                        XMW,VPM,TMM,XKOWM,PC)
C CALC NONDIMENSIONAL PARAMETERS
      TAU   = DP*TSEC/XLEN/XLEN
      VEPCC = VEP*1.0E6
```

```
      ALPHA = PC*VEPCC/SAP/XLEN
      WRITE(IW,320)TAU,ALPHA
      FRMIG = DOMMFF(TAU,ALPHA)
  201 FORMAT(6X,36A2//)
  210 FORMAT(6X,'** INPUT PARAMETERS **'/)
  211 FORMAT(6X,'POLYMER CATEGORY:',T60,'  SILICONE RUBBER ')
  212 FORMAT(6X,'POLYMER CATEGORY:',T60,'  NATURAL  RUBBER ')
  213 FORMAT(6X,'POLYMER CATEGORY:',T60,'  LDPE            ')
  214 FORMAT(6X,'POLYMER CATEGORY:',T60,'  HDPE            ')
  215 FORMAT(6X,'POLYMER CATEGORY:',T60,'  POLYSTYRENE     ')
  216 FORMAT(6X,'POLYMER CATEGORY:',T60,'  PVC(UNPLASTICIZED)')
  220 FORMAT(6X,'MOLECULAR WEIGHT OF ADDITIVE    ',T60,1PE10.2)
  221 FORMAT(6X,'TIME  (HRS)      ',T60,1PE10.2/
     1       6X,'TOTAL POLYMER SHEET THICKNESS  (CM)',T60,1PE10.2)
  225 FORMAT(6X,'USER-SPECIFIED DIFFUSION COEFFICIENT (CM2/S)',
     1       T60,1PE10.2)
  230 FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  ONE-SIDED')
  235 FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  TWO-SIDED')
C
  260 FORMAT(6X,'EXTERNAL PHASE IS         ',T60,'  AIR')
  265 FORMAT(6X,'EXTERNAL PHASE IS         ',T60,'  WATER')
  266 FORMAT(6X,'SATURATION CONC. OF MIGRANT IN POLYMER (G/CM3)',
     1           T60,1PE10.2)
  267 FORMAT(6X,'LET SATUR. CONC. IN POLYMER = INIT CONC.(G/CM3)',
     1           T60,1PE10.2)
  268 FORMAT(6X,'SATURATION CONC. IN AIR (G/CM3)',T60,1PE10.2)
  269 FORMAT(6X,'SATURATION CONC. IN WATER (G/CM3)',T60,1PE10.2)
  270 FORMAT(6X,'MIGRANT VAPOR PRESSURE (TORR)  ',T60,1PE10.2)
  275 FORMAT(6X,'MIGRANT MELT TEMP (DEG C)',T60,1PE10.2/
     1       6X,'MIGRANT OCTANOL-WATER PART. COEFF.',T60,1PE10.2)
  280 FORMAT(6X,'VOLUME OF EXTERNAL PHASE (M3)',T60,1PE10.2)
  290 FORMAT(6X,'SURFACE AREA OF POLYMER (CM2)',T60,1PE10.2)
C
  310 FORMAT(//6X,'** OUTPUT VALUES (MODULE: EQUATION 26) **'/)
  320 FORMAT(6X,'TAU                             ',T60,1PE10.2,/
     1       6X,'ALPHA                           ',T60,1PE10.2)
  331 FORMAT(6X,'USER-SPECD. PARTITION COEFFICIENT ',T60,1PE10.2)
C
      GO TO 999
  900 WRITE(IW,801)
  801 FORMAT(/6X,'PROGRAM STOP. INPUT ERROR. FOR A USER-SPECIFIED'
     1       /6X,'POLYMER CLASS, THE DIFFUSION COEFFICIENT OF    '
     2       /6X,'ADDITIVE IN POLYMER MUST BE A NON-ZERO VALUE.  ')
  999 STOP
      END
C       File DOMMFF                                          0990
C     REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C       Domain MFF:  Finite slab in contact with a finite, well-stirred bath.
C        Returns fractional migration, assuming that the solute concentration
C        in the bath is initially zero, and the distribution in the slab is
C        uniform.
C       Requires the subprogram ROOTMFF.
C       Note that TAU   = Dpt/L2
C                 ALPHA = KV/AL
C
```

```
      DOUBLE PRECISION FUNCTION DOMMFF(TAU,ALPHA)
      IMPLICIT REAL*8 (A-H,O-Z)
         COMMON/PARAM4/B(1000),NROOT,ALAST,NRTMFFMAX
         DOUBLE PRECISION PN
       COMMON/IO/IR,IW
      IF (ALAST.NE.ALPHA) NROOT=0
         EPS = 1.0d-8
         SUM = ALPHA/(1.d0+ALPHA)
         DEN1 = (1.d0/ALPHA)*(1.d0+1.d0/ALPHA)
         N = 0
 10      N = N + 1
         IF (N.EQ.NRTMFFMAX) GOTO 30
         IF (N.LE.NROOT) GOTO 20
           B(N) = ROOTMFF (N,ALPHA)
           NROOT = N
 20      PN = B(N)
         PN2 = PN*PN
         TERM = 2.d0*EXP(-PN2*TAU)/(PN2+DEN1)
         SUM = SUM-TERM
         RAT = ABS(TERM/SUM)
         IF (RAT.GT.EPS) GOTO 10
         GOTO 40
 30      WRITE(IW,101)
 101     FORMAT(/6X,'NOTE: GIVEN THE ABOVE INPUT AND THE ESTIMATED'
     1   /6X,'TAU VALUE, MIGRATION IS VERY CLOSE TO ZERO (<1.0E-04).'
     2   //6X,'RECOMMENDATION: INCREASE EXPOSURE TIME, INCREASE     '
     3   /6X,'MIGRANT-POLYMER DIFFUSION COEFFICIENT, OR REDUCE POLYMER'
     4   /6X,'THICKNESS, AND RE-RUN SCENARIO.'/)
 40      DOMMFF = SUM
         WRITE(IW,100)DOMMFF
 100     FORMAT(6X,'FRACTION MIGRATED                  ',T60,1PE10.2)
         RETURN
         END
C        ROOTMFF                                              0990
C      REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C        Finds roots of the equation Tan (BN) + ALPHA*BN = 0
C        Requires argument ALPHA = KV/AL and N = root #
         DOUBLE PRECISION FUNCTION ROOTMFF(N,ALPHA)
     IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/IO/IR,IW
         ITR = 2
         IF (N.GT.0) GOTO 3
         BNN = 0.d0
         IF (N.EQ.0) GOTO 45
         GOTO 30
3        EPS1 = 0.1d0
         EPS2 = 1.d-12
         RN = N
         PI = 3.141592653589793d0
         B2 = RN * PI
         IF(ITR.EQ.1)WRITE(IW,*)'RUNTIME ERROR.Upper bound on BN =',B2
5        B1 = (RN-0.5d0)*PI + EPS1
         IF (ITR.EQ.1)WRITE(IW,*)'RUNTIME ERROR.Lower bound on BN =',B1
         BN = B1
10       TAN1 = TAN(BN)
```

```
      COS1 = COS(BN)
      SEC2 = 1.d0/(COS1*COS1)
      R    = TAN1 + ALPHA*BN
      DR   = SEC2 + ALPHA
C     DDR  = 2.d0*TAN1*SEC2
      BNN  = BN - (R/DR)
      IF (ITR.EQ.1) WRITE (IW,*) 'New BN =',BNN,'Residual =',R
      ETEST = ABS(BNN/BN - 1.d0)
      IF (ETEST.LT.EPS2) GOTO 40
      IF (BNN.LT.BN) GOTO 20
      IF (BNN.GT.B2) GOTO 30
      BN = BNN
      GOTO 10
C     Need smaller EPS
20    EPS1 = EPS1 * 0.1d0
      IF (EPS1.GE.(100.d0*EPS2)) GOTO 5
C     Failed
30    WRITE (IW,*) 'RUNTIME ERROR.Root search failed in ROOTMFF. N = 'N
      GOTO 45
C35    WRITE (IW,*) 'RUNTIME ERROR.Root search ends with large residual in ROOTMFF'
C    +,', N =',N
C      GOTO 45
C     Found root
40    IF (ABS(R).GT.1.d0) GOTO 30
45    ROOTMFF = BNN
      RETURN
      END
```

```
C    PROGRAM NAME: EQ29              KM DILWALI 0990

C  THIS PROGRAM MODULE SERVES AS THE I/O SHELL TO
C  COMPUTE THE FRACTION OF ADDITIVE MIGRATION
C  ASSUMING THE FOLLOWING CONDITIONS:  (DFF)
C  - FINITE SLAB(POLYMER) IN CONTACT WITH ANOTHER FINITE SLAB(FOOD)
C  - FOOD PHASE CONCENTRATION INITIALLY IS ZERO
C  - MIGRANT IS UNIFORMLY DISTRIBUTED IN POLYMER
C  INPUT REQUIREMENTS:
C        IPOLY : 01-06 POLYMER TYPE (IF DIFF COEFF UNKNOWN) -
C          01= SILICONE RUBBER   04=HDPE
C          02= NATURAL  RUBBER   05=POLYSTYRENE
C          03= LDPE              06=PVC(UNPLASTICIZED)
C        XMW   : MOLECULAR WEIGHT OF MIGRANT                G/MOL
C        DP    : DIFFUSION COEFF. OF ADDITIVE IN POLYMER   CM2/S
C        THRS  : TIME                                       HRS
C        XL    : POLYMER FILM THICKNESS                     CM
C        NSIDE : 01=ONE-SIDED , 02=TWO-SIDED DIFFUSION      -
C        CINIT : INIT MIGRANT CONCN IN POLYMER G/CM3
C        NEXT  : EXT PHASE TYPE 01=AIR, 02=H2O , 03=SOLID
C        VEP   : VOL OF EXT PHASE      ,M3
C        SAP   : EXPOSED SURFACE AREA ,CM2
C        PC    : PARTITION COEFF; 0 IF UNKNOWN
C        CSATP : SAT CONCN OF MIGR IN POLYMER OR 0.,G/CM3
C        CSATA : SAT CONCN OF MIGR IN AIR     OR 0.,G/CM3
C        CSATW : SAT CONCN OF MIGR IN H2O     OR 0.,G/CM3
C        CSATE : SAT CONCN OF MIGR IN EXT.PHASE    ,G/CM3
C        VPMT  : MIGR VAPOR PRESSURE,TORR FOR CSATA CALC
C        TMM   : MIGR MELT TEMP DEG C     FOR CSATW CALC
C        XKOWM : MIGR OCT-H2O PART COEFF FOR CSATW CALC
C        JEXT  : TYPE OF EXTERNAL PHASE=0(OTHER); 01-06(POLYMER)
C        DEXT  : DIFFUSION COEFF. IN EXTERNAL PHASE, CM2/S
C*******************
      IMPLICIT REAL*8 (A-H,O-Z)
      TAU = 0.
      ALPHA = 0.
      BETA  = 0.
      NRTDFFMAX = 1000
C*******************
      COMMON/PARAM5/B(1000),NROOT,ALAST,BLAST,NRTDFFMAX
      COMMON/IO/IR,IW
      CHARACTER*2 TITLE(36)
      IR = 5
      IW = 6
      OPEN(IR,FILE='EQ29.INP')
      OPEN(IW,FILE='EQ29.LIS',STATUS='UNKNOWN')
C  READ INPUT DATA
      READ(IR,'(36A2)')TITLE
      READ(IR,'(I2)')IPOLY
      READ(IR,'(F10.2)')XMW
```

```
      READ(IR,'(F10.2)')DP
      READ(IR,'(F10.2)')THRS
      READ(IR,'(F10.2)')XL
      READ(IR,'(I2)')NSIDE
      READ(IR,'(F10.2)')CINIT
      READ(IR,'(I2)')NEXT
      READ(IR,'(F10.2)')VEP
      READ(IR,'(F10.2)')SAP
      READ(IR,'(F10.2)')PC
      READ(IR,'(F10.2)')CSATP
      READ(IR,'(F10.2)')CSATA
      READ(IR,'(F10.2)')CSATW
      READ(IR,'(F10.2)')CSATE
      READ(IR,'(F10.2)')VPMT
      READ(IR,'(F10.2)')TMM
      READ(IR,'(F10.2)')XKOWM
      READ(IR,'(I2)')JEXT
      READ(IR,'(F10.2)')DEXT
C  INITIALIZE
      XLEN = XL
      IF(NSIDE.EQ.2)XLEN=XL/2.
      TSEC = THRS*3600.
C   ECHO INPUT
      WRITE(IW,201)TITLE
      WRITE(IW,210)
      IF(IPOLY.EQ.1)WRITE(IW,211)
      IF(IPOLY.EQ.2)WRITE(IW,212)
      IF(IPOLY.EQ.3)WRITE(IW,213)
      IF(IPOLY.EQ.4)WRITE(IW,214)
      IF(IPOLY.EQ.5)WRITE(IW,215)
      IF(IPOLY.EQ.6)WRITE(IW,216)
      IF(XMW.NE.0.)WRITE(IW,220)XMW
      WRITE(IW,221)THRS,XL
      IF(DP.NE.0.)WRITE(IW,225)DP
      IF(DEXT.NE.0.)WRITE(IW,226)DEXT
      IF(NSIDE.EQ.1)WRITE(IW,230)
      IF(NSIDE.EQ.2)WRITE(IW,235)
      WRITE(IW,280)VEP
      WRITE(IW,290)SAP
      IF(NEXT.EQ.1)WRITE(IW,260)
      IF(NEXT.EQ.2)WRITE(IW,265)
      IF(NEXT.EQ.3)WRITE(IW,261)
C     IF(JEXT.EQ.0)WRITE(IW,410)
      IF(PC.NE.0.)WRITE(IW,331)PC
        IF(PC.NE.0.)GO TO 15
      IF(CSATP.NE.0.)WRITE(IW,266)CSATP
      IF(CSATP.EQ.0.)WRITE(IW,267)CINIT
      IF(NEXT.EQ.1.AND.CSATA.NE.0.)WRITE(IW,268)CSATA
      IF(NEXT.EQ.2.AND.CSATW.NE.0.)WRITE(IW,269)CSATW
      IF(NEXT.EQ.1.AND.CSATA.EQ.0.)WRITE(IW,270)VPMT
      IF(NEXT.EQ.2.AND.CSATW.EQ.0.)WRITE(IW,275)TMM,XKOWM
      IF(NEXT.EQ.3)WRITE(IW,285)CSATE
C   LIST OUTPUT
15    WRITE(IW,310)
C   CALC DIFFUSION COEFF IN POLYMER (DP) IF NOT USER-SPECIFIED
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```
      IF(IPOLY.EQ.0.AND.DP.EQ.0.)GO TO 900
      IF(DP.EQ.0.)CALL DPCALC(IPOLY,XMW,DP)
C   CALC PARTITION COEFF IF NOT USER-SPECIFIED
      VPM = VPMT/760.
      IF(PC.EQ.0.)CALL KCALC(NEXT,CSATP,CSATA,CSATW,CINIT,CSATE,
     1                       XMW,VPM,TMM,XKOWM,PC)
C   CALC DIFFUSION COEFF IN EXTERNAL PHASE(DEXT) IF NOT USER-SPECIFIED
C     IF(JEXT.GT.6)GO TO 860
C     IF(JEXT.NE.0.AND.DEXT.EQ.0.)CALL DPCALC(JEXT,XMW,DEXT)
      IF(DEXT.NE.0.)GO TO 20
      CALL DPCALC(JEXT,XMW,DEXT)
      IF(JEXT.EQ.1)WRITE(IW,411)
      IF(JEXT.EQ.2)WRITE(IW,412)
      IF(JEXT.EQ.3)WRITE(IW,413)
      IF(JEXT.EQ.4)WRITE(IW,414)
      IF(JEXT.EQ.5)WRITE(IW,415)
      IF(JEXT.EQ.6)WRITE(IW,416)
C CALC NONDIMENSIONAL PARAMETERS
20    TAU = DP*TSEC/XLEN/XLEN
      VEPCC = VEP*1.0E6
      ALPHA = PC*VEPCC/SAP/XLEN
      BETA = PC*SQRT(DEXT/DP)
      WRITE(IW,320)TAU,ALPHA,BETA
      FRMIG = DOMDFF(TAU,ALPHA,BETA)
 201  FORMAT(6X,36A2//)
 210  FORMAT(6X,'** INPUT PARAMETERS **'/)
 211  FORMAT(6X,'POLYMER CATEGORY:',T60,' SILICONE RUBBER ')
 212  FORMAT(6X,'POLYMER CATEGORY:',T60,' NATURAL  RUBBER ')
 213  FORMAT(6X,'POLYMER CATEGORY:',T60,' LDPE            ')
 214  FORMAT(6X,'POLYMER CATEGORY:',T60,' HDPE            ')
 215  FORMAT(6X,'POLYMER CATEGORY:',T60,' POLYSTYRENE     ')
 216  FORMAT(6X,'POLYMER CATEGORY:',T60,' PVC(UNPLASTICIZED)')
 220  FORMAT(6X,'MOLECULAR WEIGHT OF ADDITIVE   ',T60,1PE10.2)
 221  FORMAT(6X,'TIME  (HRS)      ',T60,1PE10.2/
     1       6X,'TOTAL POLYMER SHEET THICKNESS  (CM)',T60,1PE10.2)
 225  FORMAT(6X,'USER-SPECIFIED DIFF. COEFF. IN POLYMER (CM2/S)',
     1       T60,1PE10.2)
 226  FORMAT(6X,'USER-SPECIFIED DIFF. COEFF. IN EXTERNAL PHASE (CM2/S)',
     1       T60,1PE10.2)
 230  FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,' ONE-SIDED')
 235  FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,' TWO-SIDED')
C
 260  FORMAT(6X,'EXTERNAL PHASE IS        ',T60,' AIR')
 265  FORMAT(6X,'EXTERNAL PHASE IS        ',T60,' WATER')
 261  FORMAT(6X,'EXTERNAL PHASE IS        ',T60,' SOLID')
 266  FORMAT(6X,'SATURATION CONC. OF MIGRANT IN POLYMER (G/CM3)',
     1           T60,1PE10.2)
 267  FORMAT(6X,'LET SATUR. CONC. IN POLYMER = INIT CONC.(G/CM3)',
     1           T60,1PE10.2)
 268  FORMAT(6X,'SATURATION CONC. IN AIR     (G/CM3)',T60,1PE10.2)
 269  FORMAT(6X,'SATURATION CONC. IN WATER   (G/CM3)',T60,1PE10.2)
 270  FORMAT(6X,'MIGRANT VAPOR PRESSURE (TORR)  ',T60,1PE10.2)
 275  FORMAT(6X,'MIGRANT MELT TEMP (DEG C)',T60,1PE10.2/
     1       6X,'MIGRANT OCTANOL-WATER PART. COEFF.',T60,1PE10.2)
 280  FORMAT(6X,'VOLUME OF EXTERNAL PHASE (M3)',T60,1PE10.2)
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 285  FORMAT(6X,'SATUR. CONC. IN EXTERNAL PHASE (G/CM3)',T60,1PE10.2)
 290  FORMAT(6X,'SURFACE AREA OF POLYMER (CM2)',T60,1PE10.2)
C
 310  FORMAT(//6X,'** OUTPUT VALUES (MODULE: EQUATION 29) **'/)
 320  FORMAT(6X,'TAU                              ',T60,1PE10.2,/
     1       6X,'ALPHA                            ',T60,1PE10.2,/
     1       6X,'BETA                             ',T60,1PE10.2)
 331  FORMAT(6X,'USER-SPECIFIED PARTITION COEFFICIENT',T60,1PE10.2)
 410  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  UNDEFINED')
 411  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  SILICONE RUBBER')
 412  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  NATURAL RUBBER')
 413  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  LDPE')
 414  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  HDPE')
 415  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  POLYSTYRENE')
 416  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  PVC(UNPLASTICIZED)')
C
      GO TO 999
 900  WRITE(IW,801)
 801  FORMAT(/6X,'PROGRAM STOP. INPUT ERROR. FOR A USER-SPECIFIED'
     1       /6X,'POLYMER CLASS, THE DIFFUSION COEFFICIENT OF    '
     2       /6X,'ADDITIVE IN POLYMER MUST BE A NON-ZERO VALUE.  ')
 999  STOP
      END
C       File DOMDFF                                            0990
C      REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C       Domain DFF:  finite slab (polymer) in contact with a finite slab (food).
C        Returns fractional migration assuming the solute concentration in
C        the food is initially zero and the concentration in the polymer is
C        initially uniform.
C       Requires subprogram ROOTDFF
C       Note that TAU   = Dpt/L2
C                 BETA  = Ksqrt(De/Dp)
        DOUBLE PRECISION FUNCTION DOMDFF(TAU,ALPHA,BETA)
      IMPLICIT REAL*8 (A-H,O-Z)
        COMMON/PARAM5/B(1000),NROOT,ALAST,BLAST,NRTDFFMAX
       COMMON/IO/IR,IW
        REAL LN
C       In order to avoid problems with the rootfinding routine, ROOTDFF,
C        ALPHA is perturbed slightly.  The potential problems occur when round
C        figures are used for BETA and ALPHA, when either are simply related
C        multiples or are common factors of a larger number, because then
C        asymptotes of the two tangent functions (in the characteristic eqn.)
C        can coincide.
C     If alpha > beta it is faster to calculate migration by letting
C      alpha and beta equal their reciprocals and tau = tau times the
C      square of beta/alpha.  The value of migration thus calculated
C      is multiplied by the true value of alpha to give migration for
C      the original case.
```

```
      IF ((ALAST.NE.ALPHA).OR.(BLAST.NE.BETA)) NROOT=0
         ASAVE = ALPHA
         ALPHA = ALPHA * 1.00001d0
         EPS1 = 1.d-8
         SUM = 1.d0 - 1.d0/(1.d0 + ALPHA)
         IFLAG = 0
         N = 0
 10      N = N + 1
         IF (N.EQ.NRTDFFMAX) GOTO 40
         IF (N.LE.NROOT) GOTO 20
           B(N) = ROOTDFF(N,ALPHA,BETA)
           NROOT = N
 20      LN = B(N)
         TAN1 = TAN(LN)
         DEN = 1.d0 + ALPHA + (1.d0+ALPHA/(BETA*BETA))*TAN1*TAN1
         EN = 2.d0 * TAN1*TAN1/(DEN*LN*LN)
         ARG1 = LN*LN*TAU
         ARG2 = LOG(EN)
         TERM = 0.d0
         IF ((ARG2-ARG1).GT.-120.d0) TERM = EXP(ARG2-ARG1)
         SUM = SUM - TERM
         RAT = ABS(TERM/SUM)
         IF (RAT.LT.EPS1) GOTO 30
         IFLAG = 0
         GOTO 10
 30      IFLAG = IFLAG + 1
         IF (IFLAG.LT.3) GOTO 10
         GOTO 50
 40      WRITE(IW,101)
 101     FORMAT(/6X,'NOTE: GIVEN THE ABOVE INPUT AND THE ESTIMATED'
     1   /6X,'TAU VALUE, MIGRATION IS VERY CLOSE TO ZERO (<1.0E-04).'
     2   //6X,'RECOMMENDATION: INCREASE EXPOSURE TIME, INCREASE     '
     3   /6X,'MIGRANT-POLYMER DIFFUSION COEFFICIENT, OR REDUCE POLYMER'
     4   /6X,'THICKNESS, AND RE-RUN SCENARIO.'/)
         RETURN
 50      ALPHA = ASAVE
         DOMDFF = SUM
      WRITE(IW,100)DOMDFF
 100  FORMAT(6X,'FRACTION MIGRATED                  ',T60,1PE10.2)
         RETURN
         END
C        File ROOTDFF, function ROOTDFF                   0990
C     REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C        Finds Nth root of the equation
C           tan (LN) + BETA*tan(ALPHA*LN/BETA) = 0
C        given the parameters ALPHA and BETA.  The root for N=0 is 0.
         DOUBLE PRECISION FUNCTION ROOTDFF(N,ALPHA,BETA)
      IMPLICIT REAL*8 (A-H,O-Z)
         DOUBLE PRECISION LN1,LN2,LNN
      COMMON/IO/IR,IW
C          N     = root number; root 0 = 0
C          N1    = N + 1, used for calculation of asymptotes
C          EPS1  = desired accuracy of root
C          EPS2  = part of interval away from asymptote where the search begins
C          EPS3  = EPS2*BETA/ALPHA  if BETA < ALPHA
```

```
C             = EPS2                    if BETA > ALPHA
C         ETA = 1/(1 + BETA/ALPHA)
C         BOA = BETA/ALPHA
C         BAB = BOA     if BETA < ALPHA
C             = 1/BOA   if BETA > ALPHA
C         ETA = ETA                 if ALPHA < BETA
C             = 1/(1+ALPHA/BETA) if ALPHA > BETA
C
C       To trace program execution for diagnostic purposes, set IDIAG = 1
C        by passing a negative value of N to ROOTDFF
C
C       When roots cannot be determined, the returned root will be
C        negative. In order to trace the calculations via output
C        messages, asterisked comments C* can be activated. This module
C        can be recompiled and relinked accordingly.
        IDIAG = 0
        IF (N.LT.0) IDIAG = 1
C*      IF (IDIAG.EQ.1) WRITE (IW,*) 'N,ALPHA,BETA=',N,ALPHA,BETA
        IF (N.EQ.0) GOTO 160
        BOA = BETA/ALPHA
        BAB = BOA
        EPS1 = 1.d-12
        EPS2 = 0.1d0
        EPS3 = EPS2
C       if BETA.LT.ALPHA, change scale to do calculations
        IF (BOA.LT.1.d0) BAB = 1.d0/BOA
        IF (BAB.NE.BOA) EPS3 = EPS2*BOA
        PI1 = 2.d0*ACOS(0.d0)
        PI2 = PI1 * BAB
        N1 = N + 1
        IF (IDIAG.EQ.1) N1 = 1 - N
        RN = FLOAT(N1)
        ETA = BAB/(1.d0 + BAB)
C       Locate the two asymptotes
        DEC1 = RN*(1.d0 - ETA)
        DEC2 = RN*ETA
        TRU1 = AINT(DEC1)
        TRU2 = AINT(DEC2)
        REM1 = DEC1 - TRU1
        REM2 = DEC2 - TRU2
        DIF = ABS(1.5d0-ETA-REM1)
C*      IF (IDIAG.EQ.1) WRITE (IW,*) DEC1,DEC2,TRU1,TRU2,REM1,REM2
        IF ((REM1.GE.0.5d0).AND.((REM1.LE.1.5d0-ETA)
     +.OR.(DIF.LT.1.d-13)))
     + GOTO 20
          AS2 = (TRU2 + 0.5d0) * PI1
          IF (REM1.GT.0.5d0) AS2 = (TRU2-0.5d0)*PI1
          AS1 = (TRU2 - 0.5d0) * PI1
          IF (REM1.GT.0.5d0) AS1 = (TRU2 - 1.5d0)*PI1
          AS1T = (TRU1 + 0.5d0) * PI2
          IF ((AS1T.GT.AS1).AND.(AS1T.LT.AS2)) AS1 = AS1T
          GOTO 30
20      CONTINUE
          AS2 = (TRU1 + 0.5d0) * PI2
          AS1 = (TRU2 - 0.5d0) * PI1
```

```
30      IF (ABS(AS2-AS1).LT.(1.d-13*BOA)) GOTO 40
        IF (ABS(AS2-AS1).LT.(100.d0*EPS1)) GOTO 50
C       Have two distinct asymptotes which bound the desired root
35      IF (BAB.EQ.BOA) GOTO 60
C         revert scale (changed because BETA.LT.ALPHA)
          AS1 = AS1*BOA
          AS2 = AS2*BOA
        GOTO 60
C       Asymptotes coincide, root = asymptote
40      ROOT = -AS2
C*      IF (IDIAG.EQ.1) WRITE (IW,*) 'Asymptotes are ',AS1,AS2
C       Revert scale if BETA.LT.ALPHA
C*      WRITE (IW,*) '---asymptotes coincide, N =',N
        IF (BAB.NE.BOA) ROOT = ROOT*BOA
        GOTO 150
C       Two asymptotes within 10*EPS1 of each other (but not identical)
C*50    WRITE (IW,*) 'Asymptotes too close.  Root is arithmetic mean.'
C*      WRITE (IW,*) 'Asymptotes are ',AS1,AS2
50      ROOT = -(AS2 + AS1)/2.d0
        GOTO 150
C       The two asymptotes bound the desired root.  To find the root, we
C         start at the right and use Newton's method to 'walk down the
C         curve' to the root.  If an inflection point is encountered, we
C         start from the other direction.  If the root is within EPS3 of
C         an asymptote, an alternate form of the residual is used.
60      BMIN = 1.d0
C*      IF (IDIAG.EQ.1) WRITE (IW,*) 'Asymptotes are ',AS1,AS2
        IF (BETA.LT.1.d0) BMIN = BETA
        LEFT = 0
        LN1 = AS2 - EPS3*(AS2-AS1)
C*      IF (IDIAG.EQ.1) WRITE (IW,*) '  START FROM RIGHT'
101     LN2 = LN1/BOA
        TAN1 = TAN(LN1)
        TAN2 = TAN(LN2)
        SEC1 = 1.d0/COS(LN1)
        SEC2 = 1.d0/COS(LN2)
        R    = TAN1 + BETA*TAN2
        DR   = SEC1*SEC1 + ALPHA*SEC2*SEC2
        DDR  = 2.d0*SEC1*SEC1*TAN1 + 2.d0*(ALPHA/BOA)*SEC2*SEC2*TAN2
        LNN  = LN1 - (R/DR)
        IF (((LEFT.EQ.0).AND.(R.LT.0.d0)).OR.((LEFT.EQ.1)
     +.AND.(R.GT.0.d0)))
     + GOTO 130
        ICODE = 120
        IF ((ABS(LNN-LN1).LT.EPS1).AND.(ABS(R).LT.BMIN)) GOTO 140
        IF ((LEFT.EQ.0).AND.((DDR.LE.0).OR.(LNN.LE.AS1))) GOTO 110
        ICODE = 121
        IF ((LEFT.EQ.1).AND.((DDR.GE.0.d0).OR.(LNN.GE.AS2))) GOTO 120
C       Update guess (take one Newton step)
        LN1 = LNN
C*      IF (IDIAG.EQ.1) WRITE (IW,*) '    Take one Newton step...'
        GOTO 101
C       Newton's search stalled by inflection point.  Switch sides.
110     LEFT = 1
C*      IF (IDIAG.EQ.1) WRITE (IW,*) '  Stalled--switch to left side'
```

```
        LN1 = AS1 + EPS3*(AS2-AS1)
        GOTO 101
C       Search method unsuccessful
120     WRITE (IW,*) 'Root search failed in routine ROOTDFF, N =',N
C*      WRITE (IW,*) 'ROOT, CODE =',LNN,ICODE
        ROOT = -LNN
        GOTO 150
C       Root is 'close' to an asymptote; use alternate form for
C         the residual to minimize calculational error
130     IF (LEFT.EQ.0) AS1 = LN1
        IF (LEFT.EQ.1) AS2 = LN1
C*      IF (IDIAG.EQ.1) WRITE (IW,*) '  Switch to alternate form (root'
C*   +,' close to asymptote)'
        LEFT = 1 - LEFT
        IF (LEFT.EQ.0) LN1 = AS2
        IF (LEFT.EQ.1) LN1 = AS1
        ILEFT = 0
132     LN2 = LN1/BOA
        COT1 = 1.d0/TAN(LN1)
        COT2 = 1.d0/TAN(LN2)
        CSC1 = 1.d0/SIN(LN1)
        CSC2 = 1.d0/SIN(LN2)
        R    = COT1 + COT2/BETA
        DR   = -CSC1*CSC1 - CSC2*CSC2/(BETA*BOA)
        DDR  = 2.d0*CSC1*CSC1*COT1 + 2.d0*CSC2*CSC2*COT2/(BETA*BOA*BOA)
        LNN  = LN1 - (R/DR)
        IF (((LEFT.EQ.0).AND.(LNN.GT.AS2)).OR.
     +             ((LEFT.EQ.1).AND.(LNN.LT.AS1))) GOTO 135
        ICODE = 122
        IF ((ABS(LNN-LN1).LT.EPS1).AND.(ABS(R).LT.BMIN)) GOTO 140
C       Update guess (take one Newton step)
        LN1 = LNN
C*      IF (IDIAG.EQ.1) WRITE (IW,*) '    Take one Newton step....'
        GOTO 132
C       Step in wrong direction; switch sides
135     IF (ILEFT.EQ.0) GOTO 137
        ICODE = 123
        GOTO 120
137     ILEFT = 1
C*      IF (IDIAG.EQ.1) WRITE (IW,*) '  Stalled--switch to opposite side'
        LEFT = 1 - LEFT
        LN1 = AS1
        IF (LEFT.EQ.0) LN1 = AS2
        GOTO 132
C       Zero-th root
160     ROOT = 0.d0
        GOTO 150
C       Have located the desired root
140     ROOT = LNN
        ROOTP = ROOT + 2.d0*EPS1
        ROOTM = ROOT - 2.d0*EPS1
        RP = TAN(ROOTP) + BETA*TAN(ROOTP/BOA)
        RM = TAN(ROOTM) + BETA*TAN(ROOTM/BOA)
        ICODE = ICODE + 100
        IF (RP/RM.GT.0.d0) GOTO 120
```

```
150     ROOTDFF = ROOT
C*      IF (IDIAG.EQ.1)WRITE(IW,*)'  Variables N,ROOTDFF,R in routine'
C*   +  ' ROOTDFF are, respectively  ',N,ROOTDFF,R
        RETURN
        END
```

```
C    PROGRAM NAME: EQ31               KM DILWALI 0990

C  THIS PROGRAM MODULE SERVES AS THE I/O SHELL TO
C  COMPUTE THE FRACTION OF ADDITIVE MIGRATION
C  ASSUMING THE FOLLOWING CONDITIONS:  (DFI)
C  - FINITE SLAB(POLYMER) IN CONTACT WITH SEMI-INFINITE SLAB(FOOD)
C  - FOOD PHASE CONCENTRATION INITIALLY IS ZERO
C  - MIGRANT IS UNIFORMLY DISTRIBUTED IN POLYMER
C  INPUT REQUIREMENTS:
C        IPOLY : 01-06 POLYMER TYPE                          -
C          01= SILICONE RUBBER   04=HDPE
C          02= NATURAL  RUBBER   05=POLYSTYRENE
C          03= LDPE              06=PVC(UNPLASTICIZED)
C        XMW   : MOLECULAR WEIGHT OF MIGRANT              G/MOL
C        DP    : DIFFUSION COEFF. OF ADDITIVE IN POLYMER  CM2/S
C        THRS  : TIME                                     HRS
C        XL    : POLYMER FILM THICKNESS                   CM
C        NSIDE : 01=ONE-SIDED , 02=TWO-SIDED DIFFUSION    -
C        CINIT : INIT MIGRANT CONCN IN POLYMER G/CM3
C        NEXT  : EXT PHASE TYPE 01=AIR, 02=H2O , 03=SOLID
C        PC    : PARTITION COEFF; 0 IF UNKNOWN
C        CSATP : SAT CONCN OF MIGR IN POLYMER OR 0.,G/CM3
C        CSATA : SAT CONCN OF MIGR IN AIR     OR 0.,G/CM3
C        CSATW : SAT CONCN OF MIGR IN H2O     OR 0.,G/CM3
C        CSATE : SAT CONCN OF MIGR IN EXT.PHASE    ,G/CM3
C        VPMT  : MIGR VAPOR PRESSURE,TORR FOR CSATA CALC
C        TMM   : MIGR MELT TEMP DEG C    FOR CSATW CALC
C        XKOWM : MIGR OCT-H2O PART COEFF FOR CSATW CALC
C        JEXT  : TYPE OF EXTERNAL PHASE=0(OTHER); 01-06(POLYMER)
C        DEXT  : DIFFUSION COEFF. IN EXTERNAL PHASE, CM2/S
C********************
      IMPLICIT REAL*8 (A-H,O-Z)
      TAU = 0.
      BETA  = 0.
C********************
      COMMON/IO/IR,IW
      CHARACTER*2 TITLE(36)
      IR = 5
      IW = 6
      OPEN(IR,FILE='EQ31.INP')
      OPEN(IW,FILE='EQ31.LIS',STATUS='UNKNOWN')
C  READ INPUT DATA
      READ(IR,'(36A2)')TITLE
      READ(IR,'(I2)')IPOLY
      READ(IR,'(F10.2)')XMW
      READ(IR,'(F10.2)')DP
      READ(IR,'(F10.2)')THRS
      READ(IR,'(F10.2)')XL
      READ(IR,'(I2)')NSIDE
      READ(IR,'(F10.2)')CINIT
```

```
      READ(IR,'(I2)')NEXT
      READ(IR,'(F10.2)')PC
      READ(IR,'(F10.2)')CSATP
      READ(IR,'(F10.2)')CSATA
      READ(IR,'(F10.2)')CSATW
      READ(IR,'(F10.2)')CSATE
      READ(IR,'(F10.2)')VPMT
      READ(IR,'(F10.2)')TMM
      READ(IR,'(F10.2)')XKOWM
      READ(IR,'(I2)')JEXT
      READ(IR,'(F10.2)')DEXT
C  INITIALIZE
      XLEN - XL
      IF(NSIDE.EQ.2)XLEN-XL/2.
      TSEC - THRS*3600.
C   ECHO INPUT
      WRITE(IW,201)TITLE
      WRITE(IW,210)
      IF(IPOLY.EQ.1)WRITE(IW,211)
      IF(IPOLY.EQ.2)WRITE(IW,212)
      IF(IPOLY.EQ.3)WRITE(IW,213)
      IF(IPOLY.EQ.4)WRITE(IW,214)
      IF(IPOLY.EQ.5)WRITE(IW,215)
      IF(IPOLY.EQ.6)WRITE(IW,216)
      IF(XMW.NE.0.)WRITE(IW,220)XMW
      WRITE(IW,221)THRS,XL
      IF(DP.NE.0.)WRITE(IW,225)DP
      IF(DEXT.NE.0.)WRITE(IW,226)DEXT
      IF(NSIDE.EQ.1)WRITE(IW,230)
      IF(NSIDE.EQ.2)WRITE(IW,235)
      IF(NEXT.EQ.1)WRITE(IW,260)
      IF(NEXT.EQ.2)WRITE(IW,265)
      IF(NEXT.EQ.3)WRITE(IW,261)
      IF(JEXT.EQ.1)WRITE(IW,411)
      IF(JEXT.EQ.2)WRITE(IW,412)
      IF(JEXT.EQ.3)WRITE(IW,413)
      IF(JEXT.EQ.4)WRITE(IW,414)
      IF(JEXT.EQ.5)WRITE(IW,415)
      IF(JEXT.EQ.6)WRITE(IW,416)
      IF(PC.NE.0.)WRITE(IW,331)PC
        IF(PC.NE.0.)GO TO 15
      IF(CSATP.NE.0.)WRITE(IW,266)CSATP
      IF(CSATP.EQ.0.)WRITE(IW,267)CINIT
      IF(NEXT.EQ.1.AND.CSATA.NE.0.)WRITE(IW,268)CSATA
      IF(NEXT.EQ.2.AND.CSATW.NE.0.)WRITE(IW,269)CSATW
      IF(NEXT.EQ.1.AND.CSATA.EQ.0.)WRITE(IW,270)VPMT
      IF(NEXT.EQ.2.AND.CSATW.EQ.0.)WRITE(IW,275)TMM,XKOWM
      IF(NEXT.EQ.3)WRITE(IW,285)CSATE
C   LIST OUTPUT
15    WRITE(IW,310)
C   CALC DIFFUSION COEFF IN POLYMER (DP) IF NOT USER-SPECIFIED
      IF(IPOLY.EQ.0.AND.DP.EQ.0.)GO TO 900
      IF(DP.EQ.0.)CALL DPCALC(IPOLY,XMW,DP)
C   CALC PARTITION COEFF IF NOT USER-SPECIFIED
      VPM - VPMT/760.
```

```
      IF(PC.EQ.0.)CALL KCALC(NEXT,CSATP,CSATA,CSATW,CINIT,CSATE,
     1                       XMW,VPM,TMM,XKOWM,PC)
C   CALC DIFFUSION COEFF IN EXTERNAL PHASE(DEXT) IF NOT USER-SPECIFIED
      IF(JEXT.GT.6)GO TO 860
      IF(JEXT.EQ.0.AND.DEXT.EQ.0.)GO TO 860
      IF(JEXT.NE.0.AND.DEXT.EQ.0.)CALL DPCALC(JEXT,XMW,DEXT)
C CALC NONDIMENSIONAL PARAMETERS
      TAU = DP*TSEC/XLEN/XLEN
      BETA = PC*SQRT(DEXT/DP)
      WRITE(IW,320)TAU,BETA
      FRMIG = DOMDFI(TAU,BETA)
 201  FORMAT(6X,36A2//)
 210  FORMAT(6X,'** INPUT PARAMETERS **'/)
 211  FORMAT(6X,'POLYMER CATEGORY:',T60,'  SILICONE RUBBER ')
 212  FORMAT(6X,'POLYMER CATEGORY:',T60,'  NATURAL  RUBBER ')
 213  FORMAT(6X,'POLYMER CATEGORY:',T60,'  LDPE            ')
 214  FORMAT(6X,'POLYMER CATEGORY:',T60,'  HDPE            ')
 215  FORMAT(6X,'POLYMER CATEGORY:',T60,'  POLYSTYRENE     ')
 216  FORMAT(6X,'POLYMER CATEGORY:',T60,'  PVC(UNPLASTICIZED)')
 220  FORMAT(6X,'MOLECULAR WEIGHT OF ADDITIVE   ',T60,1PE10.2)
 221  FORMAT(6X,'TIME   (HRS)        ',T60,1PE10.2/
     1       6X,'TOTAL POLYMER SHEET THICKNESS  (CM)',T60,1PE10.2)
 225  FORMAT(6X,'USER-SPECIFIED DIFFUSION COEFFICIENT (CM2/S)',
     1       T60,1PE10.2)
 226  FORMAT(6X,'USER-SPECIFIED DIFF. COEFF.IN EXTERNAL PHASE (CM2/S)',
     1       T60,1PE10.2)
 230  FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  ONE-SIDED')
 235  FORMAT(6X,'DIFFUSION SPECIFIED AS',T60,'  TWO-SIDED')
C
 260  FORMAT(6X,'EXTERNAL PHASE IS          ',T60,'  AIR')
 265  FORMAT(6X,'EXTERNAL PHASE IS          ',T60,'  WATER')
 261  FORMAT(6X,'EXTERNAL PHASE IS          ',T60,'  SOLID')
 266  FORMAT(6X,'SATURATION CONC. OF MIGRANT IN POLYMER (G/CM3)',
     1           T60,1PE10.2)
 267  FORMAT(6X,'LET SATUR. CONC. IN POLYMER = INIT CONC.(G/CM3)',
     1           T60,1PE10.2)
 268  FORMAT(6X,'SATURATION CONC. IN AIR     (G/CM3)',T60,1PE10.2)
 269  FORMAT(6X,'SATURATION CONC. IN WATER   (G/CM3)',T60,1PE10.2)
 270  FORMAT(6X,'MIGRANT VAPOR PRESSURE (TORR)  ',T60,1PE10.2)
 275  FORMAT(6X,'MIGRANT MELT TEMP (DEG C)',T60,1PE10.2/
     1       6X,'MIGRANT OCTANOL-WATER PART. COEF.',T60,1PE10.2)
 285  FORMAT(6X,'SATURATION CONC. IN EXTERNAL PHASE  (G/CM3)',
     1           T60,1PE10.2)
 310  FORMAT(//6X,'** OUTPUT VALUES (MODULE: EQUATION 31) **'/)
 320  FORMAT(6X,'TAU                           ',T60,1PE10.2,/
     1       6X,'BETA                          ',T60,1PE10.2)
 331  FORMAT(6X,'USER-SPECD PARTITION COEFFICIENT',T60,1PE10.2)
 411  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  SILICONE RUBBER')
 412  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  NATURAL RUBBER')
 413  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  LDPE')
 414  FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1           T60,'  HDPE')
```

```
  415   FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1            T60,'  POLYSTYRENE')
  416   FORMAT(6X,'EXTERNAL PHASE POLYMER CATEGORY  :',
     1            T60,'  PVC(UNPLASTICIZED)')
        GO TO 999
 860    WRITE(IW,703)
 703    FORMAT(/6X,'PROGRAM STOP. INPUT ERROR. SOLID EXTERNAL PHASE '
     1         /6X,'MUST BE SPECIFIED AS 0(OTHER) OR 01-06(POLYMER    '
     2         /6X,'CATEGORY). FOR "OTHER" SOLIDS, THE DIFFUSION COEFF.'
     3         /6X,'MUST BE INPUT BY USER. REFER TO SEC.4.2 OF REPORT.')
        GO TO 999
  900   WRITE(IW,801)
  801   FORMAT(/6X,'PROGRAM STOP. INPUT ERROR. FOR A USER-SPECIFIED'
     1         /6X,'POLYMER CLASS, THE DIFFUSION COEFFICIENT OF     '
     2         /6X,'ADDITIVE IN POLYMER MUST BE A NON-ZERO VALUE.  ')
  999   STOP
        END
C         File DOMDFI                                         0990
C       REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C         Domain DFI:  Finite slab (polymer) in contact with a semi-infinite
C          slab (food).  Returns fractional migration assuming the food phase
C          concentration is initially zero and the solute is uniformly
C          distributed in the polymer.
C         Requires the subprograms ERFCA, SHANK
C
C         Note that TAU   = Dpt/L2
C                   ALPHA = KV/AL
C                   BETA  = Ksqrt(De/Dp)
C
C   NOTE TO USER: For very low values of TAU, migration rates approach
C   zero, and this function subroutine cannot compute a value of DOMDFI.
C   In the unlikely event of certain input conditions (low Dp,low t,etc.)
C   a FRACTION MIGRATED is not reported on screen or in the output
C   file. Nor does an error message appear if the routine cannot execute
C   the mathematics. In such instances, assume FRACTION MIGRATED is
C   negligible.
          DOUBLE PRECISION FUNCTION DOMDFI(TAU,BETA)
       IMPLICIT REAL*8 (A-H,O-Z)
        COMMON/IO/IR,IW
          NMAX = 1000
          EPS = 1.0d-8
C         Solution is indeterminate if BETA = 1
          BSAVE = BETA
          IF (BETA.EQ.1.d0) BETA = 1.00001d0*BETA
          PI = 3.1415926535898d0
          RPI = SQRT(PI)
          BP = 1.d0 + BETA
          BM = 1.d0 - BETA
          PRE = 2.d0*BETA*SQRT(TAU/PI)/BP
          SUM = 1.d0
          PRET = 2.d0*BETA/BP
          PREI = BM/BP
          PREA = PRET/PREI
          N = 0
10        N = N + 1
```

```
        IF(N.GE.NMAX)GO TO 40
        PREA = PREA*PREI
        RN = DBLE(N)
        ARG1 = RN/SQRT(TAU)
        B1 = EXP(-ARG1*ARG1)
        B2 = ARG1*RPI*ERFCA(ARG1)
        TERM = PREA*(B1-B2)
        SUM = SUM - TERM
        RAT = ABS(TERM/SUM)
        IF (RAT.GT.EPS) GOTO 10
        BETA = BSAVE
        DOMDFI = PRE*SUM
        WRITE(IW,100)DOMDFI
 100   FORMAT(6X,'FRACTION MIGRATED             ',T60,1PE10.2)
        RETURN
  40    WRITE(IW,101)
101     FORMAT(/6X,'NOTE: GIVEN THE ABOVE INPUT AND THE ESTIMATED'
     1  /6X,'TAU VALUE, MIGRATION IS VERY CLOSE TO ZERO (<1.0E-04).'
     2  //6X,'RECOMMENDATION: INCREASE EXPOSURE TIME, INCREASE     '
     3  /6X,'MIGRANT-POLYMER DIFFUSION COEFFICIENT, OR REDUCE POLYMER'
     4  /6X,'THICKNESS, AND RE-RUN SCENARIO.'/)
        RETURN
        END
C       ERFCA
C      REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C         Function ERFCA(Z) calculates the complementary error
C           function of the real, positive argument Z.  The result
C           is accurate to about 8 significant figures at
C           worst.
C       Requires function SHANK.....
        DOUBLE PRECISION FUNCTION ERFCA(Z)
     IMPLICIT REAL*8 (A-H,O-Z)
        DIMENSION S(5)
        IF (Z.LT.-Z) GOTO 30
        IF (Z.GT.12.0) GOTO 30
        Z2 = Z*Z
        RTPI = 0.17724538509055152D+01
        IF (Z.GT.4.0D0) GOTO 15
5       EPS = 1.d-16
        TERM = 2.d0*EXP(-Z2)*Z/RTPI
        SUM = 1.d0
        SUM = SUM - TERM
        L = 0
10      L = L + 1
        RN = FLOAT(L)
        TERM = TERM*2.d0*Z2/(2.d0*RN + 1.d0)
        SUM = SUM - TERM
        RAT = ABS(TERM/SUM)
        IF (RAT.GE.EPS) GOTO 10
        ERFCA = SUM
        RETURN
15      EPS = 1.d-9
        NS = 5
        SUM = EXP(-Z2)/(RTPI*Z)
        TERM = SUM
```

```
      ITERM = 0
      TERMOLD = 10.d0
      ILOC = 1
      L = 0
20    L = L + 1
      RN = FLOAT(L)
      TERM = TERM*(1.d0 - 2.d0*RN)/(2.d0*Z2)
      SUM = SUM + TERM
      RAT = ABS(TERM/SUM)
      IF (ABS(TERM).GT.TERMOLD) ITERM = ITERM + 1
      TERMOLD = ABS(TERM)
      IF (ITERM.EQ.0) GOTO 40
      S(ILOC) = SUM
      ILOC = ILOC + 1
      IF (ILOC.LE.NS+1) GOTO 40
      SX = SHANK(NS,S)
      ERFCA = SX
      RETURN
40    IF (RAT.GE.EPS) GOTO 20
      ERFCA = SUM
      RETURN
30    ERFCA = 0.d0
      RETURN
      END
C     Function SHANK, uses Shanks transform to accelerate
C     convergence of a series.                          0990
C       S is a vector (length 25) containing N consecutive
C       terms of the series.  S is destroyed during the calculation.
C    REF: GANDEK,T.P., PH.D. THESIS, M.I.T., CAMBRIDGE, MA 1986
C
      DOUBLE PRECISION FUNCTION SHANK(N,S)
   IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION S(25)
      M = N
5     DO 10 I = 1,M-2
        S(I)=(S(I+2)*S(I)-S(I+1)*S(I+1))/(S(I+2)+S(I)-2.d0*S(I+1))
10    CONTINUE
      M = M-2
      IF (M.GE.3) GOTO 5
      IF (M.EQ.2) SHANK = S(2)
      IF (M.EQ.1) SHANK = S(1)
      RETURN
      END
```

```
      SUBROUTINE DPCALC(IPOLY,DMW,DPOLY)

C SUB-PROGRAM NAME: DPCALC            KM DILWALI 0990
C THIS ROUTINE CALCULATES THE POLYMER DIFFUSION COEFF.
C AS A FUNCTION OF THE POLYMER TYPE AND MIGRANT MOLECULAR WT.
C MAIN PROGRAM : AMEM CALLS EQUATION MODULES, WHICH CALL DPCALC.
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/IO/IR,IW
      GO TO (100,200,300,400,500,600),IPOLY
C   SILICONE RUBBER
100     IF(DLOG10(DMW) .LE. 1.5) DLPOLY= -.384*DLOG10(DMW)-4.12
        IF((DLOG10(DMW) .GT. 1.5) .AND. (DLOG10(DMW) .LE. 2.125))
     1      DLPOLY= -1.31*DLOG10(DMW)-2.73
        IF(DLOG10(DMW) .GT. 2.125) DLPOLY=-2.73*DLOG10(DMW)
           GOTO 690
C   NATURAL RUBBER
200     IF(DLOG10(DMW) .LE. 1.375) DLPOLY = -.94*DLOG10(DMW)-4.53
        IF((DLOG10(DMW) .GT. 1.375) .AND. (DLOG10(DMW) .LE. 2.31))
     1      DLPOLY= -1.58*DLOG10(DMW)-3.64
        IF(DLOG10(DMW) .GT. 2.31) DLPOLY= -3.49*DLOG10(DMW)+.76
            GOTO 690
C   LDPE
300     IF(DLOG10(DMW) .LE. 1.83) DLPOLY= -1.40*DLOG10(DMW)-5.12
        IF((DLOG10(DMW) .GT. 1.83) .AND. (DLOG10(DMW) .LE. 2.55))
     1    DLPOLY= -2.01*DLOG10(DMW)-4.01
        IF(DLOG10(DMW) .GT. 2.55) DLPOLY= -4.22*DLOG10(DMW)+1.61
             GOTO 690
C   HDPE
400     IF(DLOG10(DMW) .LE. 2.05) DLPOLY= -2.0*DLOG10(DMW)-4.50
        IF(DLOG10(DMW) .GT. 2.05) DLPOLY= -4.0*DLOG10(DMW)-.40
             GOTO 690
C   POLYSTYRENE
500     IF(DLOG10(DMW) .LE. 1.625) DLPOLY= -4.0*DLOG10(DMW)-2.5
        IF(DLOG10(DMW) .GT. 1.625) DLPOLY= -10.4*DLOG10(DMW)+7.95
        IF(DLOG10(DMW) .GT. 1.825) DLPOLY= -11.104*DLOG10(DMW)+9.88
             GOTO 690
C   PVC
600     IF(DLOG10(DMW) .LE. 1.43) DLPOLY= -7.8*DLOG10(DMW)+1.70
        IF(DLOG10(DMW) .GT. 1.43) DLPOLY= -9.41*DLOG10(DMW)+4.16
690     DPOLY= 10.0**DLPOLY
       WRITE(IW,900)DPOLY
900    FORMAT(6X,'ESTD. DIFFUSION COEFFICIENT IN POLYMER (CM2/S)',
     1          T60,1PE10.2)
        RETURN
        END
```

```
      SUBROUTINE KCALC(NEXT,CSATP,CSATA,CSATW,CINIT,CSATE,
     1                      XMW,VPM,TMM,XKOWM,CPART)
C  K2M DILWALI                                0990
C  REVISIONS BY RCREID INCORPORATED IN ORIGINAL EQUATIONS.
C  THIS ROUTINE CALCS THE PARTITION COEFFICIENT DEFINED AS THE RATIO
C  OF THE SATURATION CONCN OF MIGRANT IN THE EXTERNAL PHASE TO THE
C  CONCN OF MIGRANT IN THE POLYMER.
C  INPUT REQMTS ARE AS FOLLOWS:
C   CSATP =SAT CONCN OF MIGRANT IN POLYMER      G/CM3
C   CSATA OR CSATW =SAT CONCN OF MIGRANT IN EXT PHASE  G/CM3
C     EXTERNAL PHASE= AIR> VPM =MIGRANT VAP PRESSURE @ 25C(ATM)
C     EXTERNAL PHASE= H2O> TMM =MIGRANT MELT TEMP (DEG C )
C                        XKOWM =MIGRANT OCTANOL-H2O PART COEFF.
C     EXTERNAL PHASE= SOLID> CSATE
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/IO/IR,IW
      CPART = 0.
      IF(CSATP.EQ.0.)CSATP=CINIT
      GO TO (100,200,300),NEXT
C EXT PHASE IS AIR
100   IF(CSATA.NE.0.)GO TO 110
      CSATA = VPM*XMW*40.626 *1.E-06
      WRITE(IW,510)CSATA
510   FORMAT(6X,'ESTD. SATUR. CONC. OF MIGRANT IN AIR (G/CM3)',
     1           T60, 1PE10.2)
110   CEXT  = CSATA
      GO TO 400
C EXT PHASE IS H2O -- USE REVISED EQN FOR TLOG FROM RC REID
200   IF(CSATW.NE.0.)GO TO 210
      TLOG=ALOG10(XMW)-1.123*ALOG10(XKOWM)-0.0099*TMM-2.067
      CSATW = 10.**TLOG
      WRITE(IW,520)CSATW
520   FORMAT(6X,'ESTD. SATUR. CONC. OF MIGRANT IN WATER (G/CM3)',
     1           T60, 1PE10.2)
210   CEXT  = CSATW
      GO TO 400
C EXT PHASE IS SOLID
300   CEXT = CSATE
      IF(CSATE.EQ.0.)WRITE(IW,540)
540   FORMAT(6X,'SATURATION CONCENTRATION IN EXTERNAL PHASE SPECIFIED'
     1      /6X,'AS 0.0 G/CM3. RECHECK INPUT.')
400   CPART = CEXT/CSATP
      WRITE(IW,530)CPART
530   FORMAT(6X,'ESTIMATED PARTITION COEFFICIENT',T60,1PE10.2)
      RETURN
      END
```

```
      SUBROUTINE RKCALC(NEXT,KHORZ,NPLC,AIRVEL,RSURFA,VPM,
     1 HEIGHT,WATVEL,IRWAT,RSURFW,DPIPE,XMW,RK)
C K2M DILWALI                                 0990
C REVISIONS BY RCREID INCORPORATED IN ORIGINAL EQUATIONS.
C THIS ROUTINE CALCULATES THE MASS TRANSFER COEFFICIENT RK
C THRU AIR OR WATER. FOR AIR, THE FLOW VELOCITY, POLYMER
C POSITION HORIZ OR VERT, POLYMER LOCATION INDOORS OR OUTDOORS
C AND POLYMER DIMENSIONS ARE REQD; FOR WATER, THE FLOW VELOCITY,
C AND POLYMER TYPE PLATE OR PIPE, AND DIMENSION ARE REQD INPUT.
      COMMON/IO/IR,IW
      IMPLICIT REAL*8 (A-H,O-Z)
      IF(NEXT.EQ.2)GO TO 200
C AIR FLOW TRANSFER CASES
C CALC LAMINAR BULK FLOW CONVECTION TERM
       RKA=2.0*(AIRVEL**0.5)/((((2.5 + (XMW**0.333))**1.33)
     + *(RSURFA**0.5)))
C CALC THERMAL CONVECTION TERM FOR INDOORS ONLY
       IF(NPLC.EQ.1)DAIR=3.3/((2.5 + (XMW)**.333)**2.0)
       IF(NPLC.EQ.1)RKB=I.3*DAIR
C CALC DENSITY DRIVEN CONVECTION TERM FOR VERTICAL SURFACES ONLY
       IF(KHORZ.EQ.2)RKC=(0.41*VPM/HEIGHT)**.25
C USE APPROPRIATE MASS TRANS COEFF EQN BASED ON POSN & LOCN
       IF((KHORZ.EQ.1).AND.(NPLC.EQ.2))GO TO 110
       IF((KHORZ.EQ.1).AND.(NPLC.EQ.1))GO TO 120
       IF((KHORZ.EQ.2).AND.(NPLC.EQ.2))GO TO 130
       IF((KHORZ.EQ.2).AND.(NPLC.EQ.1))GO TO 140
110    RK=RKA
       RETURN
120    RK=(1.0/RKA + 1.0/RKB)**(-1.0)
       RETURN
130    RK=(1.0/RKA + 1.0/RKC)**(-1.0)
       RETURN
140    RK=(1.0/RKA + 1.0/RKB + 1.0/RKC)**(-1.0)
       RETURN
C  WATER FLOW TRANSFER CASES
200   IF(IRWAT.EQ.1)GO TO 300
C   WATER FLOW OVER A PLATE
       RE=100.0*RSURFW*WATVEL
       IF(RE .GT. 1000000.0) GOTO 250
C  LAMINAR PLATE FLOW
       RK = 5.2E-04*SQRT(WATVEL/RSURFW)
       RETURN
C  TURBULENT PLATE FLOW
250    RK= 1.2E-04*(WATVEL**0.8)/(RSURFW**0.2)
       RETURN
C   WATER FLOW THROUGH A PIPE
300    RE=100.0*WATVEL*DPIPE
       DMIG= 7.45E-05/(XMW**0.408)
       IF(RE .GT. 2100.0) GOTO 350
C   LAMINAR FLOW SITUATION
       RK=3.65*DMIG/DPIPE
       RETURN
C   TURBULENT FLOW SITUATION
350    RK= 7.2E-05*(WATVEL**0.8)/(DPIPE**0.2)
       RETURN
       END
```

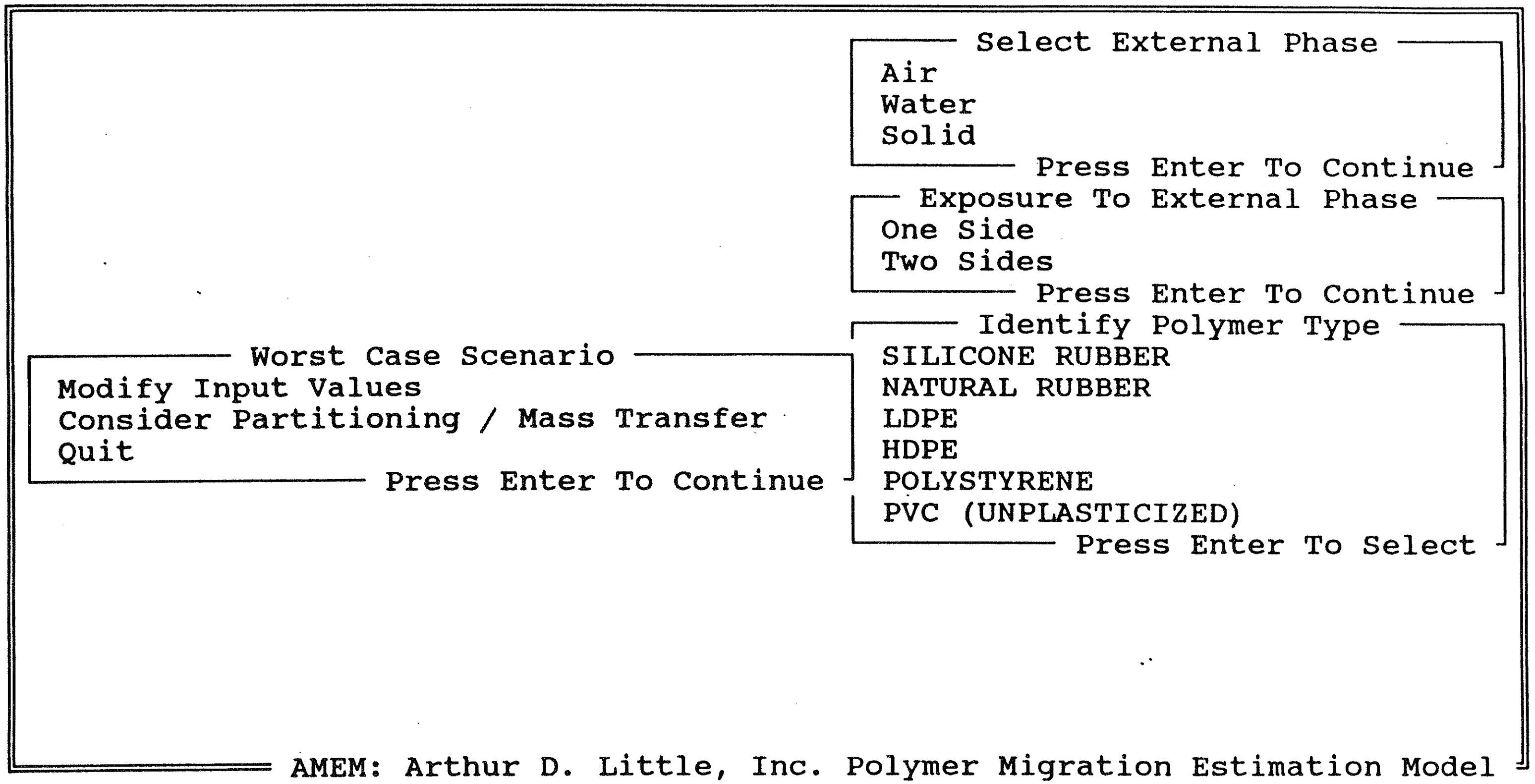
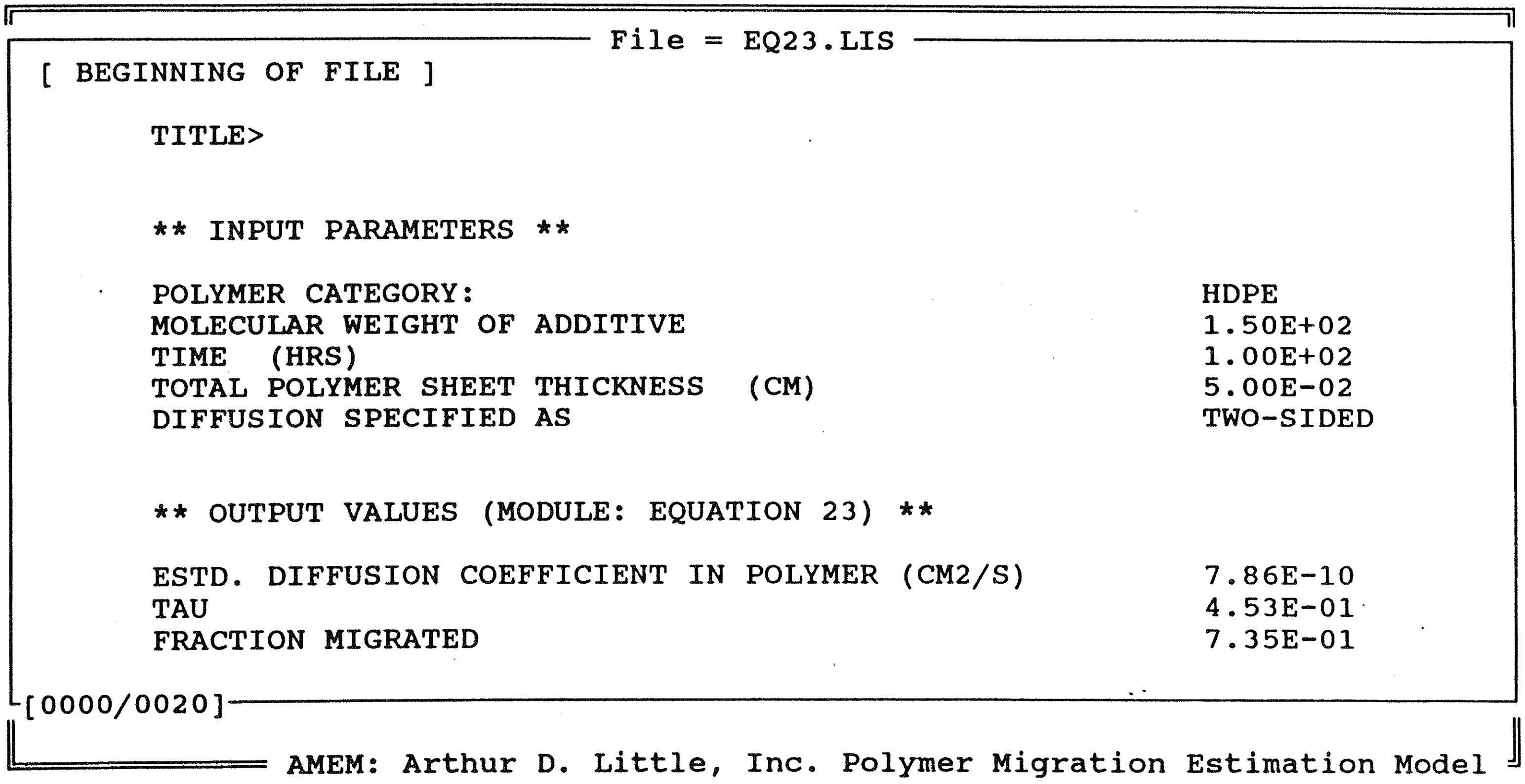


Figure A-2. Example of AMEM menu screen.



```
──────────────────────────── File = EQ23.LIS ──────────────────────────
[ BEGINNING OF FILE ]

      TITLE>


      ** INPUT PARAMETERS **

      POLYMER CATEGORY:                                      HDPE
      MOLECULAR WEIGHT OF ADDITIVE                           1.50E+02
      TIME  (HRS)                                            1.00E+02
      TOTAL POLYMER SHEET THICKNESS  (CM)                    5.00E-02
      DIFFUSION SPECIFIED AS                                 TWO-SIDED


      ** OUTPUT VALUES (MODULE: EQUATION 23) **

      ESTD. DIFFUSION COEFFICIENT IN POLYMER (CM2/S)         7.86E-10
      TAU                                                    4.53E-01
      FRACTION MIGRATED                                      7.35E-01

[0000/0020]────────────────────────────────────────────────────────────
══════════ AMEM: Arthur D. Little, Inc. Polymer Migration Estimation Model
```

Figure A-3. Example of AMEM output screen for worst case migration prediction using Eq. (3-23).

APPENDIX B

AMEM EVALUATION

1. INTRODUCTION

The methods for estimating migration from polymeric materials provided in Volume 11 and the computer program AMEM (Arthur D. Little, Inc., Migration Estimation Model) were derived from diffusion and mass transfer theory. They require inputs of physical property data and values describing physical characteristics of the system. In many cases, the properties or characteristics are not known and must be estimated. Furthermore, there were several important assumptions and constraints used to develop the AMEM. These factors lead to questions of the validity and limitations of the methods as practical means for predicting migration. In Section 5 of Volume 11, example calculations were presented to illustrate use of the predictive model. Several examples were based on conditions of actual migration testing. Other examples, however, were unrealistic although they did demonstrate application of the methods developed.

The objective of this appendix is to evaluate the range of applicability and the limitations of the methods by comparing predicted migration with migration data published in the technical literature. The focus is data for situations in which either air or water was the external phase. Furthermore, there was the constraint that the experimental conditions associated with the published data be sufficiently described so that the model inputs could be specifically stated, readily deduced, or closely approximated. Based on these criteria, 13 example cases were selected. Descriptions of the 13 cases, and the application of the methodology to predict migration for each case follow.

2. CONCLUSIONS AND RECOMMENDATIONS

The methods for estimating migration were validated by comparing predictions generated with the AMEM computer program with those measured experimentally. The thirteen examples documented herein as summarized in Table B-1. In most of the examples the agreement between the model and the experimental results was within an order of magnitude. Those cases in which good agreement is not achieved appear to be in two categories:

- The first category is those migrants for which the diffusion coefficient, D_p, in the polymer is not known and the molecular weights (MW) are greater than those used to develop the D_p versus MW correlation (i.e., Figures 5 and 6 in Volume 11). For these migrants, it appears that the D_p predicted by the AMEM is too low, especially in the case of rigid polyvinyl chloride (PVC). Another possibility is that the very low migration levels reported in some examples may be accounted for by release from the surface rather than a diffusional process.

- The second category involves migrants, such as an antioxidant, that migrate rapidly but have a low solubility and degrade in the external phase. In its present form, the AMEM model does not take into account chemical reaction of the migrating species.

As areas for continued improvement of the AMEM model, we recommend better quantification of mass transfer coefficients for conditions of particular concern to the EPA. These conditions might include conditions in rooms and buildings under various forms of ventilation, in water storage containers, and in automobile interiors. There is also the need to develop and validate procedures for applying the AMEM methodology at temperatures outside the 20-30°C range of the present model. We also recommend continued monitoring of the technical literature for migration data that can be used to further validate and establish limits for application of the AMEM model. Finally, we recommend tailoring the AMEM model interface to address exposure scenarios of particular interest to the EPA.

TABLE B-1. MIGRATION DATA EXAMPLES USED TO VALIDATE AMEM MODEL

Example No.	Polymer	Migrant, Initial Loading (wt %)	External Phase	Temp. (°C)	Time (days)	Fraction Migrated		Comments
						Measured	AMEM	
1	Rigid PVC	Stearyl alcohol, 0.6%	Water	20	60	0.00005	<0.0001	Good agreement
2	Rigid PVC	Irgastab 17 MOK, 1%	Water	20	60	0.00008	<0.0001	Good agreement
3	Rigid PVC	Calcium stearate, 1.4%	Water	25	42	0.0005	<0.0001	Fair agreement, inadequate D_p value
4	Rigid PVC	Dioctyl tin stablizer, 1.1%	Water	25	42	$7.0x10^{-7}$	<0.0001	Good agreement, inadequate D_p value
5	LDPE	Dihydroxybenzophenone, 0.03%	Water	44	10	1.0	1.0	Good agreement
6	HDPE	Dihydroxybenzophenone, 0.003%	Water	44	10	0.8	0.97	Good agreement, inadequate D_p value
7	PP	Dihydroxybenzophenone, 0.07%	Water	44	10	0.7	0.64	Good agreement
8	HDPE	3,5-Di-t-butyl-4-hydroxytoluene, 0.2%	Water	40	10	0.005	0.014-0.12	Prediction brackets measured value depending on external volume input

(continued)

TABLE B-1 (Continued)

Example No.	Polymer	Migrant, Initial Loading (wt %)	External Phase	Temp. (°C)	Time (days)	Fraction Migrated		Comments
						Measured	AMEM	
9	HDPE	Irganox 1076, 0.1%	Water	40	10	0.00065	0.007-0.051	Prediction brackets measured value depending on external volume input
10	Polystyrene	Styrene monomer, 0.1%	Water	40	0.04 7 42	0.002 0.007 0.008	0.003 0.009 0.01	Good agreement
11	Impact Polystyrene	3,5-Di-t-butyl-4-hydroxytoluene, 1%	Water	49	5 35	0.002 0.005	0.002 0.004	Good agreement
12	Plasticized PVC	Diethylhexyl adipate, 39%	Air	58	17	0.01	0.005	Fair agreement, partitioning/mass transfer important
13	Plasticized PVC	Dibutyl phthalate, 33%	Water	25	5 15	0.004 0.006	0.003 0.003	Good agreement partition equilibrium predicted

3. EXAMPLE CASES

Example #1 - Unplasticized Poly(vinyl Chloride) Sheet/Stearyl Alcohol

To better understand migration from packaging materials into foods, cosmetics and pharmaceutical products, Figge, Koch, and Freytag (1978) studied the migration of stearyl alcohol and a dioctyl tin stabilizer from unplasticized or rigid polyvinyl chloride (PVC). They also measured the migration of antioxidants from high density polyethylene. Their work on the polyethylene is used later in Examples #8 and #9.

In one series of tests, room temperature water was the external phase. The additives were radiolabelled (^{14}C) and incorporated into a PVC compound having the following composition:

	wt %
PVC resin	98.0
Irgastab 17 MOK	1.0
Stearyl alcohol	0.6
Loxiol E 10	0.4

Irgastab 17 MOK® is a trade name for 2-ethylhexyl di-n-octyltindithioglycollate, a dioctyl tin stabilizer. Two samples of the PVC blend were produced: one with the dioctyl tin stabilizer radiolabelled and the other with the stearyl alcohol carrying the radiolabel. Test samples were pressed to a thickness of 0.035 cm. The sample size was such that the two-sided exposure surface area was 9 cm^2. The samples were immersed in 1 liter of water at 20°C for 60 days after which the concentration of the migrant in the water was measured. The results for the migration of stearyl alcohol follow while the results for the dioctyl tin stabilizer are reported in Example #2.

The results for the 60-day migration experiment were reported as a percentage of the initial additive amount so that only a direct conversion is required to compare the measured result with the fraction migrated value predicted by the AMEM model. Figge et al. found that 0.005 weight percent of the stearyl alcohol originally present in the PVC migrated into the water. This is equivalent to a fraction migrated of 0.00005 or 5 x 10^{-5}.

Prediction of migration under these conditions using AMEM requires the following input data and conditions:

Migration:	To water
Exposure:	Two sides
Thickness:	0.035 cm
Time:	1440 hours (60 days)
Polymer:	PVC (Unplasticized)
Migrant:	Stearyl alcohol, MW = 270.48
Migrant Initial Concentration:	0.6 wt% or 8.4 x 10^{-3} g/cm^3 [(0.006 g/g PVC)(1.4 g/cm^3) at a polymer density of 1.4 g/cm^3]

External Phase:	Stagnant water at 20°C Volume: 0.001 m^3 (1 liter)
Surface Area:	9 cm^2
Surface Length:	2 cm

Because no value was reported, the diffusion coefficient for stearyl alcohol in the polymer was estimated using AMEM. This was done by entering 1 at the diffusion coefficient entry screen (to estimate), selecting PVC (Unplasticized) from the polymer type screen, and entering the migrant molecular weight. The D_p estimated by AMEM is 1.88×10^{-19} cm^2/s. With these minimum inputs of $D_p = 1.9 \times 10^{-19}$ cm^2/s, time = 1440 hours, and thickness = 0.035 cm, the worst case fraction migrated was predicted to be < 0.0001 using Eq. (3-23)*. (Note: As reported in Section 6 of Volume 11, AMEM does not report fraction migrated values lower than 0.0001 for Eq. (3-23) prediction involving small values of τ.) This prediction is in good agreement with the measured value of 5×10^{-5} fraction migrated.

Because the migrant is essentially insoluble in water and the degree of mixing was not reported, partitioning and mass transfer resistances may act to reduce migration even further. In this example, however, the worst case migration is already predicted to be quite low so that further reductions in the migration prediction will not be apparent. Figge et al. gives no information as to the degree of mixing in the water, so a good estimate for a mass transfer coefficient is difficult to make. However, using the polymer surface length of 2 cm and an essentially stagnant water velocity of 10 cm/s, the mass transfer coefficient for flow over a plate was estimated by AMEM as 1.2×10^{-3} cm/s. The saturation concentration for stearyl alcohol in water is reported as less than 1 ppm or 1×10^{-6} g/cm^3. On the basis of the initial stearyl alcohol concentration in the polymer (because the saturation concentration of stearyl alcohol in the polymer is not known) and an aqueous solubility of 1×10^{-6} g/cm^3, the partition coefficient was estimated by AMEM as 1.2×10^{-4}. Considering these partitioning and mass transfer conditions, AMEM again predicts < 0.0001 of the stearyl alcohol initially present to migrate in 1,440 hours using Eq. (3-17).

Example #2 - Rigid Poly(vinyl Chloride) Sheet/Dioctyl Tin Stabilizer

The migration of Irgastab 17 MOK, a dioctyl tin stabilizer, also was measured from the same PVC sheet samples to water after 60 days at 20°C. The result was that 0.008 wt% or 0.00008 of the stabilizer initially present migrated to the water. Migration under these conditions was estimated using AMEM and the following input data:

Migration:	To water
Exposure:	Two sides
Thickness:	0.035 cm
Time:	1440 hours (60 days)
Polymer:	PVC (Unplasticized)
Migrant:	Irgastab 17 MOK, MW = 750.69 g/mol

---

* In this addendum, the equations referred to are those in Volume 11.

Migrant Initial Concentration:	1.0 wt% or 0.014 g/cm^3 (at a polymer density of 1.4 g/cm^3)
External Phase:	Stagnant water at 20°C Volume: 0.001 m^3
Surface Area:	9 cm^2
Surface Length:	2 cm

Again, a value was not reported for the diffusion coefficient of the dioctyl tin stabilizer in the PVC so it was estimated by AMEM using the migrant molecular weight and the correlation for PVC (Unplasticized). D_p was estimated as 1.3 x 10^{-23} cm^2/s. Note that the migrant molecular weight is at the upper bound of the diffusion coefficient versus log(molecular weight) correlation shown in Figure 5 of Volume 11. Thus, the estimate D_p value is uncertain and may underestimate the actual value. The worst case migration predicted using Eq. (3-23) and the values for D_p, polymer thickness, and time was < 0.0001 fraction migrated. This prediction is in good agreement with the measured value of 8 x 10^{-5}.

Again, partitioning and mass transfer resistances can be considered but will not result in a further reduction of the fraction migrated prediction. For the same Example #1 conditions of a 10 cm/s water velocity and a 2 cm polymer surface length, the mass transfer coefficient, k, was estimated as 1.2 x 10^{-3} cm/s. The water solubility of Irgastab 17 MOK is reported as less than 25 ppm or 2.5 x 10^{-5} g/cm^3. The partition coefficient K was estimated by AMEM as 1.8 x 10^{-3} using the aqueous solubility value and the initial concentration in the polymer of 1.4 x 10^{-2} g/cm^3. Although partitioning and mass transfer resistances in the external phase may act to reduce the migration rate, the Eq. (3-17) prediction by AMEM was again a fraction migrated of < 0.0001.

Example #3 - Rigid Poly(vinyl Chloride) Pipe/Calcium Stearate

Dietz, Banzer, and Miller (1979) studied the migration of additives from pipe fabricated from a PVC compound having the following composition:

	phr
PVC resin	100.0
Dioctyl tin stabilizer	1.2
Titanium dioxide	1.0
Wax	1.1
Calcium stearate	1.5

In compounding, phr stands for parts per hundred resin on a weight basis. For example, in the above formulation there are 1.2 grams of stabilizer for every 100 grams of PVC resin.

Sections of a one-inch diameter, schedule 40 pipe were used as the test specimens. They were 14-cm in length and eight such lengths were placed in a glass jar containing two liters of water. This surface to volume ratio (pipe surface to water volume), according to the authors, corresponds to 4 mL of water per square inch of pipe surface as recommended by the National Sanitation Foundation. The temperature was held at 25°C. Migration of the calcium stearate and dioctyl tin stabilizer was measured. The results are presented here for calcium stearate and in Example #4 for the dioctyl tin stabilizer.

Results for the calcium stearate migration were reported as a part per million concentration found in the two-liter volume of water. To convert this to a fraction migrated, the polymer sample volume and initial migrant concentration in the polymer must be calculated. To calculate the sample volume, the following dimensions of schedule 40 pipe were required:

Inner Diameter	2.664 cm
Outer Diameter	3.340 cm
Wall thickness	0.338 cm

On the basis of these dimensions, the exposed surface area (inner and outer) of each pipe specimen was 264.1 cm^2, and its volume 44.63 cm^3. Thus, for the eight samples used in the experiment, the total surface area was 2112.8 cm^2 and the total pipe volume was 357 cm^3 in the two liters of water.

The initial concentration of the calcium stearate in the PVC compound was 1.5 phr. To convert this to a concentration, the weight fraction of the calcium stearate in the PVC is multiplied by the density of the compound, which is assumed to be that of PVC or 1.4 g/cm^3:

$$(1.5\ \text{g}/104.8\ \text{g})(1.4\ \text{g/cm}^3) = 0.02\ \text{g/cm}^3$$

Therefore, there was (0.02 g/cm^3)(357 cm^3) or 7.15 g of calcium stearate initially present in the 357 cm^3 of the pipe samples.

After six weeks (1,008 hours) immersion of the pipe samples, the concentration of calcium stearate in the water was measured to be 1.91 ppm. To convert this to a mass of calcium stearate, one must multiply by the mass of water present:

$$(1.91\ \text{g calcium stearate}/1 \times 10^6\ \text{g H}_2\text{O})(2000\ \text{g H}_2\text{O}) = 0.0038\ \text{g}$$

Therefore, (0.0038 g/7.15 g) or a 0.00053 fraction of the calcium stearate initially present in the PVC pipe migrated into the water at the end of 1,008 hours.

To predict migration under these conditions, the inputs to AMEM were:

Migration:	To water
Exposure:	Two sides
Thickness:	0.338 cm
Time:	1,008 hours
Polymer:	PVC (Unplasticized)
Migrant:	Calcium stearate, MW = 607 g/mol
Migrant Initial Concentration:	0.02 g/cm^3
External Phase:	Stagnant water at 20°C Volume: 0.002 m^3

Surface Area:	2112.8 cm^2
Surface Length:	14 cm

Since no diffusion coefficient was reported by the researchers, one was estimated by AMEM using the migrant molecular weight. For PVC (unplasticized), the diffusion coefficient was estimated as 9.34×10^{-23} cm^2/s. The worst case migration predicted by Eq. (3-23) was < 0.0001 fraction migrated, which is lower than the measured value of 5×10^{-4}.

Mass transfer resistance and partitioning effects were also considered. With a water flow velocity set equal to 10 cm/s and a pipe surface length of 14 cm (treated as flow over surface and not flow through pipe because the samples are small sections and involve 2-sided exposure), the mass transfer coefficient estimated by AMEM is 4.4×10^{-4} cm/s. The saturation concentration of calcium stearate in water is reported as 25 ppm or 2.5×10^{-5} g/cm^3. The fraction migrated predicted by Eq. (3-17) again was < 0.0001.

From both Eq. (3-23) and Eq. (3-17), the predicted value is lower than the measured fraction migrated. The reason for the lack of agreement is not known. For Examples #1 and #2, Figge et al. commented that the migration may be due to a surface release rather than a diffusional process. If this were the case in this example, the model would not be applicable. Another possibility is that the correlation by which the diffusion coefficient is estimated is inadequate. With reference to Figure 5 in Volume 11, the molecular weight of the stabilizer is higher than that for which data are available. Perhaps the correlation cannot be extrapolated.

Example #4 - Rigid Poly(vinyl Chloride) Pipe/Tin Stabilizer

In a separate experiment under the same conditions as Example #3, the migration of the dioctyl tin stabilizer, di(n-octyl)tin s,s'-bis(iso-octylmercaptoacetate), was measured from eight, schedule 40 PVC pipe specimens into a two-liter volume of water. In this case the initial concentration of the migrant was 1.2 phr or:

$$(1.2\ g/104.8\ g)(1.4\ g/cm^3) = 0.016\ g/cm^3$$

Thus, $(0.016\ g/cm^3)(357\ cm^3)$ or 5.7 g of the dioctyl tin stabilizer were initially present in the 357 cm^3 PVC pipe specimens. After the six weeks, the concentration of the stabilizer measured in the water was less than the detection limit of 0.002 ppm. In 2 liters or 2,000 g of water, this concentration corresponds to a stabilizer mass of less than 4.0×10^{-6} g or 4 μg. Converting this mass to a fraction of the initial migrant concentration indicates that less than a 7×10^{-7} fraction migrated in the 1,008 hours.

For this example, the inputs to AMEM were:

Migration:	To water
Exposure:	Two sides
Thickness:	0.338 cm
Time:	1,008 hours

Polymer:	PVC (Unplasticized)
Migrant:	Dioctyl tin stabilizer, MW = 751.8 g/mole
Migrant Initial Concentration:	0.016 g/cm^3
External Phase:	Stagnant water at 25°C Volume: 0.002 m^3
Surface Area:	2112.8 cm^2

Again, because no diffusion coefficient was reported for the stabilizer in the PVC, a value was estimated using the migrant molecular weight. The estimate for D_p was 1.25×10^{-23} cm^2/s. The worst case migration predicted by AMEM was again < 0.0001 fraction migrated.

Similar to Examples #1 through #3, partitioning and mass transfer resistances can be considered but will not reduce the fraction migration prediction because of the very low prediction under worst case conditions. For a 10 cm/s water flow velocity and a 14 cm polymer surface length, the mass transfer coefficient, k, was estimated as 4.4×10^{-4} cm/s. The solubility of the dioctyl tin stabilizer in water at 25°C is reported as less than 25 ppm or 2.5×10^{-5} g/cm^3. For this solubility in water and the initial concentration in the polymer, the partition coefficient, K, was estimated as 1.6×10^{-3}. The fraction migrated predicted by Eq. (3-17), which considers partitioning and mass transfer resistances, is again the same as that predicted with Eq. (3-23).

Example #5 - Low Density Polyethylene/Dihydroxybenzophenone

The migration of 2,4-dihydroxybenzophenone from three polyolefins was studied by Westlake and Johnson (1975). They performed both diffusion and migration studies to characterize the migration process. In the diffusion experiments, they measured the diffusion coefficient and the saturation concentration of the stabilizer in each polymer. Then, in migration tests, they measured the fraction migrated into water after 10 days. Both experiments, however, were conducted at 44°C, a temperature higher than the 20-30°C range for which the AMEM estimation procedures were developed. The results for low density polyethylene (LDPE) follow, while the results for high density polyethylene (HDPE) are reported in Example #6 and for polypropylene (PP) in Example #7.

The LDPE diffusion study was performed at 44°C using a coupon 0.15-cm thick and 3.5-cm in diameter. One side of the coupon was saturated with radiolabelled 2,4-dihydroxybenzophenone. The increase in the radioactive counting rate on the downstream side of the coupon, initially free of stabilizer, was monitored. The counting rate was monitored until an equilibrium rate was attained. At this point, the diffusion process had reached equilibrium and the polymer was saturated with the migrant. From the counting rate data, the diffusion coefficient was calculated to be 2.7×10^{-9} cm^2/s. The saturation concentration of 2,4-dihydroxybenzophenone in the LDPE was measured as 0.03 wt%.

In the migration experiment, a saturated LDPE coupon, 0.022-cm in thickness, was immersed in 10 mL of water at 44°C with both surfaces in contact with the water. The amount of stabilizer lost from the coupon after 10 days was determined from the concentration of the stabilizer in the water, which was changed periodically over the test duration. An important factor not reported was the frequency at which the 10 mL volume of water was changed. The authors only state that "the volume of water was well-mixed and changed at appropriate intervals" and that "the solubility of the stabilizer in water must be high relative to the concentrations encountered during the experiment."

After 240 hours (10 days), all of the stabilizer initially present in the LDPE had migrated into the water. For comparison purposes, the diffusion coefficient calculated from the migration data was reported as 4.2 x 10^{-9} cm^2/s, which is slightly higher than the value measured in the diffusion experiment.

Thus, the data input to predict migration under these conditions were:

Migration:	To water
Exposure:	Two sides
Thickness:	0.022 cm
Time:	240 hours
Polymer:	LDPE
Migrant:	2,4-dihydroxybenzophenone, MW = 214.21 g/mol
Migrant Initial Concentration:	0.03 wt% or 2.76 x 10^{-4} g/cm^3) (at a polymer density of 0.92 g/cm^3)
External Phase:	Water at 44°C Volume: 1 x 10^{-5} m^3 (10 cm^3) that is frequently changed and well-mixed
Surface Area:	19.24 cm^2

In this example, we used the D_p value measured in the diffusion experiment, 2.7 x 10^{-9} cm^2/s, as input to AMEM. Under worst case conditions using Eq. (3-23), AMEM predicts that all of the dihydroxybenzophenone migrates to the water in 240 hours, as was found in the migration experiment.

If the diffusion coefficient value was not reported, D_p could be estimated using AMEM, however, the value will underestimate the actual D_p in this case because the estimation technique applies only to the 20-30°C temperature range. The value predicted by AMEM from the molecular weight diffusion coefficient correlation for LDPE was 2.0 x 10^{-9} cm^2/s, which is only slightly lower than the value measured in the diffusion experiment. Using this estimated D_p value, AMEM also predicts a fraction migration of 1.0.

Although the external phase was reported to be well-mixed and frequently changed, partitioning and mass transfer effects can be considered if certain assumptions are made regarding the external phase. Although reported as well-mixed, we estimated a mass transfer coefficient value using a 10 cm/s water flow rate and a 3.5 cm surface length. The estimated value, 8.8 x 10^{-4} cm/s, thus represents a value approximating that for stagnant water. For partitioning effects, a value for K was estimated using the reported saturation concentration in the polymer, 2.76 x 10^{-4} g/cm^3, and a value for the saturation concentration in water, 1 x 10^{-4} g/cm^3 (Merck Index, 1990). Thus, K was estimated as 0.36. The volume of water was assumed to be only 1 x 10^{-5} m^3 (10 cm^3), which may underestimate the actual total volume because the 10 cm^3 volume was changed repeatedly. With these input values, AMEM predicts a fraction migrated of 0.95 using Eq. (3-17); thus partitioning and mass transfer resistances contribute only a very small effect. Because of the good agreement between the worst case model prediction and the data, mass transfer and partitioning factors apparently are not relevant. Even when using conservative assumptions, these conditions only reduce the fraction migrated prediction from 1.0 to 0.95.

Example #6 - High Density Polyethylene/Dihydroxybenzophenone

Similar diffusion and migration experiments were performed with HDPE coupons. From the diffusion experiment at 44°C, the diffusion coefficient was measured to be 5.8×10^{-10} cm^2/s and the saturation concentration of the 2,4-dihydroxybenzophenone in HDPE was reported as 0.003 wt%. In the migration experiment, a 0.8 fraction of the stabilizer initially present in the HDPE migrated into the water after 240 hours. Again, details regarding the mixing, total volume, and frequency of changing the water were not reported.

The following input data were used with AMEM:

Migration:	To water
Exposure:	Two sides
Thickness:	0.022 cm
Time:	240 hours
Polymer:	HDPE
Migrant:	2,4-Dihydroxybenzophenone, MW = 214.21 g/mol
Migrant Initial Concentration:	0.003 wt% or 2.88×10^{-5} g/cm^3 (at a polymer density of 0.96 g/cm^3)
External Phase:	Water at 44°C Volume: 1×10^{-5} m^3 (10 cm^3) that is frequently changed and well-mixed
Surface Area:	19.24 cm^2

As in the previous example, the diffusion coefficient value measured in the diffusion experiment, 5.8×10^{-10} cm^2/s, was first used to estimate the worst case migration. With this value, the worst case prediction using Eq. (3-23) would be that all of the dihydroxybenzophenone migrates to the water in the 240 hours. This prediction is close to but exceeds the reported value of 0.8 fraction migrated. Possibly, mass transfer or partitioning effects are factors in this case.

Again, although all values were not reported, some approximations can be made to judge whether partitioning or mass transfer affect migration. Although reported as well-mixed, we estimated a mass transfer coefficient value using a 10 cm/s surface flow rate and a 3.5 cm surface length. The estimated value was 8.3×10^{-4} cm/s. For partitioning effects, we estimated a value for K using the reported saturation concentration in the polymer and the value for the saturation concentration in water. Thus K was estimated as 3.47, which is quite high. The volume of water was assumed to be only 10 cm^3, which may underestimate the actual volume. With these input values, AMEM predicts a fraction migrated of 0.99 using Eq. (3-17); thus partitioning and mass transfer resistances are predicted to contribute only a small reduction in the fraction migrated. Consequently, the slight lack of agreement is attributed to the D_p value used, which overestimates the migration behavior. In fact, Westlake and Johnson report that a lower value of D_p was calculated from the migration test results as compared with the value from the diffusion experiment.

If a value for D_p had not been reported, one could be estimated using AMEM. The estimation technique, however, was developed for the temperature range from 20-30°C. At the molecular weight of 214.21 g/mol, AMEM estimates a value for D_p equal to 1.9×10^{-10} cm^2/s. For this value for estimated value of D_p, the fraction migrated prediction was 0.971 using Eq. (3-23) for worst case conditions, and a fraction migrated of 0.966 using Eq. (3-17) to consider mass transfer and partitioning limitations.

Example #7 - Isotactic Polypropylene/Dihydroxybenzophenone

Data were also reported by Westlake and Johnson for diffusion and migration experiments with an isotactic PP sample. The polypropylene polymer was reported to be 65% crystalline with a density of 0.9 g/cm^3. From the diffusion study at 44°C, the saturation concentration of the 2,4-dihydroxybenzophenone in the polypropylene coupon was reported as 0.07% by weight and the diffusion coefficient was reported as 5.5×10^{-11} cm^2/s. In the migration experiment, 0.7 of the stabilizer initially present migrated into the water after 240 hours. The input data to AMEM are:

Migration:	To water
Exposure:	Two sides
Thickness:	0.022 cm
Time:	240 hours
Polymer:	Isotactic PP, 65% crystalline
Migrant:	2,4-Dihydroxybenzophenone, MW = 214.21 g/mol
Migrant Initial Concentration:	0.07 wt% or 6.3×10^{-4} g/cm^3 (at a polymer density of 0.90 g/cm^3)
External Phase:	Water at 44°C Volume: 1×10^{-5} m^3 that is frequently changed and well-mixed
Surface Area:	19.24 cm^2

The diffusion coefficient measured in the diffusion experiment, 5.5×10^{-11} cm^2/s, was used to predict migration. In this case, AMEM predicts the worst case migration using Eq. (3-23) as 0.69 fraction migrated, which is in very good agreement with the measured value of 0.7.

As in Examples #5 and #6, partitioning and mass transfer effects can be considered if some assumptions are made regarding the experimental conditions. If the stagnant water scenario again assumed, the mass transfer coefficient is estimated as 8.8×10^{-4} cm/s. For partitioning effects, K was estimated as 0.16. Again, the total water volume was assumed to be 1×10^{-5} m^3. For these input values, AMEM predicts a fraction migrated of 0.64 using Eq. (3-17). The fraction migrated prediction is reduced somewhat when partitioning and mass transfer effects are considered. The difference, however, is quite small considering that several of the assumptions made regarding the required input values would exaggerate the influence of these effects.

Migration values could also be predicted using AMEM to estimate a value for D_p. In this case, however, one must consult Section 4.2, Table 7, and Figure 6, in Volume 11 because polypropylene is not one of the polymers for which D_p can be estimated directly by AMEM. To estimate D_p, one must select the polymer group representative of polypropylene in Table 3 and use Figure 6 to locate the value of D_p corresponding to the migrant's molecular weight. Isotactic polypropylene with a high degree of crystallinity (65%) is found at the bottom of the Polyolefins-II group. For MW = 214.21, and log (MW) = 2.33, the estimated value of D_p is 1×10^{-11} cm^2/s, which is close to the measured value of D_p. The measured value is higher because it was measured at 44°C whereas the data plotted in Figure 6 are for 20-30°C. With this value of D_p, AMEM predicts a worst case fraction migrated of 0.3 using Eq. (3-23), only approximately one half of the measured value. Again, this lower prediction is the result of using an estimated value for D_p that applies at lower temperatures.

Example #8 - High Density Polyethylene/3,5-Di-t-Butyl-4-Hydroxytoluene

In addition to their study of additive migration from rigid PVC, Figge, Koch and Freytag (1978) also investigated the migration of antioxidants from HDPE. The migration of two antioxidants, 3,5-di-t-butyl-4-hydroxy-toluene (BHT) and Irganox 1076®, was measured into water after 10 days at 40°C. The study involved a radiotracer technique in which the additives were synthesized with a ^{14}C label and incorporated into a HDPE compound that was then formed into sheet. The composition of the HDPE sheet specimens was:

	wt %
HDPE resin	99.7
BHT	0.2
Irganox 1076	0.1

Irganox 1076 is a trade name for octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate. Two samples of this blend were produced; one with the BHT radiolabelled and the other with the Irganox 1076 carrying the radiolabel. Test samples were pressed to a thickness of 0.035 cm and sample size was such that the exposed surface area was 9 cm^2. The exposure of the HDPE coupon was two-sided. The volume of the water used in the migration experiments, however, was not reported. The results for BHT follow and the results for Irganox 1076 are reported in Example #9.

The results for the 10-day migration experiment are given as a percentage of the initial additive amount. Figge et al. found that 0.48 weight percent or a fraction of 0.0048 of the BHT originally present had migrated into the water. Prediction of the migration under these conditions using AMEM requires the following data:

Migration:	To water
Exposure:	Two sides
Thickness:	0.035 cm

Time:	240 hours (10 days)
Polymer:	HDPE
Migrant:	BHT, MW = 220.4 g/mol
Migrant Initial Concentration:	0.2 wt.% or 1.92 x 10^{-3} g/cm^3 (at a polymer density of 0.96 gm/cm^3)
External Phase:	Stagnant water at 40°C
Surface Area:	9 cm^2
Surface Length:	1.2 cm

A value for the diffusion coefficient of BHT in the polymer was not reported but was estimated by AMEM based on the migrant molecular weight. The estimated D_p value was 1.7 x 10^{-10} cm^2/s. The fraction migrated estimated by the model is 0.75 under worst case conditions using Eq. (3-23). This estimate is more than two orders of magnitude higher than the 0.0048 fraction migrated reported by the authors and indicates that partitioning or mass transfer resistances may be controlling the migration rate. Mass transfer effects were considered by assuming that the stagnant volume of water has a low flow rate of about 10 cm/s over the 1.2-cm polymer surface length. The estimated mass transfer coefficient was 1.5 x 10^{-3} cm/s.

BHT is considered "insoluble" in water with a saturation concentration less than 1 ppm or 1 x 10^{-6} g/cm^3. A value for the saturation concentration at 40°C was estimated based upon the migrant molecular weight, melt temperature, and octanol water partition coefficient. For BHT, with a melt temperature equal to 70°C and log K_{ow} equal to 5.98, the water solubility was estimated by AMEM as 8.5 x 10^{-8} g/cm^3 at 25°C and 4.2 x 10^{-7} g/cm^3 at 40°C using the temperature extrapolation method (Eq. 8.15.5) in Reid et al. (1977). For this external phase saturation concentration and the initial concentration of BHT in the HDPE, the partition coefficient was estimated as 2.2 x 10^{-4}. This low value suggests that partitioning may affect the migration rate unless a very large volume of water is used as the external phase. Unfortunately, the authors do not report the volume of water used.

If an external phase volume of 1 x 10^{-4} m^3 (100 cm^3) is assumed, mass transfer and partitioning effects are predicted to reduce the fraction migrated to 0.12 when Eq. (3-17) was used. If an external phase volume of 1 x 10^{-5} m^3 (10 cm^3) was assumed, Eq. (3-17) predicts a fraction migrated 0.014. Thus, a change of one order of magnitude in external phase volume results in a reduction in the predicted migration by a factor of ten. This example demonstrates how the migration behavior can be strongly influenced by the external conditions and illustrates the importance of considering the specific conditions under which polymer products may be used when performing exposure assessments.

Example #9 - High Density Polyethylene/Irganox 1076

The migration of Irganox 1076 from the same HDPE sheet samples to water also was measured over a period of 10 days at 40°C. The result was that 0.065 wt% or 0.00065 of the antioxidant initially present migrated to the water. The following input data were used with AMEM to estimate migration under these conditions:

Migration: To water
Exposure: Two sides
Thickness: 0.035 cm
Time: 240 hours (10 days)
Polymer: HDPE
Migrant: Irganox 1076, MW = 530.9 g/mol
Migrant Initial Concentration: 0.1 wt% or 9.6×10^{-4} g/cm^3 (at a polymer density of 0.96 g/cm^3)
External Phase: Stagnant water at 40°C
Surface Area: 9 cm^2

As in Example #8, the volume of the external phase was not reported for this experiment. Neither was a value reported for the diffusion coefficient of Irganox 1076 in HDPE. A value at 20-30°C was estimated by AMEM using the migrant molecular weight and the correlation for HDPE. D_p was estimated as 5.0×10^{-12} cm^2/s. The worst case migration predicted using Eq. (3-23) was 0.13, which greatly exceeds the 0.00065 fraction migrated measured experimentally. However, if partitioning and mass transfer resistances are considered, the predicted migration is much lower.

For a 10 cm/s stagnant water flow velocity and the 1.2-cm surface length, the mass coefficient, k, was estimated as 1.5×10^{-3} cm/s. The solubility of Irganox 1076 is listed in the manufacturer's literature as less than 0.2 ppm or 2.2×10^{-7} g/cm^3 at 25°C and 1.1×10^{-6} g/cm^3 at 40°C. As for the estimation of partitioning effects, the partition coefficient, K, was estimated by AMEM as 1.15×10^{-3} using the saturation concentration in water at 40°C and the initial concentration of Irganox 1076 in the HDPE. A volume of 1×10^{-4} cm^3 (10 cm^3) was assumed because a value was not reported. For this volume, the fraction migrated predicted using Eq. (3-17) is 0.0508. If the external phase volume is further reduced to 1 cm^3, the Eq. (3-17) fraction migrated prediction is reduced to 0.007 which approaches the measured value.

Example #10 - Polystyrene/Styrene

General purpose polystyrene is widely used in food packaging applications. Commercial, food-grade polystyrene used in contact with food normally has a residual monomer concentration of less than 0.1% by weight. Arthur D. Little, Inc. (1981) measured the migration of styrene from crystalline polystyrene specimens into water at 40°C. Commercial polystyrene beads were blended with radiolabelled styrene and pressed into sheet at a thickness of 0.0254-cm. The monomer was incorporated into the polymer sheet at a level of 800 ppm. In the experiment, 13 sample coupons were immersed in 31 cm^3 of water, for a two-sided exposure, at 40°C. The total surface area of the coupons was reported as 100 cm^2. The test cell was agitated using a temperature controlled shaker bath. The concentration of styrene in the water was measured as a function of time and reported as a percentage of the styrene originally available for migration.

Data were reported at the following time intervals:

Time (hrs)	Percent Migrated	Fraction Migrated
1	0.16	0.0016
168	0.66	0.0066
1013	0.75	0.0075

Use of AMEM to predict the migration of styrene requires the following inputs:

Migration:	To water
Exposure:	Two sides
Thickness:	0.0254 cm
Time:	1 hour 168 hours 1013 hours
Polymer:	Polystyrene
Migrant:	Styrene, MW = 104 g/mol
Migrant Initial Concentration:	800 ppm or 8.32×10^{-4} g/cm^3 (at a polymer density of 1.04 g/cm^3)
External Phase:	Agitated water at 40°C Volume: 3.1×10^{-5} m^3 (31 cm^3)
Surface Area:	100 cm^2
Surface Length:	2 cm

The diffusion coefficient of the monomer in the polystyrene was reported as 3.3×10^{-13} cm^2/s, which was noted as being in good agreement with values reported in the literature. The measured value was used as input to AMEM to eliminate possible errors resulting from a value estimated at 25°C.

In this experiment the external phase was agitated but a flow velocity was not reported, so a value of 100 cm/s was used to approximate the water flow velocity over the 2.0-cm polystyrene surface length. Under these conditions, AMEM estimates the mass transfer coefficient as 3.7×10^{-3} cm/s. The solubility of styrene monomer in water at 40°C was determined experimentally by Lane (1946) and was reported as 400 ppm or 4.0×10^{-4} g/cm^3. Since styrene monomer is infinitely soluble in polystyrene, the saturation concentration in the polymer was set equal to the monomer density or 0.9 g/cm^3. This results in an estimated partition coefficient equal to 4.4×10^{-4}.

The predicted fractions migrated as a function of time under both worst case conditions and when considering mass transfer and partitioning effects were:

Time (hrs)	Fraction Migrated Worst Case Eq. (3-23)	Mass Trans./Part. Eq. (3-17)
1	0.0033	0.0025
168	0.040	0.009
1013	0.098	0.010

Although AMEM did not predict that complete partitioning had occurred using Eq. (3-17), it does indicate that the migration rate is so slow that little migration occurs during the period from 168 hours to 1,013 hours. The Eq. (3-17) predicted values again are in good agreement with the measured migration values.

Example #11 - Impact Polystyrene/3,5-Di-t-Butyl-4-Hydroxytoluene

Impact polystyrene (IPS) is used to package food products and has been investigated as pipe for water transport. IPS derives its impact resistance from rubber particles (usually polybutadiene) that are uniformly dispersed in the polystyrene matrix. Additives, such as antioxidants, lubricants, and processing aids, are also added to retard thermal degradation and to facilitate processing.

The migration of radiolabelled BHT from IPS into water at 49°C was measured by Arthur D. Little, Inc. (1981). The labelled antioxidant was incorporated into the commercially obtained polymer at a level of 1090 ppm. Sample sheets were pressed to a thickness of 0.045-cm. Six sample coupons, approximately 2-cm in diameter, were immersed in 16.3 cm^3 of water so that the exposure was two-sided. The test cell was agitated using a temperature controlled shaker bath. The concentration of the BHT in the water was measured after 5 and 35 days. The amount migrated was reported as μg of BHT per dm^2 of polymer surface area.

After 5 days (119 hours), 4.0 $\mu g/dm^2$ of BHT were measured in the water. To convert this number to a fraction of the initial BHT present, one must calculate the amount of BHT initially in the test sample. The total, two-sided surface area of the six sample coupons was reported as 46 cm^2 which is equivalent to a single-sided surface area per sample coupon of 3.83 cm^2. Multiplying this area by the 0.045-cm sample thickness results in an individual coupon volume of 0.1725 cm^3, and a total polymer volume of 1.035 cm^3. In this volume, there initially was 1,090 ppm of the BHT or:

$$[(1090 \text{ g BHT})/(1 \times 10^6 \text{ g IPS})](1.04 \text{ g IPS/cm}^3)(1.035 \text{ cm}^3) = 0.001173 \text{ g BHT}$$

at an IPS density of 1.04 g/cm^3. Given the total surface area of 46 cm^2 (or 0.46 dm^2), the 4.0 $\mu g/dm^2$ measured in the water represents 1.84 μg of BHT migrated and a fraction migrated of 0.0016. Similarly, the results after 35 days (840 hours) were reported as 12.5 $\mu g/dm^2$. This corresponds to 5.75 μg of BHT and a fraction migrated of 0.005.

With AMEM, the required input data are:

Migration: To water
Exposure: Two sides
Thickness: 0.045 cm
Time: 119 hours
840 hours
Polymer: Impact Polystyrene
Migrant: BHT, MW = 220 g/mol
Migrant Initial Concentration: 1090 ppm or 1.13×10^{-3} g/cm^3
(at a polymer density of 1.04 g/cm^3)
External Phase: Agitated water at 49°C
Volume: 1.63×10^{-5} m^3 (16.3 cm^3)
Surface Area: 46 cm^2
Surface Length: 2 cm

The diffusion coefficient of the BHT in the impact polystyrene was reported as 3.0×10^{-15} cm^2/s. This reported value was used as an input to AMEM. If a value had not been reported, one would estimate the diffusion coefficient in polystyrene using the molecular weight of the BHT. For the best accuracy, one would also need to account for the temperature difference between 49°C and the 20-30°C temperature range for which the D_p correlation was developed; a capability not now provided by AMEM.

Under worst case conditions, Eq. (3-23) predicts a fraction migrated of 0.0025 after 119 hours and a fraction migrated of 0.0048 after 840 hours. These estimates are both in good agreement with the measured values. Mass transfer and partitioning effects may also be considered. As in Example #10, a 100 cm/s flow velocity was assumed for the agitated water flow over the 2-cm polymer surface length. Under these conditions, k was estimated as 3.7×10^{-3} cm/s by AMEM. The manufacturer's literature reports BHT as "insoluble" but a value in g/cm^3 may be estimated at 25°C using the AMEM estimation procedure. BHT has a melt temperature of 70°C and a log (octanol/water partition coefficient) equal to 5.98. Using these parameters, the solubility in water was estimated by AMEM as 8.5×10^{-8} g/cm^3 at 25°C. This value was extrapolated to 49°C using Eq. 8.15.5 in Reid et al. (1977) with the estimated value equal to 1×10^{-6} g/cm^3. The partition coefficient, K, was estimated by AMEM as 8.9×10^{-4}.

When mass transfer and partitioning effects were considered, the fractions migrated predicted by AMEM were 0.0016 after 119 hours and 0.0037 after 840 hours. In this example, mass transfer and partitioning considerations reduce the migration predictions only by a small amount and remain in good agreement with the measured values.

Example #12 - Plasticized Poly(vinyl Chloride)/Di-2-ethylhexyladipate

Migration of a plasticizer was measured at 58°C from plasticized PVC into an air stream moving at about 1 ft^3/min by Quackenbos (1954). Quackenbos measured the migration of di-2-ethylhexyladipate (DEHA) from one side of a 0.1-cm thick PVC film of surface area 1000 cm^2 over a period of 400 hours. The plasticizer was initially present at a concentration of 65 phr. To calculate the concentration of plasticizer initially present in the polymer sample, parts per hundred resin was converted to g/cm^3 using the density of the plasticized PVC:

$$[(65)/(100+65)](1.22\ \text{g/cm}^3) = 0.48\ \text{g/cm}^3$$

Thus, initially there were 48 g of DEHA present in the 100 cm^3 of PVC sample. After 400 hours, Quackenbos measured the migration loss as 500 µg/cm^2 or:

$$(500\ \mu\text{g/cm}^2)(1000\ \text{cm}^2) = 5 \times 10^5\ \mu\text{g} = 0.5\ \text{g}$$

This mass represents a fraction migrated of 0.01.

To estimate migration under these conditions, AMEM was used with the following inputs:

Migration:	To air
Exposure:	One-side
Polymer:	Plasticized poly(vinyl chloride)
Thickness:	0.1 cm
Time:	400 hours
Migrant:	Di-2-ethylhexyladipate, MW = 371 g/mol
Migrant Initial Concentration:	65 phr or 0.48 g/cm^3
External Phase:	Air at 58°C, flowing at 1 ft^3 Volume: 680 m^3 (24,000 ft^3 after 400 hours)
Surface Area:	1000 cm^2

The diffusion coefficient for DEHA, at the reported initial concentration and 58°C, was calculated by Quackenbos to be 4.4 x 10^{-9} cm^2/s.

In a separate test, Quackenbos measured the mass transfer coefficient. A piece of cloth saturated with DEHA was placed in the warm air flow in place of the PVC film. After 400 hours, the cloth was weighed and a plasticizer loss of 0.0008 g/cm^2 was reported. Thus, the average loss rate was:

$$(0.0008\ \text{g/cm}^2)/[(400\ \text{hr})(3{,}600\ \text{s/hr})] = 5.6 \times 10^{-10}\ \text{g/cm}^2\text{-s}$$

From this loss rate, one may calculate the mass transfer coefficient, k, using the following relationship:

$$\text{Rate} = k \times C_{sat}$$

where C_{sat} is the saturation concentration of the migrant in the air external phase. Quackenbos reports a vapor pressure of 6.6 x 10^{-3} Pa for DEHA at 58°C. The saturation concentration was estimated using the vapor pressure, molecular weight, and temperature, as follows:

$$C_{sat} = (P_{vp})(MW)/(RT) = (6.6 \times 10^{-3})(371)/(8.314)(331)(10^{6}) = 8.9 \times 10^{-10} \text{ g/cm}^3$$

Using this saturation concentration and the average evaporation rate, the mass transfer coefficient was calculated:

$$k = \text{Rate}/C_{sat} = (5.6 \times 10^{-10} \text{ g/cm}^2\text{-s})/(8.9 \times 10^{-10} \text{ g/cm}^3) = 0.63 \text{ cm/s}$$

AMEM was first used to estimate migration under worst case conditions. The measured value of D_p equal to 4.4×10^{-9} cm^2/s was used. The fraction migrated predicted using Eq. (3-23) was 0.83, which is much higher than the measured value of 0.01.

Partitioning and mass transfer effect were then considered. The measured value for k was used with Quackenbos' value of D_p. AMEM estimated the partition coefficient as 9.6×10^{-10} using the value for C_{sat} and the saturation concentration of DEHA in the polymer set equal to the DEHA density of 0.925 g/cm^3 (because of its infinite solubility in PVC). K is low due to the low solubility of the plasticizer in air. However, the total volume of air to which the polymer surface is exposed is quite large, 680 m^3, since fresh air was continuously flowing over the surface. For these conditions, the fraction migrated predicted by AMEM using Eq. (3-17) is 0.005, much closer to the measured value of 0.01. In this example, mass transfer and partitioning limitations strongly influence the migration rate.

Example #13 - Plasticized Poly(vinyl Chloride)/Dibutyl Phthalate

Kampouris (1975) measured the migration of the plasticizer dibutyl phthalate (DBP) from a PVC film to water. The PVC film was initially plasticized at a level of 50 phr. Migration tests using a radiolabel technique were performed using 2-cm wide by 5-cm long by 1-mm thick samples, exposed on one side to 250 cm^3 of water. The amount of DBP that migrated into the water was measured after periods of 5 and 15 days.

After 5 days (120 hours), Kampouris measured 6.0×10^{-6} g/cm^3 in the 250 cm^3 of water. After 15 days (360 hours), the concentration was measured as 1.0×10^{-5} g/cm^3 in the 250 cm^3 of water. These concentrations correspond to a plasticizer mass of 0.0015 g after 120 hours and 0.0025 g after 360 hours. To calculate the fraction of DBP that migrated, one must calculate the amount of plasticizer initially present in the polymer sample at 50 phr:

$$[(50 \text{ g})/(150 \text{ g})](1.22 \text{ g/cm}^3) = 0.41 \text{ g/cm}^3$$

and

$$(2 \text{ cm})(5 \text{ cm})(0.1 \text{ cm}) = 1 \text{ cm}^3$$

Thus, there were initially 0.41 g of DBP in the PVC samples. The resulting fractions migrated were 0.0037 at 120 hours and 0.0062 at 360 hours.

Migration under these conditions was estimated by AMEM using the following input data:

Migration:	To water
Exposure:	One-side
Thickness:	0.1 cm
Time:	120 hrs 360 hrs
Polymer:	Plasticized poly(vinyl chloride)
Migrant:	Dibutyl phthalate, MW = 278 g/mol
Migrant Initial Concentration:	50 phr or 0.41 g/cm^3 (at a polymer density of 1.22 g/cm^3)
External Phase:	Stagnant water at 25°C Volume: 2.5×10^{-4} m^3 (250 cm^3)
Surface Area:	10 cm^2

No value for the diffusion coefficient was reported by the researchers. As indicated in Table 7 of Volume 11, the few experimentally measured values of D_p for plasticizer migration from PVC at 25°C reported in the literature fall within the Polyolefins-II category. Thus, an approximate value for D_p was estimated using Figure 6 and the DBP molecular weight. The estimated value for D_p was 2×10^{-11} cm^2/s. Migration under worst case conditions was first predicted by AMEM as 0.033 after 120 hours and 0.057 after 360 hours using Eq. (3-23), which exceed the measured values by about one order of magnitude.

Mass transfer resistances and partitioning limitations were then considered. A stagnant water flow velocity of 10 cm/s was again assumed and the 5-cm polymer plate surface length, was used to estimate the mass transfer coefficient. A value of 7.4×10^{-4} cm/s was estimated by AMEM. Because plasticizers are infinitely soluble in PVC, the density of DBP at 25°C, 1.046 g/cm^3, was used as the saturation concentration of the migrant in the polymer. If the density of the migrant or the true saturation concentration in the polymer was not known, then the 0.41 g/cm^3 initial concentration of DBP in the PVC compound could be used. Use of the initial concentration instead of the saturation concentration results in an estimate of K, the partition coefficient, greater than or equal to the true K, because additives are usually present at concentrations below their solubility limits.

The saturation concentration of the DBP in the water was reported by Haward (1943) and Monsanto (1983) as 0.0011 wt% or 1.1×10^{-5} g/cm^3 at 25°C. The partition coefficient was estimated by AMEM as 1.05×10^{-5} using the saturation concentration in water and the density of DBP. Based on these input values, AMEM predicts a fraction migrated of 0.0025 after 120 hours and 0.0026 after 360 hours using Eq. (3-17). Both these estimates are in fairly good agreement with the measured values, but underestimate the fraction migrated after 360 hours. Over the period from 120 to 360 hours, AMEM predicts that a partition equilibrium is approached and the migration process essentially stops.

REFERENCES

Arthur D. Little, Inc., "Migration from Styrene-Based Polymers: Styrene from Crystal Polystyrene and BHT from Impact Polystyrene," Summary report on FDA Contract No. 223-77-2360, 1981.

Bellobono, I.R., B. Marcandalli, E. Selli and A. Polissi, "A Model Study for Release of Plasticizers from Polymer Films Through Vapor Phase," J. Appl. Polym, Sci., Vol. 29, pp. 3185-3195, 1984.

Dietz, G.R., J.D. Banzer and E.M. Miller, "Water Extraction of Additives from PVC Pipe," J. Vinyl Tech., Vol. 1 (3), pp. 161-163, 1979.

Figge, K., J. Koch, and W. Freytag, "The Suitability of Simulants for Foodstuffs, Cosmetics and Pharmaceutical Products in Migration Studies," Rd. Cosmet. Toxicol., Vol. 16, pp. 135-142, 1978.

Haward, R.N., "Determination of the Solubility of Plasticizers in Water," The Analyst, Vol. 68, pp. 303-305, 1943.

Kampouris, E.M., "Study of Plasticizer Migration Using Radioactive Labelling," Rev. Gen. Caoutch. Plast., Vol. 54 (4), pp. 289-292, 1975.

Lane, W.H., "Determination of the Solubility of Styrene in Water and of Water in Styrene," Ind. and Eng. Chem., Vol. 18 (5), 295-296, 1946.

The Merck Index, 11th Ed., S. Budavari, Ed., Merck Co., Inc., Rahway, New Jersey, 1989.

Monsanto Co., "Plasticizer Performance in Polyvinyl Chloride Resin," Plasticizers and Resin Modifiers Book, 1983.

Quackenbos, H.M., Jr., "Plasticizers in Vinyl Chloride Resins, Migration of Plasticizer," Ind. and Eng. Chem., Vol. 46 (6), pp. 1335-1344, 1954.

Reid, R.C., J.M. Prausnitz and T.K. Sherwood, The Properties of Gases and Liquids, 3rd Ed, McGraw-Hill Book Co., New York, 1977.