

An overview of microphase catalysis

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Microphase catalysis denotes the use of a microdispersed phase (micelles, fine particles, emulsified droplets, etc.) to alter the rate and selectivity behaviour of a multiphase reaction system. This paper presents a concise review of the salient features of microphase catalysis. It dwells upon the types of modelling concepts and techniques used to devise pseudo-homogeneous analyses for the intensification effects of a microphase on multiphase reaction rates. With minimal emphasis on mathematical descriptions, the basic structure of the microphase strategy is brought out. The evolution of models to account for the growing complexity of the physical situations encountered over a wide range of cases is discussed.

Intensification of multiphase reactions

Multiphase reaction systems are perhaps the most commonly encountered situation in industrial practice and therefore form the very core of chemical reaction engineering. The rates of multiphase reactions are normally limited by the diffusion of a sparingly soluble solute in the phase in which the reaction takes place¹. The objective in such reaction systems, is to bring in contact, reactants which normally reside in different phases. For this to happen, at least one of the reagents must be transferred from its original phase of residence to the other wherein it interacts and reacts with the other reagent. Obviously, here the simplest case of two reactants—two phases is being referred to; additional complexity is imparted to the system if *both* the reactants 'leak' from their original phase into the other phase. The multiplicity of reactants and products, reaction schemes, physical phases are indeed all sources of considerable complexity.

Figure 1 shows a process that occurs near the interface formed by the two original phases (hereafter referred to as the macrophases, the interface between them being referred to as the macrointerface). Solute A, resident in phase I, diffuses into phase II where it undergoes a reaction with resident reactant B, homogeneously. In the situation being considered, diffusional gradients of solute A in phase I have been neglected as usually A will show a high solubility/concentration in its original phase. Typically, however, for lean gas mixtures (phase I being the gas phase) this may not be true and diffusional gradients will occur here also. Also, B is taken to be nonvolatile such that it does not enter phase I. Solute A usually shows a sparing solubility in phase II and the concentration of B in this phase may

be order(s) of magnitude higher than the typical values for A; in such a situation, B will not deplete in the vicinity of the interface and its diffusional gradients may be neglected.

Consider first, the effect of chemical reaction on the physical situation: usually the concentration gradients become steeper and from Fick's conventional constitutive equation, $R_A = -D_A \partial A / \partial x|_{x=0}$, we have that the rate of interphase mass transfer (of A) becomes larger than in the absence of such reaction. The elaborate theory of mass transfer with chemical reaction including complex multiphase, multisolute, multireaction systems may be found elsewhere¹. In the simplest instance (as well as most other instances) discussed here one of the main aims is to maximize the interphase mass transfer flux, very often referred to as the specific rate of reaction (absorption, extraction, dissolution depending upon phase I being a gas, liquid or solid, respectively), so that the reactor size may be minimized; other aims may include maximization of certain product yields, selective removal of one solute in a multisolute system etc. A variety of strategies have been investigated for this purpose, such as, for instance, the use of phase transfer catalysts which facilitate the transfer of solute A into phase II by forming, dissolved, reversible complexes²; the use of emulsifying agents which lower the interfacial tension, most dramatically for liquid-liquid systems, lead to an increase in the macrointerface area per unit reactor volume³.

Yet another set of strategies now labelled under the class of 'microphase catalysis' have been investigated very comprehensively over the last decade or so, its origins, however, lying even earlier. Microphases are constituted by tiny, dispersed phase particles/droplets whose characteristic size is much smaller than the diffusional length scales of the rate limiting, diffusing solute, A. Thus, a microdispersion of any phase (solid/liquid or even gas) in phase II and immiscible with it would constitute a micro-phase, the totality of the continuous phase and the microphase being referred to as the microheterogeneous media. Typical microphases are micelles, microemulsion droplets, fine particles of reactants or adsorbent/catalysts such as activated carbon, an emulsified second liquid phase and fine bubbles.

Intensification of multiphase reactions through the use of a microphase involves varieties of physical mechanisms which basically exploit one or more of the special properties of the microphase with respect to the

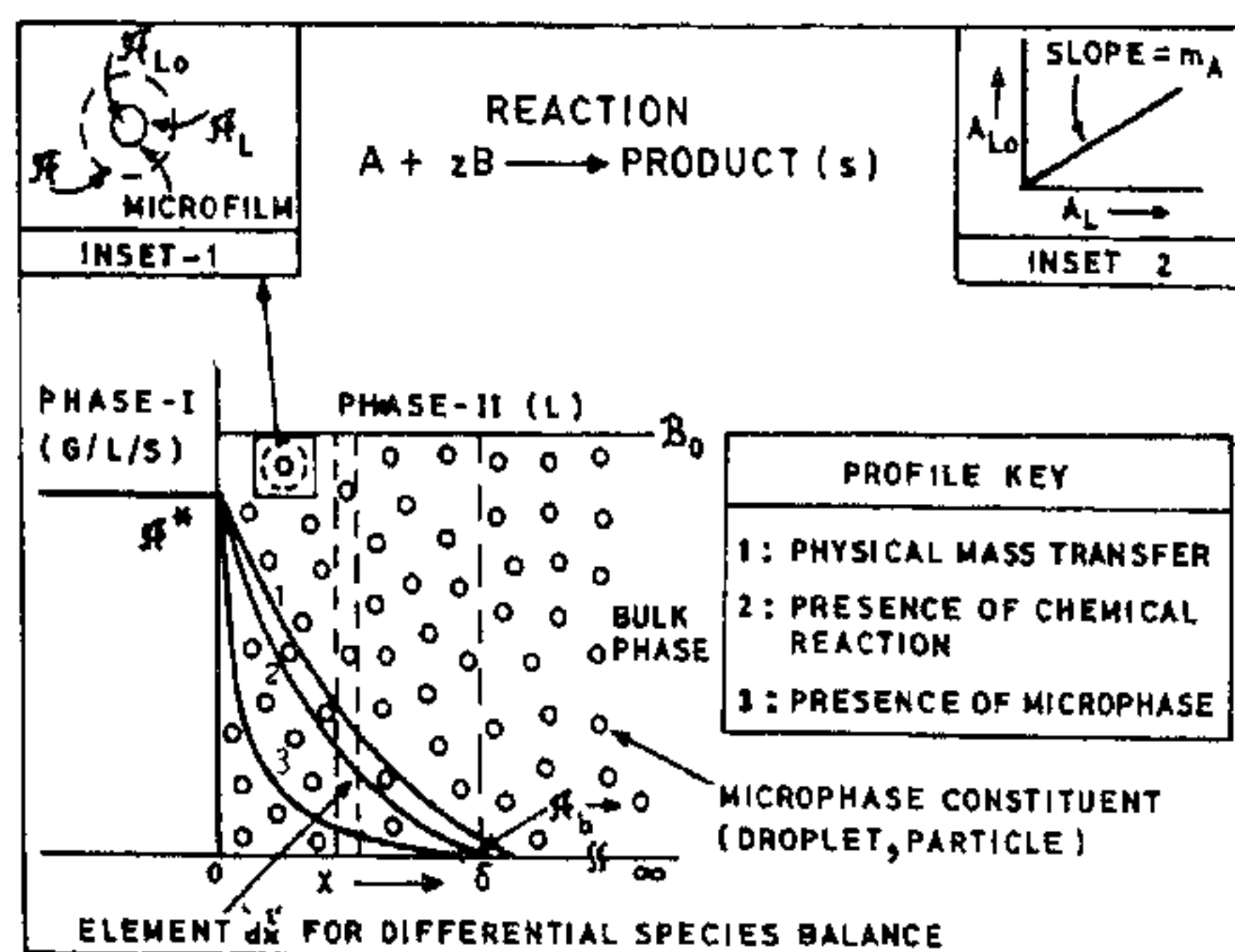


Figure 1. Physical picture for mass transfer with chemical reaction in presence of a microphase.

sparingly soluble solute A. Special properties that are relevant in this context include selective solubilizing action/adsorption and reversible chemical reaction. The essential action of the microphase is to interact with the diffusing solute A, near the macrointerface, formed by the original macrophases, in such a way so as to remove it from the vicinity of the macrointerface either by reaction or by accumulation (solubilization) and subsequent release into the bulk of the continuous phase II. In order that the microphase and the diffusing solute interact, the physical dimensions of the microphase constituents must be smaller than the diffusional length scales in the original system. Normally, the constituent sizes lie in the micron and the submicron size ranges and it is of pertinence that it is the relative size of the microdispersed material that is significant rather than the absolute degree of smallness. Figure 1 shows the effect of the microphase-solute interaction on the concentration profile of the diffusant; the gradients, just like in the case of a chemical reaction, become steeper leading to enhanced interphase fluxes.

Table 1 gives information for some typical systems, the basic phenomena under consideration, microphase action and category as well as system and reference details. For purposes of generality, microphases may be divided into three major classes, with respect to the solute A, namely: (a) sinks for the diffusing solute A—a sink may be physically or chemically active but releases no extrinsic species into the continuous phase. Thus, an emulsified second liquid phase or a slurry of insoluble reactant particles would constitute sinks; (b) catalysts providing for reactive interaction between A and B within or on them—a catalyst may be distinguished from other types of chemical sinks in that it provides no extraneous, truly identifiable species capable of interacting with either of the original reactants, i.e. A and B other than what may be classified as catalytic sites within or on the microphase constituent. Instances

Table 1. Some examples of microphase catalysis.

Original system	Phenomena*	Microphase/action
Carbonation of lime slurry	Dissolution	Lime slurry/reactant ⁸
Oxidation of Na ₂ S	Absorption	Carbon particles/catalyst ⁹
Oximation of cycloalkanones	Dissolution	Micelles/solubilization/catalyst ¹¹
Alkaline hydrolysis of solid esters	Dissolution	Carbon particles/adsorbent ¹⁰
Alkaline hydrolysis of solid esters	Dissolution	Emulsified second phase/physical solubilization ¹²
Absorption of olefinic gases into aqueous H ₂ SO ₄ solutions	Absorption	Emulsified second phase/physical solubilization ¹²
Oxidation of Na ₂ SO ₃	Absorption	Emulsified second phase/physical solubilization
Absorption of hydrogen in metal alloy hydride suspended in oil	Absorption**	LaNi ₅ H _x alloy slurry/insoluble reactant ¹⁵
Absorption of H ₂ S in iodine solutions	Absorption	Product sulphur/adsorbent ¹⁶
Oximation of cycloalkanones and alkaline hydrolysis of solid esters	Dissolution	Microemulsions/solubilization/catalyst

*Accompanied by reaction in the continuous phase.

**No reaction in oil phase.

are provided by fine carbon particles, micelles and microemulsions; (c) sources of liquid phase (II) reactant B or an independent reactant C—this definition is restricted to slurry sources whose material is at least sparingly soluble in the continuous liquid phase. It is obvious that a source for B (or C) is equivalent to a sink for A since either of the former reactants consume A by reaction. However, this reaction does not occur within or on the microphase but in the continuous phase. A typical example would be the slurry of sparingly soluble hydroxide in an aqueous medium reacting with the diffusing (dissolved) gas, such as carbon dioxide/sulphur dioxide. In some instances, a microphase may invoke more than a single mechanism, like a combination of solubilization (accumulation) and reaction, thus providing an example of mixed behaviour. The categorization of a microphase sometimes is a matter of preference; someone's adsorbent may be somebody else's insoluble reactant.

Mass transfer models

Having outlined the basic features of microphase action, it is required now to understand how these interactions may be incorporated into established models for mass transfer processes. The discussion is restricted to the case of diffusional gradients present only in phase II (only the mass transfer coefficient in this phase is of interest).

One-parameter models of mass transfer are used most commonly in engineering literature partly because they provide reasonably good estimates of the transfer rates and partly because in the more complex two-parameter models it is conceptually not possible to relate both parameters to the single empirically known quantity—the mass transfer coefficient. More fundamental approaches like, for instance, the boundary layer models, often give rise to intractable mathematics without any essential gain in accuracy.

For these reasons, single parameter models, describing the overall effects of diffusion coupled with convective transport are ubiquitous in the literature and have been successfully extended to include the effects of an accompanying chemical reaction^{1,4}. Of these, the simplest model describing the steady state transfer process is the film model which incorporates the resistance to transfer within a thin, fictitious film near the macrointerface. This model, however, is inherently limited in application to steady state situations and cannot be used if transient phenomenon like accumulation are significant. Time-dependent phenomenon are therefore more readily characterized by the unsteady models of Higbie and Danckwerts. Both these models make use of a time (or frequency)-based parameter, thus making it conceptually possible for transient processes to be incorporated within them. Unsteady models provide for elements of fluid which arrive at the interface, absorb the solute and return to the bulk fluid to lose their identity. These surface eddies spend a fixed, constant time (contact time, t_c) at the macrointerface according to Higbie's model (which is somewhat unrealistic) and have an exponentially decaying surface age distribution in Danckwerts' model. It has been shown that the estimates of the mass transfer rates are affected only marginally by the age distribution⁵. The commonly employed technique of transforms to solve the species balance equations of transport problems, as written for these models, may give rise to algebraic expressions in the transformed domain which are fairly difficult to invert as is the case for Higbie's model. The Danckwerts' model obviates this problem by using an exponential age distribution to find averages such that the surface renewal frequency becomes identical to the transform (*Laplace*) domain variable. Herein lies the power of the Danckwerts' model, its limitation being the applicability of the technique usually to linear formulations. The definition of the specific rate, from Danckwerts' theory of mass transfer, is given as $R_A = s \mathcal{L}(-D_A \partial \mathcal{A} / \partial x|_{x=0})$ where s , the *Laplace* domain variable can be equated to k_L^2 / D_A , as an outcome of the averaging process. This is so because the fraction of surface elements spending a time between t and $t + dt$ was assumed by Danckwerts to be $s \cdot \exp(-st)$ which implies that the average flux for elements of all ages (whole surface) is given by

$\int_0^{\infty} (-D_A \partial \mathcal{A} / \partial x|_{x=0}) s \cdot \exp(-st) dt$, which is in fact directly related to the definition of the *Laplace transform*.

In microheterogeneous media, especially where accumulation of the rate limiting solute is extremely significant, transient models have to be used and it is pertinent to note that the different unsteady models yield answers which are only marginally different from each other.

The basic idea, then, is to use sophisticated extensions of these conventional mass transfer models to account for the effect of the microphase. Such models are classified as pseudohomogeneous ones; the implications of pseudohomogeneity are brought out clearly later in the paper.

The uptake process

The way in which the microphase constituents interact with the diffusing solute A needs to be outlined first, in order that its incorporation into the mass transfer models is understood.

The uptake process consists of many steps such as the diffusion of the solute to the surface of the microphase constituent and its subsequent internal diffusion accompanied by adsorption/reaction on/within it. The primary complexity encountered here is the size and shape of the microphase constituents; even though all microphase samples are likely to have a definite particle size distribution, it is customary to work with an 'average' size of the microphase rather than develop intricate population balance-based models. Similarly, different shapes can usually be treated by the use of shape factors rather than focusing on the actual curvature of the constituent which may be quite random and jagged; conventionally, a spherical particle is usually analysed. The next conceptual problem is the nature of the relative motion of the microphase constituent with respect to the continuous medium. In the well-stirred bulk phase this relative motion may be quite substantial but near the macrointerface, within the surface element which is deemed to be stagnant and rigid, such motion may be neglected. For very small particles, however, there may be a nonnegligible intensity of Brownian motion of the microparticles which may have a substantial effect on the uptake rates. It can be shown that such effects usually are active only for a short range of the operating parameters and may usually be ignored⁶. The microparticles may therefore be assumed to be stationary in the fluid element and in such a case the external film-based mass transfer coefficient for uptake may be calculated by assuming Sherwood number = 2, even though this is an approximation for a spherical particle immersed in an infinite medium. For this approximation to hold good, at least the external film which surrounds a single microphase

constituent must not overlap with any other film associated with a neighbouring microparticle; this requires the fractional hold up of the microphase to be quite low—a condition normally incorporated in the assumption of pseudohomogeneity. For the usual case when the microphase has a much higher solubility for the diffusing solute compared to the continuous phase, the controlling resistance to uptake will lie in the external phase film. It has been shown that an internal Sherwood number based on the concentration difference at the surface of the particle and the average amount of solute it contains is equal to $2\pi/3$ so that a distribution coefficient (microphase/continuous) $\gg 3$ will ensure no internal diffusional resistance⁶. This however need not be true for cases such as that of (inverted) water-in-oil media⁷. The above considerations would also apply to the diffusion of the species B or C from the microphase constituent, in the case of a type (c) microphase.

The solute A may simply accumulate in/on the microphase or may undergo adsorption, reversible complexation or even irreversible chemical reaction. Some of these processes may occur simultaneously, such as accumulation and reaction, though usually one may be dominant. The uptake process would therefore be expected to be function of the diffusion coefficients, the distribution coefficient and the kinetic parameters associated with the complexation/reaction/adsorption, etc. It is very necessary to note, however, that uptake by the microphase and chemical reaction in the continuous medium are mutually competitive in that both 'consume' the solute and therefore reduce its accessibility for the other process.

Theoretical developments

The earliest works in this area have been concerned with the microphase as reactant (type (c)), such as the carbonation of lime slurry⁸. Subsequent investigations have involved the use of fine carbon particles as catalysts/adsorbents^{9,10} and micellar solutions¹¹. In all these instances, the film theory has been used dominantly and in most cases suffices well. Unsteady models reported for many of these systems have been used out of considerations inherent to the basic system (such as D_A and D_B being very different) rather than any complexity introduced by the microphase¹.

A unified view of these pseudohomogeneous, film theory-based models, is summarized below for type (a) and (b) microphases only:

Species balance equation for A in phase II film at the macrointerface

$$D_A \frac{d^2 \mathcal{A}}{dx^2} = k_1 \mathcal{A} + l_0 k_0 \mathcal{A} \quad (1)$$

with the boundary conditions

$x=0$ (macrointerface) $\mathcal{A} = \mathcal{A}^*$ (interfacial solubility of A

in phase II); $x=\delta$ (film/bulk boundary) $\mathcal{A} = \mathcal{A}_b = 0$ (usually). (2)

No balance on the species B is required if it is assumed not to deplete near the macrointerface. The solution for the specific reaction rate (interphase flux) is given by

$$R_A = -D_A \left. \frac{d\mathcal{A}}{dx} \right|_{x=0} = k_L \mathcal{A}^* (\text{Ha}')^{1/2} / \tanh(\text{Ha}')^{1/2} \quad (3)$$

where $\text{Ha}' = \text{modified Hatta number} = D_A (k_1 + l_0 k_0) / k_L^2$. The enhancing effect of the microphase (specific rate in presence of the microphase divided by that in its absence) is given by the ratio

$$\Phi = \left\{ \frac{\text{Ha}'}{\text{Ha}\delta} \right\}^{1/2} \frac{\tanh(\text{Ha})^{1/2}}{\tanh(\text{Ha}')^{1/2}} \quad (4)$$

where $\text{Ha} = \text{Hatta number} = D_A k_1 / k_L^2$ and $\delta = D_A / k_L$ as per the basic definition from the film model¹. When Ha and $\text{Ha}' \gg 10$, the enhancement factor becomes

$$\Phi = (1 + l_0 k_0 / k_1)^{1/2} \quad (5)$$

k_1 being the pseudo first order reaction rate constant ($= k_2 \cdot \bar{\mathcal{B}}_0$) in the continuous (external) phase, l_0 being the fractional volumetric hold up of the microphase and k_0 being a suitable uptake coefficient whose various forms are discussed below:

CASE I

$k_0 = k_{SL} a_p = 12 D_A / d_p^2$ (Sherwood no. = 2 $\Rightarrow k_{SL} = 2 D_A / d_p$; $a_p = 6 / d_p$) for external film coefficient controlled uptake, the concentration of A in/on the microphase being zero due to relatively rapid internal reaction⁹. (6)

CASE II

$k_0 = m_A k_{1m}$ for internal, irreversible reaction controlling in the microphase constituent locally saturated with A, i.e. when $(k_{SL} a_p \gg m_A k_{1m})^{11}$. (7)

CASE III

$k_0 = \left[\frac{1}{k_{SL} a_p} + \frac{1}{m_A k_{1m}} \right]^{-1}$ for a mixed control when

the concentration of A in/on the microphase constituent is non-zero¹⁰. (8)

A similar analysis for type (c) situations is only slightly more complex and was first reported by Ramachandran and Sharma⁸.

The use of the steady state approach, in the above cases, is facilitated by the process of accumulation of

the solute A in the microphase constituent being rendered negligible because of the equality in the rate of uptake and the internal rate of irreversible reaction. Such a steady state is not possible if there is no internal reaction. Therefore, for a purely physically active microphase which acts only by solubilizational/adsorptive accumulation (and subsequent discharge of this into the bulk phase where the concentration of A is low), it is imperative to use the unsteady state models of mass transfer. The film theory is incompatible with such inherently transient situations. The unsteady models are summarized below⁶:

Species balance equation for A in phase II in the continuous phase of the surface element

$$D_A \frac{\partial^2 \mathcal{A}}{\partial x^2} = (1-l_0) \frac{\partial \mathcal{A}}{\partial t} + (1-l_0) k_1 \mathcal{A} + l_0 k_{SL} a_p (\mathcal{A} - \mathcal{A}_L) \quad (9)$$

Accumulation equation for A in a single microphase droplet

$$m_A \frac{\partial \mathcal{A}_L}{\partial t} = k_{SL} a_p (\mathcal{A} - \mathcal{A}_L) = k_{1m} \mathcal{A}_L \quad (10)$$

Even though this model becomes important when $k_{1m} = 0$, for the sake of generality, the internal reaction term has been included in eq. (10); the last term in eq. (9) represents the rate of uptake by the microphase. The accompanying conditions are given by

$$\text{IC: } t=0 \text{ all } x \mathcal{A} = \mathcal{A}_L = \mathcal{A}_b = 0 \quad (11)$$

$$\text{BCs: } t > 0 \text{ } x=0 \mathcal{A} = \mathcal{A}^*, \text{ } x \rightarrow \infty \mathcal{A} \rightarrow \mathcal{A}_b r(t).$$

The expression for the interphase flux is now given by:

Higbie's model:

$$R_A = \frac{1}{t_c} \int_0^{t_c} D_A \frac{\partial \mathcal{A}}{\partial x} \Big|_{x=0} dt = \mathcal{A}^* [D_A (1-l_0)]^{1/2} I/t_c$$

$$\text{where } I = \int_0^{t_c} [f(u) + b f_1(u) + c f_2(u)] [g(u) h(u)] du;$$

$$f(u) = \text{erf}(m_1 u) / (\pi u)^{1/2}; f_1(u) = \text{erf} [(-m_1 u)^{1/2}] / (-m_1)^{1/2};$$

$$f_2(u) = \int_0^u f_1(y) dy; g(u) = \exp [(m_2 - \omega)(t_c - u)/2];$$

$h(u) = I_0 [(m_2 + \omega)(t_c - u)/2]$; I_0 is the modified Bessel function of zeroth order; and $b = k_1 + l_0 k_{SL} a_p / (1-l_0) +$

$$k_{SL} a_p / m_A + k_{1m}; c = k_1 k_{SL} a_p / m_A + k_1 k_{1m}$$

$$+ l_0 k_{SL} a_p k_{1m} / (1-l_0);$$

$$\omega = k_{SL} a_p / m_A + k_{1m} \text{ and } m_1 \text{ and } m_2 \text{ are the roots of the equation } v^2 + b v + c = 0. \quad (12)$$

Also, from Higbie's model $t_c = 4D_A / \pi k_L^2$.

Danckwerts' model:

$$R_A = s \int_0^\infty -D_A \frac{\partial \mathcal{A}}{\partial x} \Big|_{x=0} \exp(-st) dt = \mathcal{A}^* [D_A (1-l_0)]^{1/2} I_1$$

where $I_1 = [(s^2 + b s + c)/(s + \omega)]^{1/2}$ the constants b, c and ω being as defined above and $s = k_L^2 / D_A$ (surface renewal frequency). (13)

Simplified cases:

I. When $k_{1m} / (k_{SL} a_p / m_A) \gg 1$ (rate of internal reaction \gg uptake rate) and $[(1-l_0)k_1 + l_0 k_{SL} a_p] t_c / (1-l_0) \ll 1$ eqs. (12) and (13) reduce to eq. (6). This is also known as the *transport controlled regime*.

II. When $k_{1m} / (k_{SL} a_p / m_A) \ll 1$ (rate of internal reaction \gg uptake rate; leads to internal saturation) and $[(1-l_0)k_1 + l_0 m_A k_{1m}] t_c / [(1-l_0) + l_0 m_A] \gg 1$, eqs. (12) and (13) reduce to eq. (7).

III. When $k_{1m} / (k_{SL} a_p / m_A) \ll 1$ and the second condition for the above case II is reversed, the specific rate of reaction is given by

$$R_A = k_L \mathcal{A}^* [(1-l_0) + l_0 m_A]^{1/2} \quad (14)$$

Cases II and III come under the purview of the *relative solubility controlled regime*.

The last equation (14) is particularly interesting and brings out the role of a physically solubilizing microphase clearly, when all internal reactive effects may be neglected and unsteady state analyses become indispensable. The microphase constituents which load themselves with the solute A near the macrointerface, discharge this solute into the bulk phase where the concentration of A is much lower than at the macrointerface. In fact, if the rate of consumption of A by reaction in the bulk phase is too low, the presence of a solubilizing microphase will cause this bulk phase concentration to become higher, due to discharge of loaded solute, compared to the situation when the microphase is absent, thus reducing its efficacy as a 'catalytic' agent. On the other hand if the value of the pseudo first order reaction rate constant becomes too large, the relative contribution of the microphase towards enhancing the specific rate goes down as consumption of A by reaction near the macrointerface reduces the amount of A available to the microphase for uptake. Hence the optimal situation is one where the (continuous) liquid phase reaction rate constant is

efficiently high to keep the bulk concentration of A near zero, in the presence of a solubilizing microphase, but still not high enough to manifest itself noticeably near the macrointerface. A more detailed, quantitative discussion, involving non-zero bulk phase concentrations of A has been reported by Mehra *et al.*¹²

Figure 2 shows the enhancement factor for a stated set of operating conditions, in the presence of a physically solubilizing microphase. For very small microconstituent sizes the enhancement factor becomes sensitive to this size and depends solely upon the distribution coefficient. In this situation the microphase is always locally saturated with the solute; in other words partitioning equilibrium is attained almost instantaneously.

A comprehensive theory of microphase catalysis covers a large variety of cases. Table 2 shows the significant situations which come under the purview of this strategy. Most of these analyses are now available in the literature^{6, 12, 13}

An important case which brings out the power of the Danckwerts' model with respect to linear systems, when combined with the method of linear operators, is that of desorption of a solute in the presence of a microphase, which is generated by a reversible chemical reaction. Herein a physically solubilizing microphase acts to transport the generated solute from the microheterogeneous bulk phase to the macrointerface from where it is sorbed.

Figure 3 shows the concentration profiles in a surface element, for solute A which is being desorbed, in the presence of a nonreactive, emulsified second liquid phase. Solute A is generated by the reaction scheme, $A \xrightleftharpoons[k_{-1}]{k_1} B$ in the original liquid phase and it is assumed that the microphase has an exclusive preference for A while it is inert with respect to B. The mathematical representation of this process in matrix form is given by

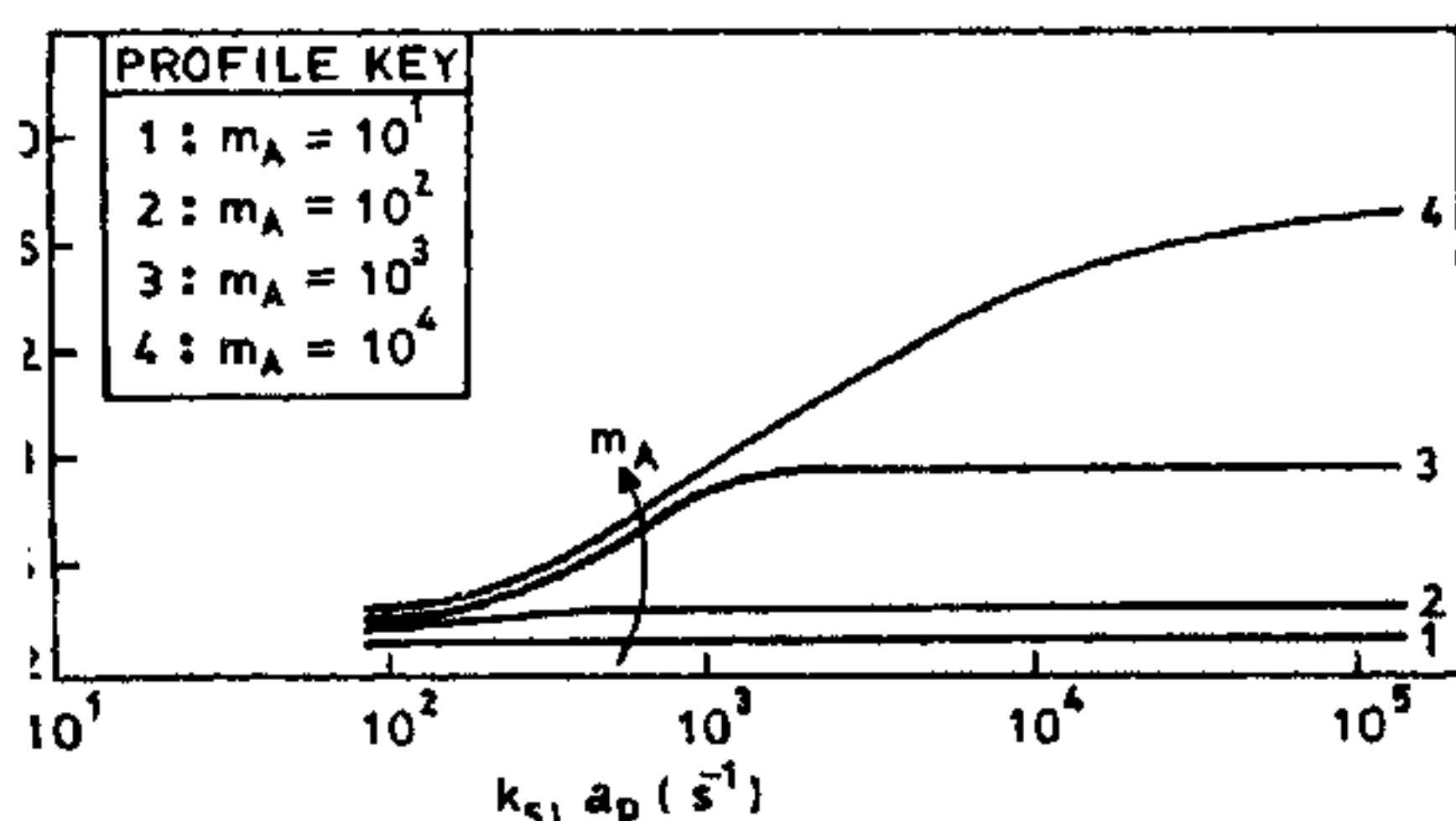


Figure 2. Plot of enhancement factor vs uptake transfer coefficient distribution coefficient as parameter. Data used: $k_L = 3 \times 10^{-5}$ m/s, 1 s^{-1} , $k_{1m} = 0$, $D_A = 7 \times 10^{-10}$ m²/s, $l_0 = 0.1$, d_p range covered through $k_{SL} a_p [= (2D_A/d_p)(6/d_p)]$ 0.1–10 μm .

Table 2. Cases covered by the theory of microphase catalysis.

Title	Remarks	Reference
Brownian motion of particles	Danckwerts' model and linear operators used	6, 13
Stationary droplet approximation	Simple rate expression from Danckwerts' model	6, 12
Finite (non-zero) bulk concentrations	Macrobalances for batch mode reported	12
Instantaneous reaction between A and B	Moving boundaries lead to error function solutions	6
Reversible complexation (reaction)	Shows analogy between 'solubilization' and reaction	13
Desorption preceded by reversible reaction	Danckwerts' model and linear operators used	13
Separation of gas mixtures	Utilization of differences in affinity for microphase	16
Manipulation of selectivity and product distribution	Preliminary analysis: advantages and cautions indicated	13
Product as microphase (autocatalytic)	Growth and nucleation treated separately	13, 18
Inverted systems (water in oil media)	Internal gradients; Danckwerts' model used	7
Exhaustible microphases	Nonlinear solute partitioning leads to moving boundaries and error functions	15

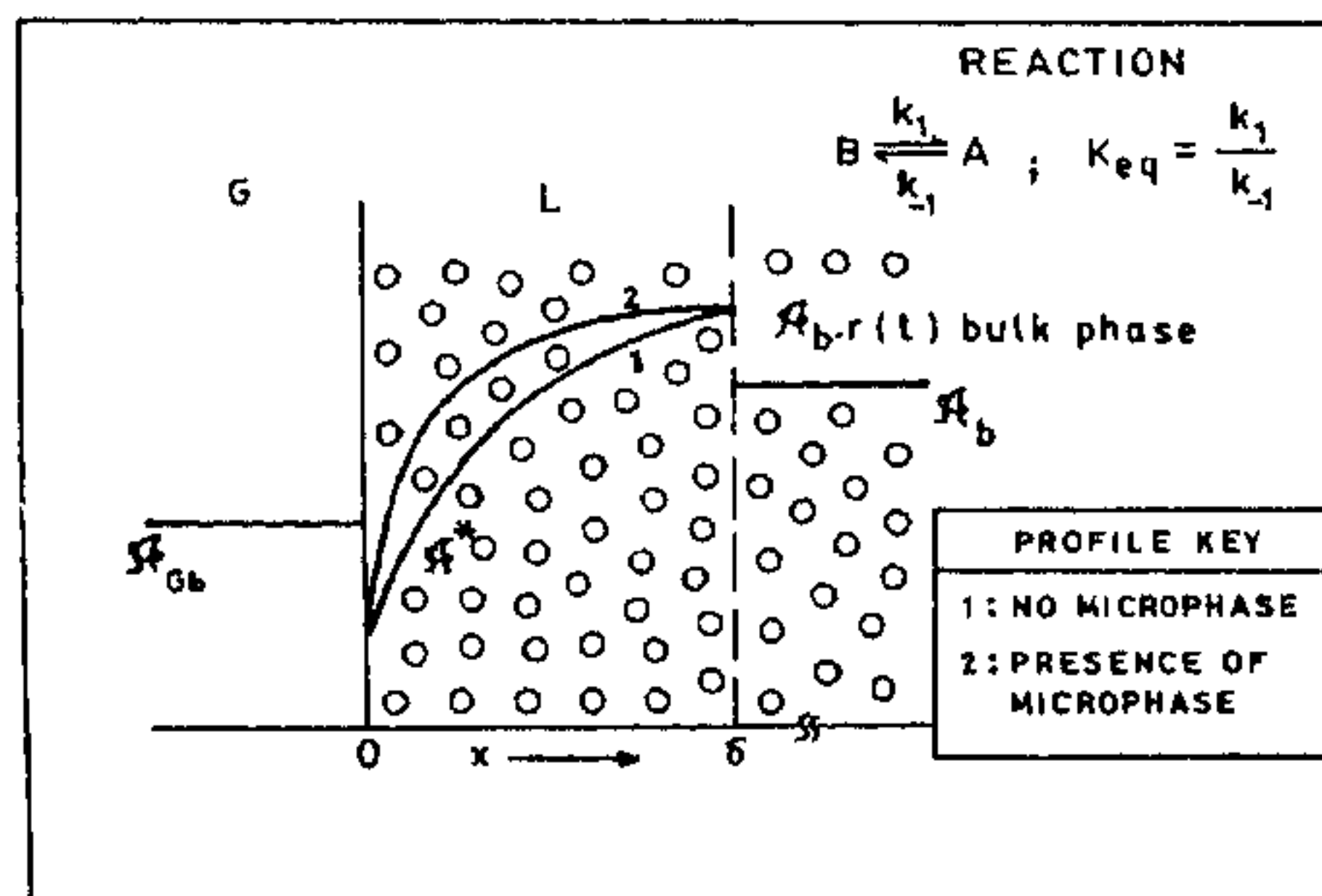


Figure 3. Physical picture for desorption preceded by reversible chemical reaction in presence of a microphase. Solute A is desorbed while B is nonvolatile.

$$\frac{\partial^2 \mathbf{a}(s)}{\partial x^2} = \mathbf{k}(s) \mathbf{a}(s) - \mathbf{c}(s) \quad (15)$$

where $\mathbf{a}(s)$ is a concentration vector in the Laplace domain and $\mathbf{k}(s)$ is a coefficient matrix (2×2) which is a function of the forward and backward rate constants (k_1, k_{-1}), the uptake coefficient ($k_{SL} a_p$), the distribution coefficient (m_A) the volumetric hold up (l_0) of the microphase and the surface renewal frequency (s). The final rate expression for the interphase desorption flux involves the eigenvalues of the matrix $\mathbf{k}(s)$ as well as its

determinant. The linear operator formalism treats the vectors and matrices as single variables and uses the Sylvester expansion of a matrix to compute the function of a matrix argument (such as $\exp(\mathbf{k})$, for instance)¹⁴. It is evident that the use of Higbie's model, instead, would have given rise to intractable mathematics due to the problem of inversion of the Laplace domain expression into the real time domain.

Figure 4 shows the variation in the enhancement factor with the equilibrium constant, $K_{eq} = k_1/k_{-1}$, (with distribution coefficient as parameter). It may be seen that for large values of K_{eq} , as the reaction approaches irreversibility, there is no effect on the enhancement factor. For the lower range of K_{eq} values, the enhancement factor decreases with the value of the equilibrium constant. This is because for a fixed k_1 , low K_{eq} implies that k_{-1} is increased and the rate of consumption of A by reaction near the gas-liquid interface goes up; so much so that the A discharged by the microphase is also consumed leading to a lower value of the enhancement factor. This competitive effect is also observed in the case of gas absorption wherein consumption by reaction and 'consumption' by the microphase are somewhat mutually competing⁶.

The effect of Brownian motion of the microphase constituents on the interphase flux has also been assessed using this combination of linear operators and Danckwerts' model⁶.

Another instructive analysis, this time of an inherently nonlinear situation, which needs to be formulated in terms of moving boundaries within the surface element is that of homogeneous, instantaneous reaction between A and B in the continuous phase. This, however, is true in the presence as well as absence of the microphase. A more novel situation where moving boundaries occur because of the microphase is that where the solubilization/adsorption equilibrium for the partitioning of solute A is nonlinear in nature (nonconstant distribu-

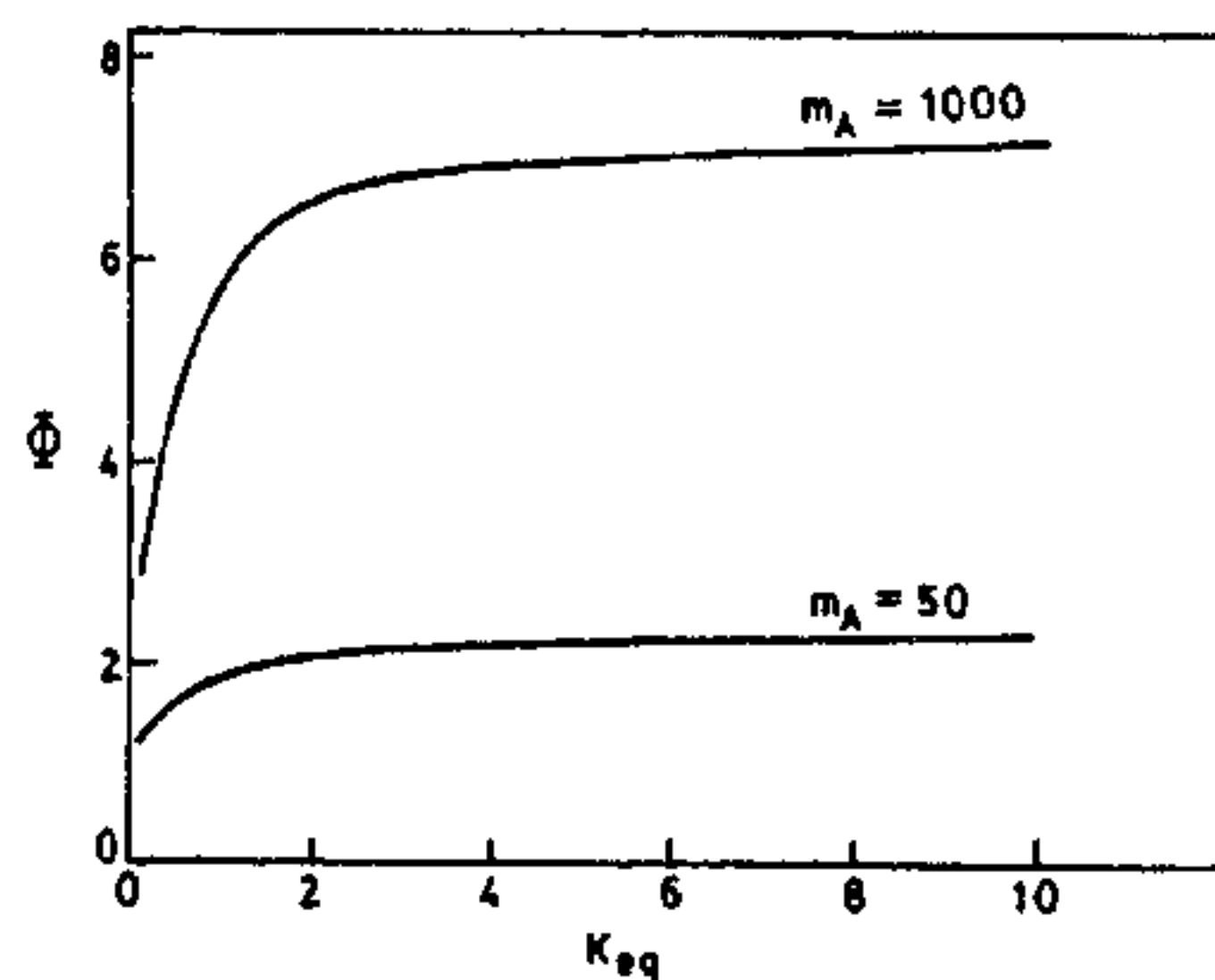


Figure 4. Plot of enhancement factor vs equilibrium constant for the desorption of A with distribution coefficient as parameter. Data used: $k_L = 1 \times 10^{-4}$ m/s, $k_1 = 10$ s⁻¹, $D_A = D_B = 1 \times 10^{-9}$ m²/s, $a^* = 1 \times 10^{-3}$ kmol/m³, $a_b = 5 \times 10^{-3}$ kmol/m³, $K_{eq} = k_1/k_{-1}$.

tion coefficient). Here the actual nonlinear curve may be linearized piecewise, each linear segment representing a constant value of the distribution coefficient. A surface element may thus be divided into separate zones each of which corresponds to the different linear segments of the equilibrium curve. Figure 5 explains this in a schematic manner. The inset shows the piecewise linear approximation to the actual nonlinear equilibrium curve. The corresponding physical zones and their motion with time is marked on the main figure.

The solutions obtained here for the specific rates are in terms of error functions and belong to the classical family of solutions derived for the analyses of processes such as zone melting¹⁵.

Microphases may also be used for the purposes of separation of solutes by exploiting the difference in the relative affinity of the solutes for the microphase. Some theoretical considerations have been reported in the literature¹⁶.

Experimental observations

Table 3 shows some comparisons between experiment and theory for some selected systems. The observed agreements may be regarded as excellent and demonstrate the validity of the modelling approaches discussed above.

Critical comments

The approach discussed here concerns pseudohomogeneous models and is rigorously valid only for low hold ups of the microphase. Hence the solute diffusivity in the continuous phase is assumed to be the same as in

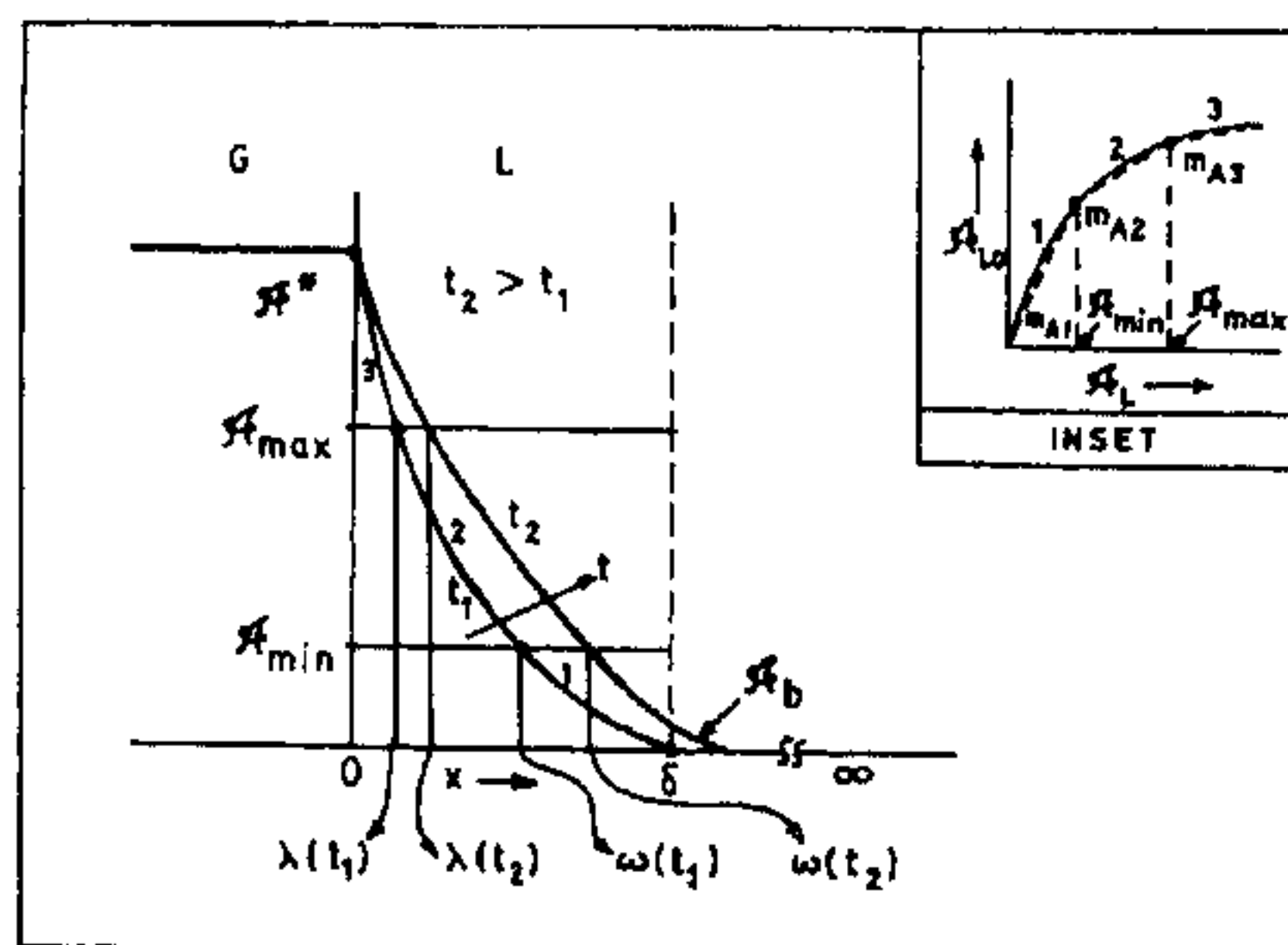


Figure 5. Physical picture for mass transfer in presence of an exhaustible microphase (nonlinear solute partitioning); no chemical reaction. Three-zone approximation is shown. Segments 1, 2 and 3 in inset correspond to physical zones 1, 2 and 3 in main figure as marked on the curve $t = t_1$ by dots. a_{max} and a_{min} are the zone-dividing concentrations.

Table 3. Some comparisons between experiment and theory.

System name	System properties	Microphase hold up (vol %)	Φ (Theory)	Φ (Expt.)
Isobutylene absorption in emulsions of chlorobenzene in aqueous sulphuric acid	$k_L = 1.74 \times 10^{-5}$ m/s $k_1 = 3.21 \times 10^{-1}$ s $^{-1}$ $d_p = 2.0 \times 10^{-6}$ m $m_A = 1617$ $D_A = 1.14 \times 10^{-9}$ m 2 /s	0.01	2.85	2.11
		0.05	6.10	5.78
		0.20	12.10	11.00
		Equipment: stirred cell with flat interface		
<i>Remarks: Mildly stirred gas-liquid system; bulk concentration of A is zero</i>				
Butene-1 absorption in emulsions of chlorobenzene in aqueous sulphuric acid	$k_L = 1.27 \times 10^{-5}$ m/s $k_1 = 2.48 \times 10^{-1}$ s $^{-1}$ $d_p = 8.0 \times 10^{-7}$ m $m_A = 2014$ $D_A = 6.19 \times 10^{-10}$ m 2 /s	0.02	7.92	7.29
		0.05	12.43	12.31
		0.10	17.51	17.98
		Equipment: stirred cell with flat interface		
<i>Remarks: Mildly stirred gas-liquid system; bulk concentration of A is zero</i>				
2,4-dichlorophenyl benzoate hydrolysis in emulsions of chlorobenzene in aqueous alkali hydroxides	$k_L = 9.8 \times 10^{-6}$ m/s $k_1 = 5.8 \times 10^{-1}$ s $^{-1}$ $d_p = 3.5 \times 10^{-6}$ m $m_A = 8890$ $D_A = 5.9 \times 10^{-10}$ m 2 /s	0.02	3.45	4.00
		0.05	5.70	6.73
		0.10	8.00	9.10
		Equipment: mechanically agitated contactor		
<i>Remarks: Intensely stirred solid-liquid system; bulk concentration of A is zero</i>				
Phenyl benzoate hydrolysis in emulsions of chlorobenzene in aqueous alkali hydroxides	$k_L = 1.2 \times 10^{-5}$ m/s $k_1 = 3.8 \times 10^{-2}$ s $^{-1}$ $d_p = 3.5 \times 10^{-6}$ m $m_A = 5170$ $D_A = 6.4 \times 10^{-10}$ m 2 /s	0.02	4.63	3.00
		0.04	6.78	4.80
		0.05	7.73	5.80
		Equipment: mechanically agitated contactor		
<i>Remarks: Intensely stirred solid-liquid system; bulk concentration of A is non-zero</i>				

the absence of the microphase. Furthermore, the interfacial area between the macrophases is treated as 'unhindered' by the presence of the microconstituents and the microfilms surrounding these microparticles are assumed not to overlap. This also implies that the value of the basic parameter of the mass transfer model used (t_c or s), which essentially represents the lumped hydrodynamic effects, remains unaltered in the presence of the microphase. Pseudohomogeneous models are popular, often analytically presentable and conceptually simple to formulate. Truly heterogeneous models, which are applicable for high hold ups of the microphase are comparatively complicated and at the current moment have been discussed in the literature in a tentative, ad-hoc manner; however, very recently, an excellent, truly heterogeneous, steady state analysis has been reported¹⁷. The development of these models is essential for the mass transfer theory to advance into the realms of densely packed media.

The analysis of microphase-bearing situations has not yet focused on the use of population balances, agglomeration and coalescence frequencies, etc. to construct more rigorous models and these must be explored in a phased way to assess whether the mathematical complexities introduced are necessary from the

point of view of the physics, the required degree of accuracy and the extent of error and uncertainty in the experimental data. Such an approach is likely to prove indispensable when analysing situations involving: (i) autocatalytic effects (product acts as microphase— nucleation and growth of the product precipitate need to be accounted for); (ii) intense turbulence so that agglomeration/coalescence and redispersion of the microphase constituents become very significant; (iii) relatively broad constituent size distributions are obtained inherently in the process of creating the microdispersion. Very limited experimental data exist involving the above mentioned conditions; in fact, the only reported experimental work¹⁸, on a system of considerable industrial importance in the area of hydrogen sulphide removal from gas streams, deals with autocatalytic and rapid agglomeration complexities occurring simultaneously; these data have been analysed with the help of lumped models only¹⁸. Even in the absence of sufficient experimental data, however, population balance-based approaches can provide a theoretical basis for the effects that are to be expected and with what magnitude.

In this context it is important to note that surfactant-based systems may provide excellent and flexible model

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systems in the laboratory for the generation of experimental data. Considerable amount of model testing carried out till now has been with emulsified phases, micelles and microemulsions¹².

A comprehensive review of 'microphase catalysis' including the cases listed in Table 2, heterogeneous models, breakdown limits of the pseudohomogeneous approach etc. has been reported recently¹³.

Nomenclature

A	volatile diffusing species
\mathcal{A}	concentration of dissolved A in continuous liquid phase, kmol/m ³
\mathcal{A}_b	bulk concentration of A in continuous liquid phase, kmol/m ³
\mathcal{A}_L	concentration of A in the microphase on an equivalent continuous phase basis, kmol/m ³
\mathcal{A}_{L0}	concentration of A in the microphase, kmol/m ³
\mathcal{A}^*	interfacial solubility of \mathcal{A} at operating partial pressure on gas side, kmol/m ³
a_p	specific microphase-continuous phase interfacial area per unit volume of microphase, m ² /m ³
$\mathbf{a}(s)$	concentration matrix (Laplace domain)
B	non-volatile continuous liquid phase (II) reactant
\mathcal{B}	concentration of B in continuous liquid phase, kmol/m ³
\mathcal{B}_0	bulk concentration of B in continuous liquid phase, kmol/m ³
b	constant defined in eq. (12), s ⁻¹
C	independent species reactive towards A residing in the microphase
$\mathbf{c}(s)$	constant matrix in eq. (14)
c	constant defined in eq. (12), s ⁻²
D_A	diffusivity of A in continuous liquid phase, m ² /s
D_B	diffusivity of B in continuous liquid phase, m ² /s
d_p	microphase constituent size (dia.), m
$f(u)$	function defined in eq. (12), s ^{-1/2}
$f_1(u)$	function defined in eq. (12), s ^{1/2}
$f_2(u)$	function defined in eq. (12), s ^{3/2}
$g(u)$	function defined in eq. (12), dimensionless
Ha	Hatta number defined in eq. (4), dimensionless
Ha'	modified Hatta number defined in eq. (3) dimensionless
$h(u)$	function defined in eq. (12), dimensionless
I	constant defined in eq. (12), s
I_1	constant defined in eq. (13), s ^{-1/2}
K_{eq}	equilibrium constant for reversible reaction for the case of desorption ($=k_1/k_{-1}$), dimensionless
k_1	(forward) (pseudo) first order rate constant for consumption (absorption)/generation (desorption) of A, s ⁻¹

k_{1m}	(pseudo) first order internal reaction rate constant for reaction between A and C (or B), s ⁻¹
k_{-1}	(backward) first order rate constant for consumption of A (desorption), s ⁻¹
k_L	gas-liquid mass transfer coefficient (liquid side), m/s
k_{SL}	mass transfer coefficient based on external film around microparticle, for uptake/release of A, m/s
k_0	uptake coefficient for pickup/release of A, s ⁻¹
$\mathbf{k}(s)$	coefficient matrix in eq. (14)
l_0	fractional volumetric hold up of microphase (based on total liquid + microphase), dimensionless
m_A	distribution coefficient of A between microphase and continuous phase (microphase/continuous), dimensionless
m_1, m_2	roots of characteristic equation associated with eq. (12), s ⁻¹
R_A	specific rate of absorption of A, kmol/m ² .s
$r(t)$	decaying function of associated with bulk conditions; see eq. (11), dimensionless
s	Laplace domain variable; also the surface renewal frequency = k_L^2/D_A , s ⁻¹
t	time, s
t_c	contact time from Higbie's model ($=4D_A/\pi k_L^2$), s
u	dummy variable, s
v	dummy variable, s ⁻¹
x	space coordinate in a surface element, m
y	dummy variable, s
Φ	enhancement factor in the specific rate of absorption/desorption of A, defined as the rate in presence of a microphase divided by that in its absence, dimensionless
δ	thickness of the fictitious diffusion film at the gas-liquid macrointerface, m
ω	constant defined in eq. (12), s ⁻¹

1. Doraiswamy, L. K. and Sharma, M. M., *Heterogeneous Reactions*. Vol. 1, Wiley, New York, 1984.
2. Lele, S. S., Bhawe, R. R. and Sharma, M. M., *Chem. Eng. Sci.*, 1983, 38, 765.
3. Lele, S. S., Bhawe, R. R. and Sharma, M. M., *Ind. Eng. Chem.*, 1983, 22, 73.
4. Danckwerts, P. V., *Gas-Liquid Reactions*, McGraw Hill, New York, 1970.
5. Danckwerts, P. V., Kennedy, A. M. and Roberts, D., *Chem. Eng. Sci.*, 1963, 18, 63.
6. Mehra, A., *Chem. Eng. Sci.*, 1988, 43, 899.
7. Mehra, A., *Chem. Eng. Sci.*, 1989, 44, 448.
8. Ramachandran, P. A. and Sharma, M. M., *Chem. Eng. Sci.*, 1969, 24, 1681.
9. Pal, S. K., Juvekar, V. A. and Sharma, M. M., *Chem. Eng. Sci.*, 1982, 37, 327.
10. Janakiraman, B. and Sharma, M. M., *Chem. Eng. Sci.*, 1985, 40, 235.

11. Janakiraman, B. and Sharma, M. M., *Chem. Eng. Sci.*, 1985, **40**, 223.
12. Mehra, A., Pandit, A. and Sharma, M. M., *Chem. Eng. Sci.*, 1988, **43**, 913.
13. Mehra, A., *Handbook of Heat and Mass Transfer* (ed. Chermisinoff, N. P.), Gulf Publishers, New Jersey, 1990, Vol. 5.
14. Ramkrishna, D. and Amundson, N. R., *Linear Operator Methods in Chemical Engineering*, Prentice Hall, New Jersey, 1985.
15. Mehra, A., *Chem. Eng. Sci.*, 1990, **45**, 1525.
16. Mehra, A. and Sharma, M. M., *Chem. Eng. Sci.*, 1988, **43**, 2541.
17. Juvekar, V. A. and Karve, S., *Chem. Eng. Sci.*, 1990, **44**, 587.
18. Mehra, A. and Sharma, M. M., *Chem. Eng. Sci.*, 1988, **43**, 1071.

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A correlation study of radon in dwellings with radium content of soil

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Various national and international surveys have demonstrated an increase in radon (Rn) levels in dwellings and consequently there is a continuous growing concern about its health effects on the population. Rn progeny levels in dwellings are likely to be a multiple of outdoor levels. The main sources of indoor levels are the ground, the building materials, tap-water and domestic gas supplies. In houses with high concentration, the main source of Rn is the soil gas of the subjacent ground. Rn in soil gas depends on the radium content of the soil and the soil density. In India the first set of measurements were made in about 800 houses, which were identified as high background areas, and soils in these areas contain comparatively high levels of uranium and thorium. These measurements have given a geometric mean of 10.6 mWL for potential alpha energy concentration corresponding to a mean effective dose equivalent of 3.31 mSv. The second set of measurements consists of 1200 dwellings confining to mostly normal background areas. The measurements have given a mean value of 3.4 mWL corresponding to a dose equivalent of 1.16 mSv. The results of high background areas show about 2.8-fold increase compared to the background areas.

The results of the soil radioactivity content in some high background areas when compared with the measured Rn levels in dwellings in nearby locations show that as soil activity increases, Rn levels tend to increase. In some cases a positive correlation has been obtained between Rn concentration in dwellings and the radium content of the soil. However, this trend is not observed always. This may be due to the influence of meteorological parameters, that affect the emanation rate. The relation between the emanation rate and the Rn and its progeny concentration in dwellings have been discussed.

formations. Rn gas, generated within the soils, diffuses into the atmosphere in measurable amounts. The rate of emanation depends on many factors like type and meteorological parameters. Various national and international surveys have demonstrated an increase in Rn levels in dwellings and consequently there is a growing awareness about its health effect on the population. Rn progeny levels in a dwelling are likely to be a multiple of outdoor air.

The main sources of indoor levels are the ground, the building material, tap-water and domestic gas supply. In houses with higher concentrations, the main source of Rn is the soil gas of the subjacent ground. Rn in soil gas depends on the radium content of the soil and soil density.

The physical characteristics of soils, density of the gas and void fractions, influence the transport of Rn and exhalation rate of Rn in the atmosphere. The present study was undertaken with a view to finding out whether a correlation exists between the Rn levels in dwellings with radium content of the soil.

Measurement procedure

Indoor Rn levels in dwellings were measured using a passive technique. The method consists of exposing small strips of LR-115 Type II solid state nuclear track detector (SSNTD) of 2.5 × 2.5 cm affixed on a rectangular card in the dwelling. The detector card is suspended from the roof or ceiling of the dwelling environment for a known period of exposure time ranging from 40 to 60 days.

The detector cards after the exposure period were retrieved and were chemically etched in a suitable alkali

Rn-222 occurs widespread throughout nature, arising from radium-226 present in practically all natural