MULTICOMPONENT SURFACE DIFFUSION OF ADSORBED SPECIES: A DESCRIPTION BASED ON THE GENERALIZED MAXWELL–STEFAN EQUATIONS

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Abstract—Surface diffusion of n sorbed species is described using the generalized Maxwell–Stefan (GMS) formulation of irreversible thermodynamics. The approach treats the vacant sites (V) as the $(n + 1)$th component in the diffusing mixture. The diffusion coefficients defined in the GMS treatment are basically of two kinds: (i) the coefficients $Ð_{iV}$, signifying the facility for diffusive exchange between species i and the vacant sites; and (ii) the coefficients $Ð_{ij}$, describing the facility for counter-exchange between the sorbed species i and j. The GMS counter-sorption diffusivity is, in turn, relatable to the coefficients $Ð_{iV}$ and $Ð_{jV}$; the latter are estimated from single-sorbent diffusivity data. The direct influence of the fractional surface occupancies θ_i on the transfer rates is made transparent in the analysis. Several special cases have been analysed. For diffusion of a single sorbed species the Fick surface diffusivity D_{1V} is related to the GMS diffusivity $Ð_{1V}$ by

$$D_{1V} = Ð_{1V}/(1 - \theta_1)$$

a known result; the GMS coefficient $Ð_{1V}$ is commonly referred to as the "intrinsic" or "corrected" diffusivity while the Fick coefficient D_{1V} is usually termed the "apparent" diffusivity. The expression for the tracer diffusivity:

$$D^* = 1 \bigg/ \left(\frac{\theta_t}{Ð_{12}} + \frac{1 - \theta_t}{Ð_{1V}} \right)$$

derived from the GMS formulation is a convenient new result; its utility in interpretation of tracer diffusion data is demonstrated using the experiments of Pope (1967, *Trans. Faraday Soc.* **63**, 734–742). Surface diffusion of multicomponent $(n \geq 2)$ sorbed species is described by a matrix of Fick diffusivities $[D] \equiv [B]^{-1} [\Gamma]$. The elements of $[B]$ are explicitly related to the GMS coefficients $Ð_{iV}$ and $Ð_{ij}$, while the matrix of thermodynamic factors $[\Gamma]$, derivable from the adsorption isotherm, portrays the direct influence of the surface occupancies θ_i on surface transport. The results of the prediction of $[D]$ for binary sorption are in broad agreement with the Monte Carlo simulations of Palekar and Rajadhyaksha (1986, *Chem. Engng Sci.* **41**, 463–468). For constant value of the Fick matrix $[D]$, analytical solutions for transient uptake of multicomponent mixtures are obtained as n-dimensional matrix analogs of the corresponding solution for single-component sorption. The application of the suggested solution technique is demonstrated by simulation of the transient uptake of n-heptane and benzene on NaX zeolite. The model is capable of reproducing the maximum in the n-heptane kinetic sorption curve, as experimentally observed by Kärger and Bülow (1975, *Chem. Engng Sci.* **30**, 893–896). Analysis of binary counter-sorption using the GMS approach helps to explain the experimental observation that adsorption and desorption rates may be significantly different; the rationale is to be found in the dependence of the GMS counter-sorption diffusivity on surface composition. It is concluded that the GMS formulation provides the most convenient practical formulation of multicomponent surface diffusion.

INTRODUCTION

The understanding and modelling of the diffusion process inside the *micro*pores (typically having pore sizes smaller than 2 nm) of adsorbent and catalyst particles poses many challenges for the experimentalist and theoretician alike [cf. Ruthven (1984) for a recent summary of developments in this area]. With an upsurge of applications involving zeolites, the proper description of intracrystalline diffusion assumes enhanced importance because of its influence on the selectivity of separations and reactions.

There are several factors which make the description of microporous diffusion distinguishable from diffusion in *macro*pores (typically having pore sizes

exceeding 20 nm) (Weisz, 1973). Firstly, diffusion inside micropores, especially those for which the channel sizes approach molecular dimensions, is strongly affected by the parallel occurrence of surface diffusion; indeed it is difficult to separate the contributions of these two phenomena in most conventional experiments. Secondly, viewed at a molecular level, the transferring species inside the *micro*pores never really leave the force field exerted by the surface and in this sense the phenomenon is distinct from Knudsen diffusion. Haag *et al.* (1981) have demonstrated, for example, that the diffusivity of a molecule inside a narrow zeolite channel could be significantly *higher* than would be expected if one were to use the Knudsen theory. Thirdly, the diffusivity inside *micro*porous structures like zeolites exhibits a strong dependence on the surface occupancy and shows a strong exponential temperature dependence characteristic of

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an activated process; this is not the case in *macroporous* transport.

Our overall objective in this paper is to develop a generally applicable formulation of microporous, or surface, diffusion of multicomponent ($n \geq 2$) sorbed species and specifically to provide a methodology for prediction of multicomponent surface transfer rates from information on the transfer rates of the individual components. While there are several approaches to the prediction of sorption equilibrium of a mixture from sorption equilibrium of individual components [cf. Ruthven (1984)], a parallel approach for prediction of multicomponent surface transfer rates is lacking.

Published treatments of multicomponent surface diffusion use either the generalization of the Fickian concept [cf. Marutovsky and Bülow (1982) and Palekar and Rajadhyaksha (1986)] or the Onsager formulation of irreversible thermodynamics [cf. Ash and Barrer (1967), Barrer (1978) and Kärger and Bülow (1975)]; neither approach offers a methodology for prediction of multicomponent transport from information on single-species transport. Now, for the case of diffusion in non-ideal "bulk" fluid phases it is now generally well recognized that the generalized Maxwell–Stefan (GMS) formulation, which has its basis in irreversible thermodynamics (Krishna, 1987; Lightfoot, 1974; Standart *et al.*, 1979), provides the most convenient and practical description. Its superiority over the alternative, but equivalent, Onsager formalism lies in the fact that the transport coefficients defined in the GMS formulation are more easily amenable to physical interpretation and, equally importantly, the GMS formulation provides a basis for prediction of multicomponent transfer behaviour on the basis of the corresponding information for the binary pairs in the mixture (Krishna, 1977; Krishna and Standart, 1979; Krishna and Taylor, 1986). In this paper multicomponent diffusion of sorbed species is formulated by appropriate adaptation of the Maxwell–Stefan approach. The utility of the Maxwell–Stefan approach is demonstrated by considering several special cases and comparing the results of the theoretical analysis with published information.

DEVELOPMENT OF MAXWELL–STEFAN FORMULATION FOR DIFFUSION OF SORBED SPECIES

Let us consider an *n*-component mixture diffusing inside a microporous sorbent. Diffusion inside the micropores is pictured as being primarily caused by surface diffusion of adsorbed species and it is further assumed that equilibrium prevails between the adsorbed species and the bulk fluid. If we now concentrate our attention on the surface of the sorbent it is clear that, even if we retain our continuum picture of the diffusion process, we need to introduce into our formulation parameters which describe the interplay between the sorbed species and the sorbent, and in particular the ease with which the sorbed molecules move from one site to another. Drawing analogy with the dusty gas model for transport inside porous media

[cf. Jackson (1977) and Mason and Malinauskas (1983)], we view the vacant sites on the surface as the ($n + 1$)th component in the mixture. We assume all vacant sites to be equivalent and no further distinction is made between the vacant sites at different locations in the sorbent.

Let n_i^s represent the surface concentration of component i measured in moles of i adsorbed on the surface per square metre of sorbent surface. The total surface concentration n_t^s is

$$n_t^s = \sum_{i=1}^{n} n_i^s. \tag{1}$$

Let $n_{t,\text{sat}}^s$ represent the total surface concentration of the mixture when all the sorption sites are covered; in other words $n_{t,\text{sat}}^s$ reflects the saturation sorbent capacity. The fraction of available sorption sites which is actually covered by the n species is therefore

$$\theta_t = n_t^s / n_{t,\text{sat}}^s. \tag{2}$$

The fractional uncovered sites, or vacancy, is thus

$$\theta_V = 1 - \theta_t \tag{3}$$

where we use the subscript V to denote the ($n + 1$)th species or vacancy. The fraction of the total available sites occupied by each species is

$$\theta_i = n_i^s / n_{t,\text{sat}}^s \tag{4}$$

and so, by definition:

$$\theta_t = \sum_{i=1}^{n} \theta_i = 1 - \theta_V. \tag{5}$$

The n fractional coverages, or occupancies, θ_i are analogs of bulk phase mole fractions x_i in the description of surface diffusion. The surface mole fractions x_i^s, commonly used in the literature on adsorption equilibria, are related to the fractional coverages θ_i:

$$x_i^s = \theta_i / \theta_t \tag{6}$$

and these two parameters equal each other when the surface coverage is complete, i.e. $\theta_t = 1$. In the foregoing development we have defined the various terms with the monolayer adsorption mechanism in mind. However, the developed formalism is not restricted to this case; the interpretation of vacancies and the ensuing discussions on mechanisms of surface diffusion will need to be adapted for multilayer adsorption. The formalism to be developed remains generally valid.

The vacancy solution model (VSM) of Suwanayuen and Danner (1980) for the description of adsorption equilibria also treats the vacancies as pseudo-species, ascribing to them thermodynamic properties such as chemical potential. The difference between the VSM approach and the other approaches to the description of the adsorption of phase equilibria emanating from the classic work of Myers and Prausnitz (1965) is essentially concerned with the choice of the standard states for calculation of the chemical potentials (Ruthven, 1984). In contrast, a mechanistic description of surface diffusion phenomena must recognize

the properties of the sorbent, in particular the vacant sites, whose existence cannot be "ignored" by a judicious choice of a "reference" point. It is to be further emphasized that our explicit recognition of vacant sites as the $(n + 1)$th component does not imply that we necessarily have to adopt the VSM approach for description of the *equilibrium* between the sorbed species and the adjoining bulk fluid phase; the description of phase equilibria is a separate, parallel, exercise. We find it necessary to stress this point in view of the recent criticisms of the VSM for correlation of adsorption equilibria (Talu and Myers, 1988); these do not apply to our approach adopted hereunder, which only utilizes the vacancy concept for surface transport.

For surface diffusion in the $(n + 1)$-component system consisting of n sorbed species and the vacancy (species $n + 1$) we may write the GMS equations in an analogous manner to diffusion in bulk fluid phases (Krishna and Taylor, 1986; Lightfoot, 1974; Standart et al., 1979):

$$\frac{\theta_i}{RT}\nabla_{T,\Pi}\mu_i = \sum_{\substack{j=1 \\ j \neq i}}^{n+1} \frac{\theta_i N_j - \theta_j N_i}{n_t^s \mathcal{D}_{ij}}$$
$$(i = 1, 2, \ldots n + 1). \quad (7)$$

While the significance of the terms in GMS equations for bulk fluid phase diffusion is easy to comprehend [cf. Krishna and Taylor (1986)], some explanation is required here for the corresponding quantities in the surface analog eq. (7). Here μ_i represents the chemical potential of the sorbed species i and the driving force for transfer of species i is the (surface) potential gradient of species i, $\nabla_{T,\Pi}\mu_i$, at constant temperature and spreading pressure Π. In view of the Gibbs–Duhem equation (Myers and Prausnitz, 1965; Ruthven, 1984):

$$\sum_{i=1}^{n+1} \theta_i \nabla_{T,\Pi}\mu_i = 0 \quad (8)$$

only n of eqs (7) are independent.

One peculiarity of surface diffusion which is distinct from bulk fluid phase diffusion is that since the total number of sorption sites is fixed we always have equimolar counter-diffusion in the $(n + 1)$-component system under consideration:

$$N_t = \sum_{i=1}^{n+1} N_i = 0 \quad (9)$$

or, put another way, the vacancy flux N_{n+1} balances the fluxes of the sorbed species. With inclusion of the vacant sites as the $(n + 1)$th component there is no "mixture as a whole" movement or "drift" analogous to the bulk fluid diffusion case (Bird et al., 1960). Now, in the case of the dusty gas model the "dust" components are assumed to have an infinitely large molar mass; for surface diffusion we demand that the vacancy have a vanishingly small molar mass and, therefore, even though the vacancy flux is non-zero

there is no corresponding contribution to the component mass balance.

In view of the foregoing the surface diffusion fluxes J_i are identical to the N_i:

$$J_i \equiv N_i. \quad (10)$$

We discuss below, in turn, the estimation of the various parameters appearing in the GMS formulation.

Surface chemical potential gradients

The surface chemical potential of species i, μ_i, is given by the equilibrium relation

$$\mu_i = \mu_i^o + RT \ln (f_i) \quad (11)$$

where f_i is the fugacity of component i in the bulk fluid phase in equilibrium with the sorbed mixture. Now, for one-dimensional transport the driving force on the left side of eq. (7) can be rewritten in terms of the gradients of the fractional coverages:

$$\frac{\theta_i}{RT}\nabla_{T,\Pi}\mu_i = \frac{\theta_i}{RT}\sum_{j=1}^{n}\frac{\partial\mu_i}{\partial\theta_j}\frac{d\theta_j}{dz}$$
$$= \theta_i \sum_{j=1}^{n}\frac{\partial\ln(f_i)}{\partial\theta_j}\frac{d\theta_j}{dz}$$
$$= \sum_{j=1}^{n}\Gamma_{ij}\frac{d\theta_j}{dz} \quad (i = 1, 2, \ldots n) \quad (12)$$

where we have defined an n-dimensional matrix of thermodynamic factors $[\Gamma]$ with elements

$$\Gamma_{ij} = \theta_i\frac{\partial\ln(f_i)}{\partial\theta_j} \quad (i, j = 1, 2, \ldots n). \quad (13)$$

Knowledge of the adsorption isotherm defines the relationship between the bulk fluid phase fugacity f_i and the surface mole fractions x_i^s, or alternatively the surface occupancies θ_i, of the adsorbed species (Myers and Prausnitz, 1965; Ruthven, 1984), which relationship can be utilized to calculate the elements of $[\Gamma]$. For example, the Langmuir adsorption isotherm for equilibrium between a ideal gas mixture ($f_i \equiv p_i$) and a solid adsorbent is

$$\theta_i = \frac{b_i p_i}{1 + \sum_{i=1}^{n} b_i p_i}\left(b_i p_i = \frac{\theta_i}{1 - \sum_{i=1}^{n}\theta_i}\right) \quad (14)$$

and the elements Γ_{ij} are found to be

$$\Gamma_{ij} = \delta_{ij} + \frac{\theta_i}{1 - \sum_{i=1}^{n}\theta_i} \quad (i, j = 1, 2, \ldots n). \quad (15)$$

In the following discussions we shall use the Langmuir adsorption isotherm for elucidating the influence of surface coverage on surface diffusion; indeed all the essential qualitative features are contained in expression (15). It needs to be stressed here, however, that our formalism is not limited to this isotherm nor to ideal gas mixtures and for the general case we may use eq. (13) for calculation of $[\Gamma]$.

GMS diffusion coefficients

The surface diffusivities $Ð_{ij}$ defined in eq (7) are the GMS diffusion coefficients. The coefficients $Ð_{i,n+1}$, or equivalently $Ð_{iV}$, reflects the facility for exchange between sorbed species i and vacant sites. In order to explain this further we consider the mechanism for surface diffusion.

Diffusion of sorbed species is an activated process and for the movement of a species it has to cross the potential barrier. Assume that the sorbed species under consideration has been activated and is ready to execute a jump. One of the following three possibilities arise:

(A) An adjoining site is vacant; in this case the activated species will move to this site; if more than one adjoining site is vacant the species can jump to any one of these sites with equal probability.

(B) All adjoining sites are occupied; in this case the activated species must return to its original position (the activated jump has been in vain!).

(C) The activated species i arrives at a site which is just being vacated by another activated sorbed species j; if j and i are identical species the interchange between i and j is also futile and does not contribute to net transport.

The transfer of species i by mechanism (A) occurs with a certain characteristic frequency and displacement associated with it; this is reflected in the GMS diffusivity:

$$Ð_{iV} = \frac{1}{2}\lambda_i^2 v_i \tag{16}$$

where λ_i is the mean displacement distance, and v_i is the jump frequency of sorbed species i; a priori estimates of these parameters are possible with the aid of specific assumptions as has been achieved, e.g. for the hopping model (Gilliland *et al.*, 1974) and for the transition state theory for zeolite diffusion (Ruthven and Derrah, 1972). It may be noted here in passing that the inverse of the GMS diffusivity $Ð_{iV}$ has been used in the formulations of Ruthven and Derrah (1972) and is referred to by them as the drag coefficient. The interpretation of molecular diffusion process in bulk fluid phases in terms of the drag experienced by the diffusing species is the basis of the derivation of the Maxwell–Stefan relations [cf. Krishna and Taylor (1986)] and it is interesting to note the analogy in this particular respect with respect to surface transport.

The frequency with which an adsorbed species will execute a jump also depends on the degree of surface occupancy. For low surface coverages the adsorbed species will not experience interactions because, statistically speaking, these species will be far removed from one another; an adsorbed species is for the greater part surrounded by vacancies. The interactions between adsorbed species could become important at high surface coverages, affecting the frequency with which an adsorbed species attempts a jump,

because now the adsorbed species will be surrounded by other adsorbed species (Reed and Ehrlich, 1981). Whether or not the adsorbed species will interact with one another depends on the type of species. For vanishingly small surface coverages the coefficients $Ð_{iV}^0$, distinguished by a superscript 0, can be expected to be the same for both single-sorbate and multicomponent surface diffusion; this provides the basis for prediction of multicomponent behaviour from single-sorbate behaviour. Our treatment does not provide further light on the composition dependence of the $Ð_{iV}$; we shall return to this point later in the paper.

Let us examine the situation corresponding to mechanism (C) above. Here species i exchanges with species j; this counter-sorption of two species has a greater probability of occurrence at high surface coverages. Indeed, at saturation occupancy only counter-sorption (exchange) is possible. The counter-sorption facility is reflected in the GMS coefficient $Ð_{ij}$ ($j \neq V$). The Onsager reciprocal relations shows that these coefficients are symmetric (cf. Appendix A):

$$Ð_{ij} = Ð_{ji} \quad (i, j = 1, 2, \ldots n). \tag{17}$$

If j and i are identical then the exchange is futile and no net flux results, as is evidenced from eq. (7) which shows that for $j = i$ the right-hand side vanishes identically.

While the GMS coefficient $Ð_{iV}$ can be interpreted in terms of mean displacements and jump frequencies, a similar interpretation of the counter-sorption diffusivity $Ð_{ij}$ is not quite so straightforward. For the case that the surface is fully covered ($\theta_t \rightarrow 1$) and occupied almost completely by species j ($\theta_j \rightarrow 1$) the counter-sorption coefficient $Ð_{ij}$ will reflect, in terms of the jump frequency and mean displacement, the facility of transfer of species j, i.e.

$$\underset{\theta_j \rightarrow 1}{Lt} Ð_{ij} = Ð_{jV}. \tag{18}$$

Conversely, when the surface is predominantly covered by species i then the counter-sorption coefficient $Ð_{ij}$ must reflect the ease of transfer of species i:

$$\underset{\theta_i \rightarrow 1}{Lt} Ð_{ij} = Ð_{iV}. \tag{19}$$

The coefficient $Ð_{ij}$ must exhibit a continuous dependence on the surface coverages between the two extremes represented by eqs (18) and (19). If we examine the corresponding problem encountered in the multicomponent diffusion in non-ideal liquid mixtures, it is seen that the variation of the GMS diffusivity $Ð_{ij}$ with composition has also evaded a fundamental analysis [cf. Reid *et al.* (1977)] and experimental data generally appear to follow the empirical trend suggested by Vignes (1966); the Vignes dependence applied to our case yields

$$Ð_{ij} = [Ð_{jV}]^{\theta_j/(\theta_i + \theta_j)}[Ð_{iV}]^{\theta_i/(\theta_i + \theta_j)}. \tag{20}$$

Recalling that counter-sorption starts playing a significant role when the surface coverage is high, the

values of $\mathrm{Đ}_{iV}$ and $\mathrm{Đ}_{jV}$ to be used in eq. (20) are most logically the ones corresponding to high surface coverages. Equation (20) must be viewed as an empirical rule, to be checked by experiment. Our model development however does not hinge on the applicability, or otherwise, of the Vignes relationship (20); any model must recognize the composition dependence of $\mathrm{Đ}_{ij}$ and the physical constraints demanded by eqs (18) and (19).

In proceeding with our analysis it is convenient to define, in analogy with the corresponding bulk diffusion case [cf. Krishna (1977)], an n-dimensional matrix of inverted GMS diffusivities [B] with elements defined by

$$B_{ii} = \frac{\theta_i}{\mathrm{Đ}_{iV}} + \sum_{\substack{j=1 \\ j \neq i}}^{n+1} \frac{\theta_j}{\mathrm{Đ}_{ij}} \quad (i = 1, 2, \ldots n) \qquad (21)$$

$$B_{ij} = -\theta_i \left(\frac{1}{\mathrm{Đ}_{ij}} - \frac{1}{\mathrm{Đ}_{iV}} \right) [i, j \ (i \neq j) = 1, 2, \ldots n]. \qquad (22)$$

With the definitions of matrices [Γ] and [B] [cf. eqs (15), (21) and (22)], the GMS eqs (7) may be cast into convenient n-dimensional matrix notation:

$$(J) = -n_t^s [B]^{-1} [\Gamma] \frac{d(\theta)}{dz} \qquad (23)$$

which is the final working form of the GMS formulation of surface diffusion.

The Fickian formulation of multicomponent surface diffusion [cf. Marutovsky and Bülow (1982) and Palekar and Rajadhyaksha (1986)] utilizes an n-dimensional matrix of Fick diffusivities [D] defined by

$$(J) = -n_t^s [D] \frac{d(\theta)}{dz} \qquad (24)$$

but the Fick approach, on its own, provides no clue to estimation of [D]; Palekar and Rajadhyaksha (1986), therefore, had to resort to Monte Carlo simulations to estimate [D]. Comparing eqs (23) and (24):

$$[D] \equiv [B]^{-1} [\Gamma] \qquad (25)$$

which relation allows estimation of [D].

Ash and Barrer (1967) use the Onsager formulation of irreversible thermodynamics to describe surface transport; this is discussed in Appendix A, along with the interrelationships between the Fick, Onsager and GMS formulations.

We now examine several special cases to demonstrate the application of the GMS formulation of surface diffusion.

DIFFUSION OF SINGLE SORBED SPECIES

For this case $n = 1$ eqs (23)–(25) collapse to the scalar form

$$J_1 = -n_t^s \mathrm{Đ}_{1V} \Gamma \frac{d\theta_1}{dz} = -n_t^s D_{1V} \frac{d\theta_1}{dz} \qquad (26)$$

and from eq. (15) we see that the thermodynamic

factor Γ is

$$\Gamma = 1/(1 - \theta_1) \qquad (27)$$

and so the Fick diffusivity D_{1V} is related to the GMS diffusivity $\mathrm{Đ}_{1V}$ by

$$D_{1V} = \mathrm{Đ}_{1V}/(1 - \theta_1). \qquad (28)$$

In the extensive literature on microporous diffusion, the Fick diffusivity is also referred to as the "apparent" diffusivity while the GMS diffusivity is identifiable with the "corrected" or "intrinsic" diffusivity [cf. Ruthven (1984)]. Equation (28) shows that the Fick diffusivity must increase sharply as the surface coverage approaches unity. We may expect the GMS diffusivity $\mathrm{Đ}_{1V}$ to display a relatively weak dependence on surface occupancy; this expectation is indeed met in the case of diffusion of benzene in NaX zeolite for which Eic et al. (1988) have observed that $\mathrm{Đ}_{1V}$ is practically independent of surface occupancy.

The Fick surface diffusivity of SO_2 in a microporous plug has been measured by Pope (1967) and his data shows a pronounced increase in D_{1V} with surface occupancy. The GMS diffusivity $\mathrm{Đ}_{1V}$, calculated from the Fick diffusivity data using eq. (28), is however not constant but is found to be dependent on the surface coverage, decreasing with increasing surface coverage (cf. Fig. 2). It is apparent that the adsorbed SO_2 species interact with each other, causing a reduction in the GMS diffusivity with increasing surface coverage; from Fig. 2 it can be seen this variation can be represented adequately by the Vignes relationship

$$\mathrm{Đ}_{1V} = (\mathrm{Đ}_{1V}^0)^{1 - \theta_i} (\mathrm{Đ}_{1V}^1)^{\theta_i} \qquad (29)$$

where the superscripts 0 and 1 refer to the coefficients at zero and total coverages, respectively. Equations (27)–(29) provide a complete description of Fick diffusivity D_{1V} and the smooth curve in Fig. 1 has been obtained by taking $\mathrm{Đ}_{1V}^1 = 1.7 \times 10^{-8} \ \mathrm{m^2 \ s^{-1}}$, which is the extrapolated value in Fig. 2. The GMS
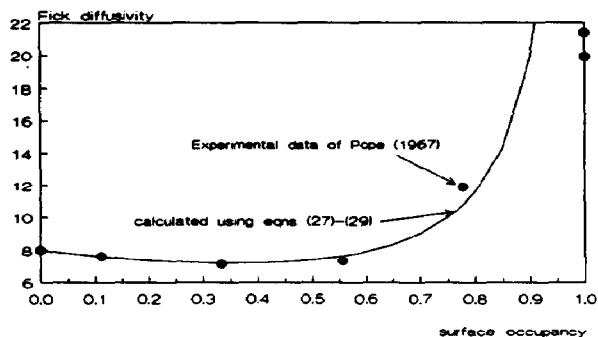

Fig. 1. Variation of the Fick surface diffusivity with surface occupancy, θ, of SO_2 in a microporous plug of spheron 6(2700) [data from Pope (1967)]. (●) Fick surface diffusivity at 0°C, (———) calculations using eqs (27)–(29), taking $\mathrm{Đ}_{1V}^0 = 8$ and $\mathrm{Đ}_{1V}^1 = 1.7 \times 10^{-8} \ \mathrm{m^2 s^{-1}}$. The surface occupancy θ_i has been calculated from the reported value of the surface concentrations and the saturation surface concentration. The units for the y-axis are $10^{-8} \ \mathrm{m^2 \ s^{-1}}$.
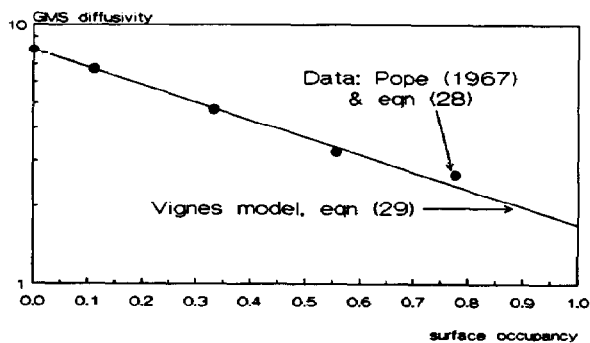
Fig. 2. Variation of the GMS diffusivity, $Đ_{1V}$, with surface occupancy, θ, for diffusion of SO_2 in a microporous plug; values calculated from the Fick diffusivity data at 0°C (Pope, 1967) using eq. (28). The units used for y-axis are $10^{-8}\,m^2\,s^{-1}$.
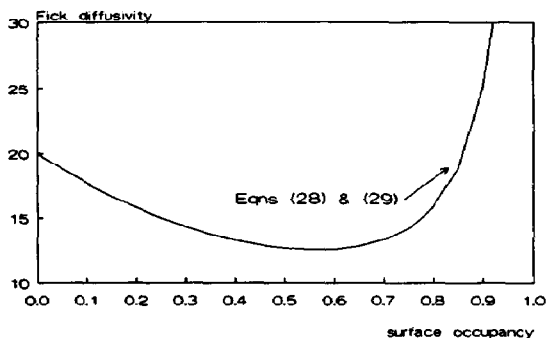

Fig. 3. Variation of Fick diffusivity, D_{1V}, with surface occupancy, θ, for $Đ_{1V}^0 = 20$ and $Đ_{1V}^1 = 2$ (arbitrary units): calculations using eq. (29).

formulation, together with the empirical Vignes dependence, describes the behaviour of the Fick diffusivity quite well, and in particular the observed minimum is properly modelled. When interactions between adsorbed molecules become more important, as will often be the case for intracrystalline diffusion in zeolites, the reduction in the GMS diffusivity with surface coverage will be large and the minimum in the Fick diffusivity will become more pronounced. This is illustrated qualitatively in Fig. 3, taking the values $Đ_{1V}^0 = 20$ and $Đ_{1V}^1 = 2$ (arbitrary units); similar pronounced minima for the dependence of the Fick diffusivity on surface concentration has been reported by Ruthven and Doetsch (1976) for diffusion of hydrocarbons in 13X zeolite.

TRACER DIFFUSION

This is an extension of the case of a single sorbed species considered above but a fraction of the molecules of component 1 is tagged or traced. In describing the diffusion process we need to differentiate between untagged species (component 1) and the tagged species (component 2); tracer diffusion is thus a special case of binary sorption. The experimental conditions are invariably maintained such that the total concen-

tration of tagged and untagged species remains constant which implies that the sum of their respective gradients vanish, i.e.

$$\frac{d\theta_1}{dz} = -\frac{d\theta_2}{dz} \tag{30}$$

and also that we have equimolar counter-diffusion between 1 and 2:

$$N_1 = -N_2, \quad J_1 = -J_2. \tag{31}$$

The equimolar condition (31) is in addition to the general equimolar requirement of surface diffusion given by eq. (9). This implies that the vacancy flux vanishes, i.e.

$$N_V = 0. \tag{32}$$

This essentially means that the total surface coverage θ_t remains constant, which conclusion is consistent with eq. (30).

Imposing constraints (30)–(32) on the general relationships for binary sorption, the tracer diffusion fluxes are

$$J_i = -n_t^s(D_{ii} - D_{ij})\frac{d\theta_i}{dz} \quad (i = 1, 2). \tag{33}$$

The species 1 and 2 transfer with equal facility, referred to as the tracer diffusivity D^*

$$D^* \equiv D_{11} - D_{12} = D_{22} - D_{21}. \tag{34}$$

D^* can be expressed explicitly in terms of the GMS diffusivities $Đ_{1V}$ and $Đ_{12}$ (see Appendix B for derivation):

$$D^* = 1 \Big/ \left(\frac{\theta_t}{Đ_{12}} + \frac{1-\theta_t}{Đ_{1V}}\right). \tag{35}$$

Pope (1967) has also reported tracer diffusivity data for the diffusion of SO_2 in the microporous plug; the data for D^* at 0°C are plotted in Fig. 4. Comparison of the data in Figs 1 and 4 shows that, unlike the Fick
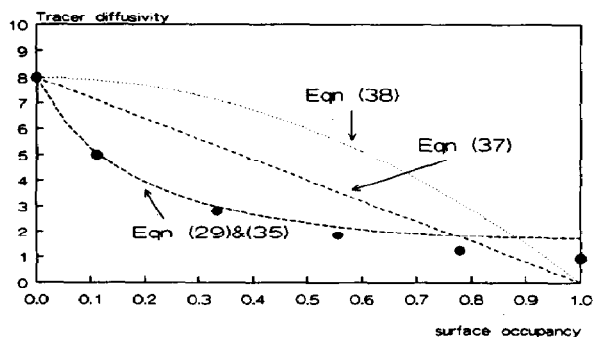

Fig. 4. Tracer diffusion (D^*) data (●) at 0°C for SO_2 in a microporous plug (Pope, 1967) as a function of surface occupancy θ. Also shown are predictions of the Riekert model [eq. (37)], Palekar and Rajadhyaksha model [eq. (38)] and GMS formulation [eqs (29) and (35)], taking $Đ_{12} = Đ_{1V}^1 = 1.7 \times 10^{-8}\,m^2\,s^{-1}$ and $Đ_{1V}^0 = 8 \times 10^{-8}\,m^2\,s^{-1}$. The units used for the y-axis are $10^{-8}\,m^2\,s^{-1}$.

D_{1V}, the tracer D^* *decreases* with increasing surface occupancy θ_t. To elucidate this behaviour we recast eq. (35) in the form

$$\frac{1}{D^*} - \frac{1-\theta_t}{Ð_{1V}} \equiv \frac{1}{D^*} - \frac{1}{Ð_{1V}} = \frac{\theta_t}{Ð_{12}}. \qquad (36)$$

The concentration dependence of $Ð_{12}$ must be expected to be negligibly small as both 1 and 2 refer to the same species, one tagged and the other untagged. Put another way, $Ð_{12}$ is concentration-independent because it does not really matter whether species 1 is surrounded by species 2 or vice versa. For constant $Ð_{12}$ a plot of the left side of eq. (36) vs the surface occupancy should be linear; Fig. 5 provides verification of this prediction.

Taking $Ð_{12} = Ð_{1V}^1 = 1.7 \times 10^{-8}\,m^2\,s^{-1}$ the calculation of D^* from eq. (35), using the Vignes dependence eq. (29), are shown in Fig. 4. The GMS simulation of tracer diffusion is found to be very good. Also shown in Fig. 4 are two other models for tracer diffusivity from the published literature: (i) due to Riekert (1971):

$$D^* = Ð_{1V}^0 (1 - \theta_t) \qquad (37)$$

and (ii) due to Palekar and Rajadhyaksha (1985):

$$D^* = Ð_{1V}^0 (1 - \theta_t^2). \qquad (38)$$

Neither of these two models is able to even qualitatively reproduce the observed variation of D^* with surface occupancy.

Hitherto, the interpretation of tracer diffusion has largely followed the classic work of Ash and Barrer (1967) which used the Onsager formulation of irreversible thermodynamics. This approach leads to the following expression for the tracer diffusivity (see Appendix B for derivation):

$$D^* = D_{1V}(1 - \theta_1 L_{12}/\theta_2 L_{11})/\Gamma \qquad (39)$$

which suffers from the disadvantage that no procedure for estimation of the cross-coefficient L_{12} is given by the treatment. In view of this shortcoming of the Onsager formulation, Palekar and Rajadhyaksha (1985) have ventured to state that "a general relationship between tracer diffusivity and intrinsic diffusivity
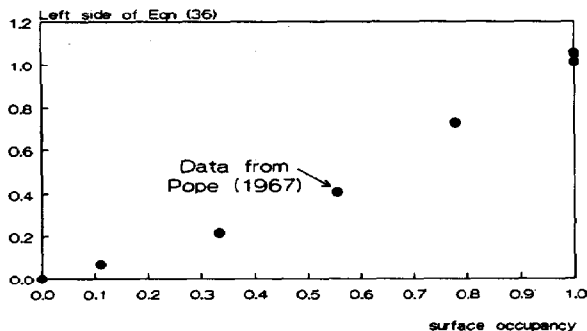
cannot be derived from Irreversible Thermodynamics". Our eq. (35), derived from the Maxwell–Stefan formulation of irreversible thermodynamics, provides the aforementioned relationship and, furthermore, the treatment developed here helps to resolve the arguments concerning the concentration dependence of the tracer diffusivity (Palekar and Rahadhyaksha, 1985; Riekert, 1971).

When the adsorbed species do not interact with each other then we should expect $Ð_{1V}$ to be independent of surface coverage, and also $Ð_{1V} = Ð_{12}$. In this case the tracer diffusivity D^* equals $Ð_{1V}$, the "corrected" or GMS diffusivity (cf. Appendix B); for diffusion of C_8 aromatics in NaX zeolite, the experimental data of Goddard and Ruthven (1986) confirm this expectation.

SURFACE DIFFUSION OF BINARY SORBED SPECIES

We now consider diffusion of two sorbed species in some detail because this binary system exhibits all the essential features of the general multicomponent case. The system behaviour is characterized by three GMS diffusivities: the intrinsic diffusivities $Ð_{1V}$ and $Ð_{2V}$ of components 1 and 2 and the counter-sorption diffusivity $Ð_{12}$. Algebraic expressions for the elements of $[B]^{-1}$, $[\Gamma]$ and $[D]$ are derivable for this case and given in Appendix B. We shall explore some of the features of binary surface diffusion by examining the structure of $[D]$, for the case where the GMS diffusivities $Ð_{1V}$ and $Ð_{2V}$ are concentration-independent. We take species 1 to be the faster moving species and evaluate the counter-sorption coefficient $Ð_{12}$ using the Vignes relationship (20).

Figure 6 shows the variation of the elements of $[D]$ with increasing (surface) mole fraction of the more mobile species 1, x_1^s ($Ð_{1V}/Ð_{2V} = 2$, $\theta_t = 0.4$). It is interesting to note that both the coefficients D_{11} and D_{12} increase with increasing x_1^s. Similarly, the coefficients D_{21} and D_{22} increase with increasing x_2^s. This implies that species i will tend to diffuse faster when it is present in a larger proportion (higher mole fraction x_i^s). The cause of this "acceleration" is the behaviour

Fig. 5. Plot of $(1/D^* - 1/D_{1V})$ vs the surface occupancy: data ($\bullet$) from Figs 1 and 4. The units used for the y-axis are $10^8\,m^{-2}\,s$.
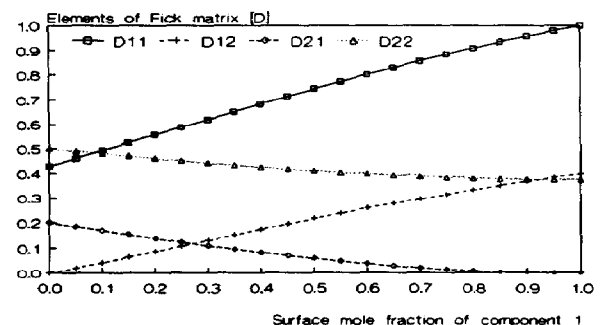
Fig. 6. Variation of the elements of Fick surface diffusivity matrix $[D]$ with surface mole fraction of faster moving species 1, x_1^s: calculations using eq. (B3), taking $Ð_{1V}/Ð_{2V} = 2$; $\theta_t = 0.4$. The elements D_{ij} are normalized with respect to the value of D_{11} corresponding to $x_1^s = 1$. The y-axis is dimensionless.
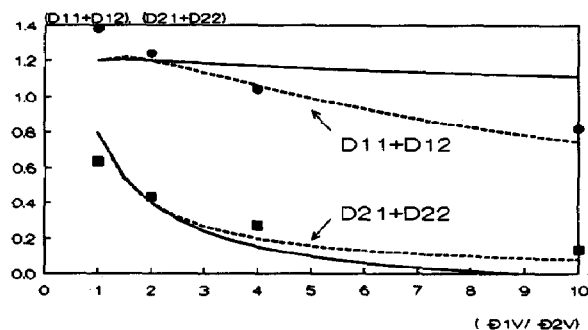
Fig. 7. Variation of $(D_{11} + D_{12})$ and $(D_{21} + D_{22})$ with the ratio $Đ_{1V}/Đ_{2V}$. The total surface occupancy $\theta_t = 0.4$ and $x_2^s = 0.25$: ($\bullet$) and ($\blacksquare$) Monte Carlo simulation results of Palekar and Rajadhyaksha (1986), (———) GMS model calculations with the counter-sorption diffusivity $Đ_{12}$ calculated using the Vignes relationship (20), (– – – –) GMS model calculations taking $Đ_{12} = Đ_{2V}$.

of the matrix $[\Gamma]$; both Γ_{11} and Γ_{12} increase with increase in x_1^s. Results similar to that presented in Fig. 5 were obtained by Palekar and Rajadhyaksha (1986) (cf. Fig. 2 of their paper), who employed Monte Carlo simulations to obtain $[D]$. A careful comparison of the results of the predictions of the GMS formulations with the Monte Carlo simulations of Palekar and Rajadhyaksha (1986) reveals that though similar trends are obtained for the variation of the elements of $[D]$ with system parameters, there are some differences in the actual calculated values. This is illustrated in Fig. 7 for the variation of $(D_{11} + D_{12})$ and $(D_{21} + D_{22})$ with $Đ_{1V}/Đ_{2V}$, for a fixed total surface occupancy $\theta_t = 0.4$ and $x_2^s = 0.25$. The full lines represent the calculations of the GMS model with $Đ_{12}$ calculated from eq. (20) and the broken lines represent our model calculations taking a constant value of $Đ_{12} = Đ_{2V}$, the diffusivity of the slower moving species. The results of Palekar and Rajadhyaksha (1986) show excellent agreement with the latter assumption, suggesting that their algorithm makes some such implicit assumption, not explicitly stated in their published paper. We are of the opinion that the counter-sorption diffusivity $Đ_{12}$ must be dependent on the surface mole fractions in the general case; we shall return to this point later when we treat transient binary counter-sorption.

Considering the totally different bases in the calculation procedures adopted by Palekar and Rajadhyaksha (1986) and ourselves, it must be concluded that the agreement between the two approaches is remarkably good, even with the GMS model in which $Đ_{12}$ is variable. The statement of Palekar and Rajadhyaksha (1986) that "irreversible thermodynamics can give only the dependence of the diffusion coefficients on sorbate concentration and offers little information regarding their magnitude" is refuted by the results presented here; the Maxwell–Stefan approach has been shown to provide fairly complete information on the magnitude of the matrix of Fick diffusion coefficients $[D]$.

TRANSIENT UPTAKE OF MULTICOMPONENT MIXTURES

The determination of the transient uptake profiles for multicomponent mixtures is important in a host of industrial separation applications including adsorptive separations and desorptive regeneration using a solvent. If an analytic solution to the problem involving diffusion of a single sorbed species is available, then the solution to the corresponding multicomponent surface diffusion problem can be simply obtained as matrix analogs of the corresponding binary solution provided we assume that the matrix of Fick diffusivities $[D]$ is constant over the surface concentration range of interest; this follows by application of the linearized theory of multicomponent mass transfer (Stewart and Prober, 1964; Toor, 1964); Krishna and Standart (1979) give a detailed account of the required computational procedures.

To illustrate the application of this linearization technique let us consider transient uptake of a multicomponent mixture on to a sorbent. For single-sorbate (component 1) uptake on to a microporous adsorbent, limited by intracrystalline (surface) diffusion, the transience is described by [cf. eq. (6.4) of Ruthven (1984)]

$$\frac{\theta_1 - \theta_{10}}{\theta_{1sat} - \theta_{10}} = 1 - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp\left(-\frac{m^2 \pi^2 D_{1V} t}{r_c^2} \right)$$

(40)

where the surface of the adsorbed particles is maintained at the concentration, or coverage, θ_{1sat}, and θ_{10} is the initial sorbate occupancy. D_{1V} is the (intracrystalline) Fick diffusivity and r_c is the crystallite radius.

The corresponding expression for the transient uptake of n sorbed species is simply the n-dimensional matrix analog of eq. (40):

$$(\theta - \theta_0) = \left[[I] - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \right.$$

$$\left. \times \exp\left(-\frac{m^2 \pi^2 [D] t}{r_c^2} \right) \right] (\theta_{sat} - \theta_0). \quad (41)$$

The matrix calculations in eq. (41) can be carried out using Sylvester's theorem [cf. Krishna and Standart (1979)]; the procedure is demonstrated for binary diffusion in Appendix C. Since the eigenvalues of $[D]$ are positive definite (cf. Appendix A), the solution to the multicomponent surface diffusion problem is always real and stable.

Let us consider a specific example of transient uptake of n-heptane (1) and benzene (2) by NaX zeolite at 359 K. The zeolite crystals are exposed to a bulk vapour mixture maintaining the surface at the saturation concentration values of 0.18 and 1.65 mmol/g for n-heptane and benzene, respectively (Kärger and Bülow, 1975), i.e. $\theta_{1sat} = 0.098$ and $\theta_{2sat} = 0.902$. The intrinsic diffusivities of n-heptane is much higher than that of benzene; we take $Đ_{1V}/Đ_{2V} = 50$ [cf. Kärger et al. (1978)]. For the initial conditions $\theta_{10} = \theta_{20} = 0$, the transient uptake profiles,
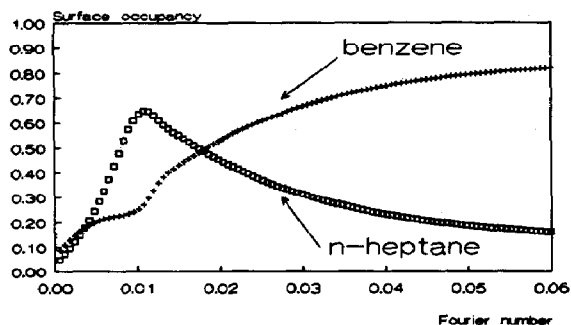
Fig. 8. Transient uptake profiles for n-heptane and benzene on NaX zeolite at 359 K, as function of the Fourier number $(Fo = \mathbb{D}_{2V} t/r_c^2)$. Initial conditions: $\theta_{10} = \theta_{20} = 0$; saturated surface conditions: $\theta_{1sat} = 0.098$, $\theta_{2sat} = 0.902$; diffusivity ratio $\mathbb{D}_{1V}/\mathbb{D}_{2V} = 50$, $\mathbb{D}_{12}$ calculated using eq. (20). [D] matrix at any Fo interval is calculated at the terminal θ_i for the previous Fo interval.

using the procedure outlined in Appendix C, are shown in Fig. 8. In the calculations $\mathbb{D}_{1V}$ and $\mathbb{D}_{2V}$ were assumed to be constant and the counter-sorption diffusivity $\mathbb{D}_{12}$ was calculated using eq. (20). Since [Γ] is a strong function of the surface coverages [cf. eq. (B2)], the matrix calculations were performed for small intervals of $Fo = 0.0006$, and the surface occupancies θ_1 and θ_2 calculated at the end of an interval were used for the calculation of [D] for the next time interval. Figure 8 shows a dramatic difference in the uptake profiles of n-heptane (which moves much faster but has a much lower saturation occupancy than benzene) and benzene (slower moving but with a much higher saturation occupancy). Of note is the maximum in the n-heptane profile with $\theta_1 = 0.65$ at $Fo = 0.01$, much higher than the final equilibrium value $\theta_{1sat} = 0.098$. It is only beyond $Fo = 0.01$ that the n-heptane gets (slowly) displaced by benzene to reach the final equilibrium. The experimentally observed uptake profiles reported by Kärger and Bülow (1975) show remarkable agreement to the profiles in Fig. 8. Our simulations correctly reproduce the experimentally reported observation that the maximum in the n-heptane profile is reached at about a sixth of the time it takes to reach a plateau in the occupancy profiles.

The transient sorption of the n-heptane–benzene system considered above is typical of a binary mixture of fast moving–less strongly adsorbed species with a slow moving–more strongly adsorbed component; analogous behaviour in the n-hexane–benzene system has been reported by Kärger et al. (1975). The reasoning behind the observed maximum in the profile for the faster moving species is as follows. Initially the surface concentration of the faster moving species (1) increases at a much higher rate than that of the slower moving species (2) due to its higher intrinsic diffusivity. As the surface coverage θ_1 increases, the elements D_{11} and D_{12} also increase (cf. Fig. 6), accelerating the uptake of component 1 and taking it beyond the saturation coverage θ_{1s}; this is possible because of

finite and large value of D_{12} which moves species 1 in the direction dictated by the driving force of component 2. This acceleration continues till a situation is reached where the tendency for θ_1 to increase (caused due to the cross-term D_{12}) balances the tendency for θ_1 to decrease to its equilibrium value θ_{1sat} (dictated by the main term D_{11}) and a maximum is reached. Beyond this point the intrinsic driving force predominates and species 1 decreases to its final equilibrium value. In summary, the unusual behaviour is to be ascribed to two factors: (i) the higher intrinsic diffusivity of component 1 and (ii) the dependence of the [D] matrix on [Γ], whose elements Γ_{11} and Γ_{12} increase with increasing occupancy of component 1. This point is emphasized further by the simulations presented in Fig. 9 where [Γ] and [B] are both calculated at the initial condition of $\theta_{10} = \theta_{20} = 0$; [Γ] equals the identity matrix for this case. The calculated profiles for uptake of n-heptane and benzene are monotonous and represent the behaviour as though each component is sorbed in the absence of the other. Since experimental results conform to the behaviour depicted in Fig. 8, we conclude that coupling between surface fluxes of sorbed species, portrayed by non-diagonal matrices [B], [Γ] and [D], is a characteristic feature of multicomponent diffusion.

Beyond the point at which n-heptane reaches a maximum counter-sorption of n-heptane and benzene dominates; in fact, when the surface occupancy is complete $(\theta_i \cong 1, \theta_V = 0)$, $\mathbb{D}_{12}$ is the only diffusivity of consequence and the GMS eqs (7) rightly recognise that the contributions of the terms involving $\mathbb{D}_{iV}$ identically vanish. We illustrate some of the essential features of binary counter-sorption by carrying out simulations of the transient uptake profiles for the case where species 1 moves faster than species 2 $(\mathbb{D}_{1V}/\mathbb{D}_{2V} = 20)$ for the following two sets of conditions.

Case A. Uptake of species 1; the initial coverage $\theta_{10} = 0.1$ and at time $t = 0$ the exterior surface of the microporous adsorbent is maintained at conditions corresponding to $\theta_{1sat} = 0.9$.
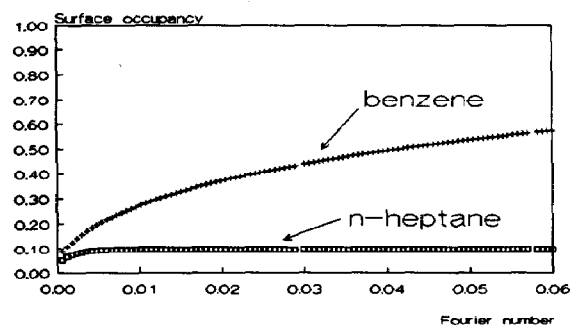

Fig. 9. Transient uptake profiles for n-heptane and benzene on NaX, as function of the Fourier number $(Fo \equiv \mathbb{D}_{2V} t/r_c^2)$, for conditions specified as in Fig. 8. The matrix [D] is assumed to be constant and calculated at the initial conditions θ_{i0}.
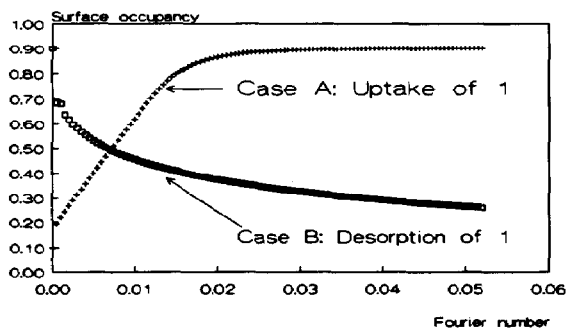
Fig. 10. Transient counter-sorption of species 1 and 2 where $D_{1V}/D_{2V} = 20$. Case A: $\theta_{10} = 0.1$, $\theta_{1sat} = 0.9$; case B: $\theta_{10} = 0.9$, $\theta_{1sat} = 0.1$. Calculations performed using eq. (40) with D_{12} replacing D_{1V}. Equation (20) used for calculation of D_{12}.

Case B. Desorption of species 1; the initial coverage $\theta_{10} = 0.9$ and at time $t = 0$ the exterior surface is maintained at conditions corresponding to $\theta_{1sat} = 0.1$.

The transient surface coverage profiles for the (mirror-image) adsorption–desorption cases A and B are shown in Fig. 10. It is interesting to note that the approach to equilibrium in the case of uptake is much faster than the case where the species with the higher intrinsic diffusivity is being desorbed. The reason for the dependence in the observed equilibration rates on the *direction* of transfer is to be found in the composition dependence of D_{12}. In the case of uptake of the faster moving species 1, this counter-sorption diffusivity increases with increasing uptake ("acceleration" effect). Conversely, when species 1 is being desorbed, the reducing concentration of species 1 reduces the counter-sorption diffusivity D_{12}. Satterfield *et al.* (1971) and Moore and Katzer (1972) have experimentally observed that the *direction* of transfer affected the rates of adsorption and desorption of hydrocarbon mixtures in zeolites; our model formulation provides a theoretical basis with which these observations can be rationalized. Also, the analysis of binary counter-sorption emphasizes the need to take proper note of the composition dependence of the counter-sorption diffusivity D_{12}; this parameter cannot be assumed to be constant, as has already been stressed in earlier remarks concerning the Monte Carlo simulation results of Palekar and Rajadhyaksha (1986).

CONCLUSIONS

Surface diffusion of n sorbed species has been described using the GMS formulation of irreversible thermodynamics. The approach treats the vacant sites as the $(n + 1)$th component in the diffusing mixture, drawing on the analogy with the dusty gas model for diffusion in porous media. The treatment defines two types of diffusivities: (i) the "intrinsic" diffusivities D_{iV}, signifying the facility for diffusive exchange between species i and the vacant sites, and (ii) the D_{ij}, describing the facility for counter-exchange between the

sorbed species i and j. For negligible interactions between sorbed species, the intrinsic diffusivities D_{iV} can be identified with the single-sorbate diffusivity. The GMS counter-sorption diffusivity, in turn, is relatable to the coefficients D_{iV} and D_{jV}; the empirical Vignes relation (20), strictly outside the scope of the GMS treatment, provides a usable procedure for calculation of D_{ij}.

The GMS approach clearly brings out the influence of the fractional surface coverages θ_i of the sorbed species on the transfer behaviour; this influence is portrayed by the matrix of thermodynamic factors $[\Gamma]$, defined by eq. (12). For the Langmuir isotherm the elements of $[\Gamma]$ are given by eq. (15).

For diffusion of a single sorbed species the Fick surface diffusivity D_{1V} has been shown to be related to the GMS diffusivity D_{1V} by eq. (28), which is well established in the literature; D_{1V} is identifiable with "intrinsic" or "corrected" diffusivity.

The expression for the tracer diffusivity D^*, eq. (34), is a new contribution of the GMS formulation and this result is verified by comparison with experimental data of Pope (1967). Some of the apparent controversies in the published literature on the dependence of the tracer diffusivity on the surface coverage, highlighted by Palekar and Rajadhyaksha (1985), have been resolved by the GMS formulation.

The GMS model calculations of the Fick surface diffusivity matrix [D] for binary sorbed phases reveal some interesting features of multicomponent transfers, e.g. the increase in the coefficients D_{11} and D_{12} with increasing surface concentration of species 1; this amounts to acceleration of species 1 and has ramifications in transient uptake processes. For a constant value of the Fick matrix [D], analytical solutions for transient uptake of multicomponent mixtures are obtained as n-dimensional matrix analogs of the corresponding solution for single-component sorption. The application of the suggested solution technique is demonstrated by simulation of the kinetic sorption curve for n-heptane–benzene on NaX zeolite. The GMS formulation is capable of reproducing the maximum in the n-heptane kinetic sorption curve, as experimentally observed by Kärger and Bülow (1975).

Analysis of binary counter-sorption using the GMS approach helps to explain the experimental observation that adsorption and desorption rates may be significantly different.

The advantages of GMS formulation over alternative Fick and Onsager formulations have been underlined in the discussions and the results presented in this paper suggest that the GMS approach provides the most convenient practical formulation of multicomponent surface diffusion.

NOTATION

$[B]$ inverted matrix of GMS diffusion coefficients with elements defined by eqs (21) and (22), m^{-2} s

b_i coefficients in Langmuir isotherm (14), N^{-1} m^2

D_{iV} Fick surface diffusivity for species, m^2 s^{-1}

D^* tracer diffusivity, m^2 s^{-1}

$[D]$ matrix of Fick diffusivities with elements D_{ij}, m^2 s^{-1}

$[D]$ $\equiv [B]^{-1}$ with elements for binary sorption given by eq. (B1), m^2 s^{-1}

$\hat{D}_i$ eigenvalues of the Fick diffusivity matrix $[D]$, m^2 s^{-1}

$Đ_{ij}$ GMS diffusivity for counter-sorption of species i and j, m^2 s^{-1}

$Đ_{iV}$ GMS diffusivity for sorption of species i, m^2 s^{-1}

f_i fugacity of component i in the bulk fluid phase, N m^{-2}

$\hat{f}_i$ eigenvalues of $[F]$ defined by eq. (C2)

$[F]$ matrix giving fractional approach to equilibrium [cf. eq. (C3)]

Fo Fourier number $[\equiv (Đ_{2V} t / r_c^2)]$

$[G]$ matrix defined by eq. (A4)

$[I]$ identity matrix with elements δ_{ij}

J_i surface diffusion flux of species i, mol m^{-1} s^{-1}

(J) n-dimensional column vector of surface diffusion fluxes, mol m^{-1} s^{-1}

$[L]$ matrix of Onsager coefficients defined by eq. (A1), m^2 s^{-1}

n number of species in mixture

n_i^s surface concentration of species i, mol m^{-2}

n_t^s total mixture surface concentration, mol m^{-2}

$n_{t,sat}^s$ total surface concentration of mixture at saturation, mol m^{-2}

N_i molar surface flux of species i in laboratory fixed coordinate reference frame, mol m^{-1} s^{-1}

N_t total mixture molar flux in laboratory fixed co-ordinate reference frame, mol m^{-1} s^{-1}

p_i partial pressure of i in bulk vapour, N m^{-2}

r_c crystallite radius, m

R universal gas constant, 8.3144 J mol^{-1} K^{-1}

t time, s

T temperature, K

x_i^s mole fraction of sorbed species i

x_i mole fraction of species i in the bulk fluid phase

z coordinate direction

Greek letters

Γ thermodynamic correction factor defined by eq. (12) for a single-component sorption

$[\Gamma]$ matrix of thermodynamic correction factors with elements defined by eq. (4) for a multicomponent mixture

δ_{ij} Kronecker delta $(= 1$ if $i = j$, $= 0$ if $i \neq j)$

θ_i fractional surface occupancy of species i

θ_t fractional surface occupancy by total mixture

(θ) n-dimensional column vector of fractional surface coverages of the n species

$[\Theta]$ n-dimensional diagonal matrix with elements δ_{ij}/θ_i

λ mean displacement, m

μ_i surface chemical potential of species i, J mol^{-1}

μ_i^o standard surface chemical potential of species i, J mol^{-1}

v_i jump frequency, s^{-1}

Π spreading pressure, N m^{-1}

Subscripts

i, j species i, j

$n + 1$ refers to vacant sites (also denoted by V)

0 initial value at time $t = 0$

t refers to total mixture

sat refers to saturation value; also refers to surface conditions in eqs (40) and (41)

T, Π refers to gradient obtained under conditions of constant temperature and spreading pressure

V refers to vacancy $(\equiv$ component $n + 1)$

Superscripts

o standard state

0 parameter at vanishingly small surface occupancy

1 parameter at total surface occupancy

s refers to surface

Matrix notation

$[\;]$ square matrix of dimension $n \times n$

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APPENDIX A: COMPARISON OF FICK, ONSAGER AND GMS FORMULATIONS

An alternative formulation of surface diffusion is based on the Onsager formulation of irreversible thermodynamics (Ash and Barrer, 1967; Barrer, 1978; Kärger, 1973; Kärger and Bülow, 1975) relating the surface diffusion fluxes to the chemical potential gradients:

$$(J) = -n_t^s[L]\ \nabla_{T,\mathbf{n}}(\mu)/RT \tag{A1}$$

where we use n-dimensional matrix notation. The Onsager reciprocal relations show that the matrix $[L]$ is symmetric, i.e.

$$L_{ij} = L_{ji}. \tag{A2}$$

Further, from considerations of the second law of thermodynamics (Krishna and Taylor, 1986) it can be shown that the matrix $[L]$ is positive definite.

The column vector of surface chemical potential gradients, $\nabla_{T,\mathbf{n}}(\mu)$, is related to the gradients of surface coverages by

$$\frac{1}{RT}\nabla_{T,\mathbf{n}}\mu_i = \sum_{j=1}^{n} \frac{\partial \ln(f_i)}{\partial \theta_j}\frac{d\theta_j}{dz} = \sum_{j=1}^{n} G_{ij}\frac{d\theta_j}{dz}$$
$$(i = 1, 2, \ldots n) \quad \text{(A3)}$$

where the Hessian matrix of the Gibbs surface free energy, $[G]$, with elements

$$G_{ij} = (\partial\mu_i/\partial\theta_j)/RT = (\partial\mu_j/\partial\theta_i)/RT = G_{ji} \tag{A4}$$

is symmetric and from thermodynamic stability considerations it can be shown to be positive definite [cf. Modell and Reid (1983)]. Combining eqs (A1) and (A3) yields the working form of the Onsager formulation of surface diffusion:

$$(J) = -n_t^s[L][G]\frac{d(\theta)}{dz}. \tag{A5}$$

If we define an n-dimensional diagonal matrix $[\Theta]$, with elements δ_{ij}/θ_i, then we have the relation

$$[G] = [\Theta][\Gamma]. \tag{A6}$$

The interrelationships between the GMS, Fick and Onsager formulations follow from the above:

$$[D] = [B]^{-1}[\Gamma] \equiv [\mathbb{D}][\Gamma] = [L][G] = [L][\Theta][\Gamma] \tag{A7}$$

where we have further defined the matrix $[\mathbb{D}] \equiv [B]^{-1}$.

We note that since $[D]$ is a product of two symmetric positive definite matrices $[L]$ and $[G]$, the eigenvalues $\hat{D}_i$ of $[D]$ are always positive and real. Also, application of the Onsager reciprocal relations (A2) to the right equalities in eq. (A7) verifies the symmetry property of GMS diffusivities given by eq. (17).

For diffusion of a single sorbed species eq. (A7) collapses to the scalar relations

$$D_{1V} = \mathbb{D}_{1V}/(1 - \theta_1) = L_{1V}/\theta_1(1 - \theta_1). \tag{A8}$$

For the general multicomponent case the matrix of Onsager coefficients $[L]$ is obtained from eqs (A6) and

(A7) in the form

$$[L] = [B]^{-1}[\Theta] \equiv [\mathbb{D}][\Theta] \qquad (A9)$$

which relation gives an explicit procedure for calculation of $[L]$ from the GMS diffusivities $\mathbb{D}_{ij}$ and θ_i.

APPENDIX B: DIFFUSION OF BINARY SORBED SPECIES AND TRACER DIFFUSION

For diffusion of binary sorbed species the n-dimensional matrix form of the GMS reduces to a 2×2 matrix and explicit algebraic expressions can be derived for the matrices $[\Gamma]$ and $[D]$; these are derived hereunder along with further simplifications which describe tracer diffusion.

The matrix $[\mathbb{D}] \equiv [B]^{-1}$ has the elements $\mathbb{D}_{ij}$ given by

$$\mathbb{D}_{11} = \mathbb{D}_{1V}[\theta_1 \mathbb{D}_{2V} + (1 - \theta_1)\mathbb{D}_{12}]/(\theta_1 \mathbb{D}_{2V}$$
$$+ \theta_2 \mathbb{D}_{1V} + \theta_V \mathbb{D}_{12})$$

$$\mathbb{D}_{12} = \theta_1 \mathbb{D}_{2V}(\mathbb{D}_{1V} - \mathbb{D}_{12})/(\theta_1 \mathbb{D}_{2V} + \theta_2 \mathbb{D}_{1V} + \theta_V \mathbb{D}_{12})$$

$$\mathbb{D}_{21} = \theta_2 \mathbb{D}_{1V}(\mathbb{D}_{2V} - \mathbb{D}_{12})/(\theta_1 \mathbb{D}_{2V} + \theta_2 \mathbb{D}_{1V} + \theta_V \mathbb{D}_{12})$$

$$\mathbb{D}_{22} = \mathbb{D}_{2V}[\theta_2 \mathbb{D}_{1V} + (1 - \theta_2)\mathbb{D}_{12}]/(\theta_1 \mathbb{D}_{2V} + \theta_2 \mathbb{D}_{1V}$$
$$+ \theta_V \mathbb{D}_{12}). \qquad (B1)$$

The elements of the thermodynamic factor matrix $[\Gamma]$ assuming a Langmuirian sorbed phase [cf. eq. (15)] are

$$\Gamma_{12} = \frac{\theta_1}{1 - \theta_1 - \theta_2}, \quad \Gamma_{11} = 1 + \Gamma_{12}$$

$$\Gamma_{21} = \frac{\theta_2}{1 - \theta_1 - \theta_2}, \quad \Gamma_{22} = 1 + \Gamma_{21}. \qquad (B2)$$

The elements of the matrix of Fick diffusivities $[D]$ are

$$D_{11} = \mathbb{D}_{11}\Gamma_{11} + \mathbb{D}_{12}\Gamma_{21}, \quad D_{12} = \mathbb{D}_{11}\Gamma_{12} + \mathbb{D}_{12}\Gamma_{22}$$
$$D_{21} = \mathbb{D}_{21}\Gamma_{11} + \mathbb{D}_{22}\Gamma_{21}, \quad D_{22} = \mathbb{D}_{21}\Gamma_{12} + \mathbb{D}_{22}\Gamma_{22}. \qquad (B3)$$

For the special case of tracer diffusion, species 1 and 2 are identical ($\mathbb{D}_{1V} = \mathbb{D}_{2V}$), and the tracer diffusivity D^* defined by eq. (34) reduces to [cf. eqs (B1)–(B3)]

$$D^* = D_{11} - D_{12} = D_{22} - D_{21} = \mathbb{D}_{11} - \mathbb{D}_{12}$$

$$= \frac{1}{\dfrac{\theta_1 + \theta_2}{\mathbb{D}_{12}} + \dfrac{\theta_V}{\mathbb{D}_{1V}}}. \qquad (B4)$$

Use of the alternative Onsager formulation, eq. (A5), leads to the following expression for the tracer diffusivity:

$$D^* = D_{11} - D_{12} \equiv L_{11}(G_{11} - G_{12}) - L_{12}(G_{22} - G_{21})$$

$$= L_{11}(\Gamma_{11} - \Gamma_{12})/\theta_1 - L_{12}(\Gamma_{22} - \Gamma_{21})/\theta_2$$

$$= L_{11}/\theta_1 - L_{12}/\theta_2 = \mathbb{D}_{1V}(1 - \theta_1 L_{12}/\theta_2 L_{11})$$

$$= \mathbb{D}_{1V}(1 - \theta_1 L_{12}/\theta_2 L_{11})/\Gamma \qquad (B5)$$

where we have invoked equalities (A6) and (A8). From eqs (A9) and (B1) we can obtain the following expression for the cross-coefficient L_{12}:

$$L_{12} = \mathbb{D}_{12}\theta_2 = \theta_1 \theta_2 \mathbb{D}_{1V}(\mathbb{D}_{1V} - \mathbb{D}_{12})/[(\theta_1$$
$$+ \theta_2)\mathbb{D}_{1V} + \theta_V \mathbb{D}_{12})]. \qquad (B6)$$

Relation (B6) shows that when $\mathbb{D}_{12} = \mathbb{D}_{1V}$ and is independent of surface occupancy, then $L_{12} \equiv 0$; under these circumstances we have the following simple expression for the tracer diffusivity:

$$D^* = \mathbb{D}_{1V} = L_{11}/\theta_1 \qquad (B7)$$

or in other words the tracer diffusivity is equal to the "corrected" diffusivity $\mathbb{D}_{1V}$.

APPENDIX C: TRANSIENT UPTAKE PROFILES FOR BINARY DIFFUSION

The first step is the calculation of the eigenvalues of $[D]$; these are given by

$$\hat{D}_{1,2} = \frac{D_{11} + D_{22}}{2} \pm \frac{D_{11} - D_{22}}{2}$$
$$\times [1 + 4D_{12}D_{21}/(D_{11} - D_{22})^2]^{1/2}. \qquad (C1)$$

The fractional approach to equilibrium is then calculated for each of the two eigenvalues calculated above:

$$\hat{f}_i = 1 - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp\left(-\frac{m^2 \pi^2 \hat{D}_i t}{r_c^2}\right). \qquad (C2)$$

The fractional approach matrix $[F]$ is given by Sylvester's theorem [cf. Krishna and Standart (1979)]:

$$[F] = \frac{\hat{f}_1}{\hat{D}_1 - \hat{D}_2}([D] - \hat{D}_2[I]) + \frac{\hat{f}_2}{\hat{D}_2 - \hat{D}_1}([D] - \hat{D}_1[I]). \qquad (C3)$$

The transient uptake profiles are given by [cf. eq. (41)]

$$(\theta - \theta_o) = [F](\theta_{sat} - \theta_o). \qquad (C4)$$

The solution matrix $[F]$ is generally non-diagonal and eq. (C4) shows that the uptake of components 1 and 2 are coupled to each other.