SKBF TEKNISK
KBS RAPPORT

83-37

Surface migration in sorption processes

A Rasmuson
I Neretnieks

Royal Institute of Technology
Stockholm, Sweden March 1983

SVENSK KÄRNBRÄNSLEFÖRSÖRJNING AB / AVDELNING KBS

POSTADRESS: Box 5864, 102 48 Stockholm, Telefon 08-67 95 40

SURFACE MIGRATION IN SORPTION PROCESSES

Anders Rasmuson
Ivars Neretnieks

Department of Chemical Engineering
Royal Institute of Technology
Stockholm, Sweden, March 1983

A list of other reports published in this series during 1983 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17) and 1982 (TR 82-28) is available through SKBF/KBS.

SURFACE MIGRATION IN SORPTION PROCESSES

Anders Rasmuson
Ivars Neretnieks

March 1983

Department of Chemical Engineering
Royal Institute of Technology
S-100 44 STOCKHOLM
Sweden

SUMMARY

Diffusion rates of sorbing chemical species in granites and clays are, in several experiments within the KBS study, higher than can be explained by pore diffusion only. One possible additional transport mechanism is transport of sorbed molecules/ions along the intrapore surfaces.

As a first step a literature investigation on surface migration on solid surfaces has been conducted. A lot of experimental evidence of the mobility of sorbed molecules has been gathered through the years, particularly for metal surfaces and chemical engineering systems. For clays, however, there are only a few articles, and for granites, none. Two classes of surface migration models have been proposed in the literature:

i) Surface flow as a result of a gradient in spreading pressure.

ii) Surface diffusion as a result of a gradient in concentration.

The surface flow model has only been applied to gaseous systems. However, it should be equally applicable to liquid systems.

The models (i) and (ii) are conceptually very different. However, the resulting expressions for surface flux are complicated and it will not be an easy task to distinguish between them. There seem to be three ways of discriminating between the transport mechanisms:

a) Temperature dependence

b) Concentration dependence

c) Order of magnitude.

CONTENTS

INTRODUCTION

In different areas of the KBS study diffusive mass transport rates, for sorbing species, of a magnitude that cannot be explained by pore diffusion alone, have been observed. This is the case in some of the diffusion experiments with bentonite, and there are also recent results on diffusion in granite that point in this direction. In the former case a high diffusivity would be negative, while in the latter case it would help in retarding escaping radionuclides. One possible explanation is the diffusion of adsorbed molecules along the pore surfaces acting in parallel with pore diffusion.

Migration of adsorbed molecules on surfaces is a process that has received considerable attention from a scientific point of view and is of considerable significance in a number of technological areas. For example: the sintering of metal and metal oxide powders is to a large extent controlled by surface diffusion (Kuczynski 1961, Rhead 1972); the rate of migration and coalescence of internal voids in metals as they are generated in nuclear reactors, is governed by surface diffusion (Willertz and Shewmon 1970); the stability of small catalyst particles that are supported on high surface area oxides may be a function of surface diffusion of adatoms across the support (Geguzin et al. 1969, Wynblatt and Gjostein 1974); the process of crystal growth from the vapor phase has been recognized to depend on surface diffusion of adatoms (Hirth and Pound 1963, Gilmer and Bennema, 1972); the technology of thin film semiconductor devices is in several ways related to the process of surface diffusion e.g. through nucleation and growth of epitaxial films (e.g. Hayek and Schwabe 1972, Bauer and Poppa 1972) and electromigration in thin films (Rosenberg, 1972).

Diffusion on solids is important in many chemical and chemical engineering processes as well. The mobility of atoms and other dissociation products formed on the surface of a catalyst has an important bearing on the course of reactions occuring at the surface (e.g. Satterfield 1970). Adsorption of organics on activated carbon is often strongly influenced by surface diffusion (e.g. Suzuki and Fujii

1982). Surface diffusion is also of importance in many gas phase adsorption processes (e.g. Okazaki et al. 1981).

The scientific interest stems from the fact that quantitative measurements of surface mobility give information about atomic and molecular behavior on solid surfaces. In a sense, an atom moving over a crystal can be viewed as a convenient probe of local properties

A number of reviews and summarizing articles on surface diffusion are available in the literature. A list of recent reviews has been compiled in Table 1. However, it should be recognized that most of them deal with diffusion on metal surfaces.

Table 1. Recent reviews of surface diffusion.

Title	Author
Surface structure and diffusion	Gomer (1959)
Surface self-diffusion	Gjostein (1963)
Surface diffusion	Blakely (1963)
Surface diffusion of adsorbed molecules	Dacey (1965)
Zur Oberflächendiffusion und oberflächennahen Diffusion auf Kristallen	Meyer (1968)
Diffusion along a real crystal surface	Geguzin (1969)
In situ measurements of surface self-diffusion of metals	Bonzel and Gjostein (1969)
Surface diffusion of oxides	Robertson (1969)
Surface self-diffusion on metals	Hirano and Tanaka (1970)
Surface grain boundary and dislocation pipe diffusion	Gjostein (1970)
Surface diffusion	Satterfield (1970)
Regularities of surface diffusion	Gal and Borisov (1971)
Surface self-diffusion of metals	Neumann and Neumann (1972)
Mobility of atoms and molecules over solid surfaces	Geuss (1972)
Short circuit diffusion	Gjostein (1973)
Transport of matter at surfaces	Bonzel (1975)
Surface diffusion	Ehrlich and Stolt (1980)
Surface diffusion of adsorbed species	King (1980)
Surface diffusion	Gomer (1982)

ADSORPTION

Surface migration cannot be significant unless appreciable adsorption occurs (number of molecules in adsorbed state), yet if adsorbed molecules are held so strongly as to be essentially immobile, surface diffusion will be insignificant. Accordingly, the equilibrium relationship is essential for interpreting surface migration. From a dynamic point of view, adsorption may be classfied as mobile or nonmobile. In the former case a molecule may move about while on the surface, remaining in the adsorbed state all the time. In the latter case it does not leave its adsorbed position until it desorbs and return to the fluid phase. The mobility is dependent on temperature. For example Milchev and Paunov (1981), used a simplified model to describe the gradual transition from localized to mobile adsorption with increasing temperature.

Adsorption is usually said to be either physical or chemical. This distinction is based mainly on the magnitude of the heat of adsorption and is not very precise. Physical adsorption is due to the operation of forces between the solid surface and the adsorbate molecules that are similar to the van der Waal´s forces between molecules. These forces are undirected and relatively nonspecific. The energies of adsorption involved are of the order of 10-40 kJ per mole. Physical adsorption is generally quite readily reversible. In contrast with physical adsorption, chemisorption is the result of much stronger binding forces, comparable with those leading to the formation of chemical compounds. The adsorption may be regarded as the formation of a sort of surface compound. The energies of adsorption range from about 40 to 400 kJ per mole. Chemisorption is seldom reversible.

Chemisorption is completed when a surface is covered by an adsorbed monolayer, but there is good evidence that physisorption can lead to adsorbed layers several molecules thick. Sometimes a physically adsorbed layer may form on top of an underlying chemisorbed layer.

Accordingly, adsorption may also be classified as monolayer or multilayer. The former deals with low surface concentrations up to where the surface is covered with one layer of adsorbed molecules and the latter with all coverage above this. The distinction is not too exact because multilayers may begin to build up before the monolayer is completed; hence the properties of these two types of adsorption often overlap. According to Moore (1962, p. 749) adsorption from solution does not in general appear to lead to layers more than one molecule thick.

Finally, we may also distinguish between localized and nonlocalized adsorption. In localized adsorption the adsorbed molecules take up fixed positions, and although in some cases they are free to move from position to position, they are at equilibrium with the surface only when occupying adsorption sites. In contrast to this, nonlocalized adsorption occurs when the molecules are stable at any point on the surface and there are no favored positions of lower potential energy. This does not mean that the surface is energetically uniform; some regions may have higher heats of adsorption than others but the adsorbed molecules are not limited to specific points of attachment.

Adsorption is described mathematically in equilibrium adsorption isotherm models. In these the concentration in the solid C_s is related to the concentration in the fluid C_p through the equilibrium relationship:

$$C_s = f(C_p) \qquad (1)$$

where f in general is a nonlinear function of C_p.

A compilation of common adsorption isotherm models is given by Belfort (1980) (Table 2).

			Initial investigators	
Models	**Important assumptions**	**Comments**	**Gas-vapor phase (founders)**	**Liquid phase recent**
Gibbs adsorption isotherm	Hypothetical 2-D adsorbed-surface phase in equilibrium with solution and obeying the fundamental property relation with *P*, *V*, replaced by π and *A*.	In several multisolute adsorption applications (at a specific π), theory proved more useful for dilute rather than concentrated solutions.	Gibbs (1906); Myers and Prausnitz (1965) (extended to multicomponent sorption)	Radke and Prausnitz (1972) (extended to multicomponent sorption)
Monomolecular (Langmuir) isotherm	Uniform adsorption energy, maximum amount adsorbed is a saturated monolayer; surface forces operate between molecules and atoms that actually contact the surface; no transmigration in the plane of the surface.	Generally applicable at low pressure (for gas phase) and concentrations (for liquid phase); assumptions not always met for liquid phase adsorption.	Langmuir (1916)	—
Multilayer (BET) adsorption isotherm	Langmuir model applies to successive layers; layers need not fill before next layers begin to grow.	Several versions of this model have been proposed; assumptions probably not always met for liquid-phase adsorption.	Brunauer, Emmet, and Teller (1938)	—
Capillary condensation isotherm	Vapors are condensed as bulk liquid in pores owing to the lowering of vapor pressure due to the effects of surface tension.	Capillary forces cannot be used to explain sorption upon planar surfaces or the sorption of gases.	Zsigmondy (1911)	—
Thick compressed-film (Polanyi adsorption potential) isotherm	Equipotential and equal-compression planes exist in the adsorbed phase, heterogeneous adsorption energy allowed.	Although the validity of the model has been severely criticized, the empirical plotting procedure appears to be simple and useful; the surface area of the adsorbent is not explicitly mentioned.	Polanyi (1914); Eucken (1914)	Manes (1962) (single and multicomponent sorption)
Exponential empirical (Freundlich) isotherm	Empirical and meant to apply within a narrow range of the adsorption isotherm curve, beyond the Henry's law region.	Should not be projected outside the narrow range of experimental fit.	Freundlich (1922)	—

Table 2. Widely used equilibrium adsorption models (Belfort. 1980)

In addition some three-parameter adsorption isotherms are given by Jossens et al. (1978). Each of these reduces to Henry´s law at very low concentrations and each contains three adjustable parameters.

The isosteric heat of adsorption may be obtained from the equilibrium relationship using van´t Hoff´s relation:

$$q_{st} = R\,\frac{d\ell nK_A}{d(1/T)} \qquad (2)$$

where $K_A = K_A(C_p)$ is the equilibrium constant. The differential heat of adsorption is then obtained as:

$$q = q_{st} - RT \qquad (3)$$

Adsorption of electrolytes

The interaction of an electrolyte with an adsorbent may take one of several forms. The electrolyte may be totally adsorbed, in which case the situation is similar to that for molecular adsorption. It is more often true, however, that ions of one sign are held more strongly, with those of the opposite sign forming a diffuse or secondary layer. The surface may be polar, with a potential ψ, so that primary adsorption can be treated in terms of the Stern model, or the adsorption of interest may involve exchange of ions in the diffuse layer.

In the case of ion exchangers, the primary ions are chemically bonded into the framework of the ion exchanger, and the exchange is between ions in the secondary layer.

The potential difference across an interface may be pictured as an electrical double layer. One phase acquires a net negative charge and the other acquires a net positive charge. In the diffuse double layer theory proposed by Stern, the charge on the solid is rigidly fixed.

Adsorbed on top of this there may be a practically immobile layer of oppositely charged molecules of the liquid (Stern layer). Further in the solution there is a diffuse layer of charge, which may have a sign either the same as or opposite from that of the adsorbed layer (Gouy layer). Only this diffuse region is free to move. The potential drop ζ in the diffuse layer is called the zeta potential. The so called Stern equation may be put in a form somewhat analogous to the Langmuir equation (Adamson 1976, p. 411):

$$\theta/(1-\theta) = C_2 \exp\left[(ze\psi + \phi)/kT\right] \qquad (4)$$

where

z valence of ion
e charge of electron
ψ electrical potential
ϕ additional chemical adsorption potential

The effect is to write the adsorption free energy or, approximately. the energy of adsorption q as a sum of electrostatic and chemical contributions. Surface charge may be controlled or fixed by a potential determining ion. Table 3 (from Fuerstenau, 1971) lists the potential determining ion and its concentration giving zero charge on the mineral. There is a large family of minerals for which hydrogen (or hydroxide ion) is potential determining - oxides, silicates, phosphates, carbonates etc. For these, adsorption of surfactant ions is highly pH dependent.

Material	Potential determining ion	Point of zero charge
Fluorapatite, $Ca_5(PO_4)_3(F, OH)$	H^+	pH 6
Hydroxyapatite, $Ca_5(PO_4)_3(OH)$	H^+	pH 7
Alumina, Al_2O_3	H^+	pH 9
Calcite, $CaCO_3$	H^+	pH 9.5
Fluorite, CaF_2	Ca^{2+}	*p*Ca 3
Barite (synthetic), $BaSO_4$	Ba^{2+}	*p*Ba 6.7
Silver iodide	Ag^+	*p*Ag 5.6
Silver chloride	Ag^+	*p*Ag 4
Silver sulfide	Ag^+	*p*Ag 10.2

Table 3. Potential determining ion and point of zero charge (Fuerstenau, 1971).

EXPERIMENTAL EVIDENCE FOR THE MOBILITY OF ADSORBED MOLECULES

Metal surfaces

Three recent reviews have focused on the diffusion of adsorbed species on metal surfaces: Bonzel (1975), Ehrlich and Stolt (1980) and King (1980). The investigations include:

diffusion in monolayers of metals
diffusion of chemisorbed gases (on metals).

It must be emphasized that the studies are made at elevated temperatures.

A few of the features qualitatively important in surface diffusion on metals may be inferred from experiments performed. It is clear that in most adsorbed layers diffusion is rapid at temperatures considerably below those at which evaporation occurs. The barrier to diffusion of atoms chemisorbed on metals is quite small on the scale of the desorption energy. This is not surprising, as on a metal one expects interactions of adatoms with the substrate to be somewhat insensitive to their exact location on the surface. The concentration of the adsorbed layer also has a strong effect on atomic motion.

To gain more insight into the process, studies have also been made on well-defined crystal planes. An interesting result has been given by Chen and Gomer (1979). They found a significant dependence on surface concentration for the diffusion of oxygen on tungsten (Figure 1).

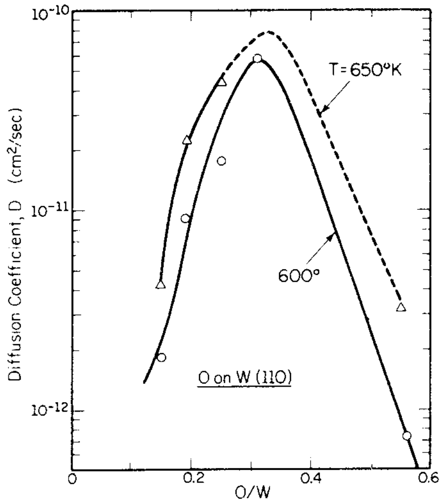

Figure 1. Concentration dependence of diffusion coefficient for oxygen on W(110) (Chen and Gomer, 1979).

The maximum in the curve is a result of two competing effects: activation energy which rises with increasing concentration and the dynamics of molecular motion which is more rapid at higher concentrations.

An interesting new line of research in this area has been made possible by the development of the field ion microscope (FIM). The atomic resolution of this instrument offers a direct view of atomic displacements, and diffusivities can thus be derived from a random walk formalism. Unfortunately, the FIM techniques are immediately applicable only to metal adatoms, which are not seriously affected by the act of observation.

Physicochemical and Chemical Engineering systems

The enhancement of diffusive mass transport in porous materials by surface diffusion is well documented in chemical engineering literature of both gaseous and liquid separations (Schneider and Smith, 1968; Knoblauch et al., 1969; Horiguchi et al., 1971; Furusawa and Smith, 1973; Komiyama and Smith, 1974; Gilliland et al., 1974; Lee and O´Connell, 1975; Suzuki and Kawazoe, 1975; Suzuki et al.,1976; Ponzi et al., 1977; Sudo et al., 1978; Johansson and Neretnieks, 1980; Okazaki et al., 1981 a,b; Suzuki and Fujii, 1982).

Furusawa and Smith (1973) found surface diffusion in the liquid-filled pore transport of benzene adsorbed from aqueous solutions on activated carbon. Effective diffusivities for the liquid-filled pores were much larger than values predicted from the molecular diffusivity of benzene in water using a normal tortuosity factor. A surface diffusivity of about $6 \cdot 10^{-13}$ m^2/s was obtained. Surface diffusion of organics adsorbed from aqueous solutions on activated carbon has also been independently recorded by Knoblauch, Juntgen and Peters (1969). Komiyama and Smith (1974) measured the adsorption rates from 25 °C to 75 °C for benzaldehyde on polymeric, porous Amberlite particles (poly-styrene). When the benzaldehyde was dissolved in methanol, the adsorption capacity was very low. Data for methanol solutions gave reasonable values for intraparticle diffusivities based solely on transport in the pore volume. For adsorption from aqueous solution (where the adsorption capacity was high), the contribution of surface diffusion was important.

Suzuki and Kawazoe (1975) measured the adsorption of fifteen kinds of volatile organics from aqueous solution on activated carbon in a batch system. It was assumed that the rate of adsorption was controlled by intraparticle surface diffusion. The effective surface diffusion coefficients were successfully correlated to the ratio of the boiling point of adsorbate to adsorption temperature as:

$$D_s = 1.1 \cdot 10^{-8} \exp(-5.32\, T_b/T),\ \mathrm{m^2/s} \qquad (5)$$

In the case of activated diffusion we have:

$$D_s = D_{so} \exp(-E/RT) \qquad (6)$$

Equations (5) and (6) suggest that the activation energy, E, can be related to the heat of vaporization, q_v, because the boiling point for non-polar substances is thought to be approximately proportional to q_v by Trouton´s rule:

$$q_v = 21.0\, T_b,\ \mathrm{cal/^oK,\ mol} \qquad (7)$$

Then from equations (5) - (7) the activation energy E is given as:

$$E = 0.5\, q_v \qquad (8)$$

In a later paper by Suzuki et al. (1976) the adsorption of polyoxyethylene of various molecular weights from aqueous solutions on activated carbon was investigated. It was found that the effective surface diffusion coefficient decreased in proportion to the square root of the molecular weight of the polymer.

Sudo et al. (1978) made an experimental investigation of the concentration dependence of effective surface diffusion coefficients in aqueous phase adsorption on activated carbon. Five chlorinated aromatics as well as benzoic acid were used as adsorbates. The data could be represented by the relationship:

$$D_s = D_{so} \exp (a s_\infty) \tag{9}$$

with $a = 0.88$ g/mole
s_∞ is the equilibrium amount adsorbed, mole/g

The increase of D_s with s_∞ was explained as a decrease of the heat of adsorption with surface concentration.

Johansson and Neretnieks (1980) did an experimental study of adsorption on activated carbon in countercurrent flow. For the organics adsorbed the determined surface diffusivities show a concentration dependence similar to equation (9).

Suzuki and Fujii (1982) performed a Wicke Kallenbach type steady state diffusion experiment for varying concentrations of propionic acid solution through activated carbon pellets. Concentration dependence of the surface diffusion coefficient was determined from the variation of diffusion flux with concentration. The strong dependence of the surface diffusion coefficient on the amount adsorbed was partially interpreted in terms of the change of heat of adsorption with surface coverage as determined from separate equilibrium runs. The following relation was obtained:

$$D_s = D_{so} (a \cdot s)^n \qquad (10)$$

where s is the amount adsorbed (mol/kg).

Schneider and Smith (1968) have reported that for hydrocarbons on silica gel, in some instances 70-80 % of the transport within the silica gel occurred on the surface even at temperatures in excess of room temperature. The diffusivities obtained correspond to very low surface coverages (fraction of a monolayer of the order of 10^{-4}) and should represent limiting values. A survey of available surface diffusion literature, all at higher coverages, indicated that the results reported by the authors are at the lower end of the range of diffusivities. The activation energy (obtained from $D_S = D_S(T)$) and heat of adsorption (from $K_A = K_A(T)$), for example for n-butane, were 4.4 and -7.8 kcal/mole, respectively.

An experimental investigation of the effect of surface energetic heterogeneity on surface diffusion was reported by Horiguchi et al. (1971). Two porous solids were chosen - Vycor and Graphon. The former is characterized as having an energetically heterogeneous surface because its heat of adsorption decreases markedly with the amount adsorbed, while the latter has an energetically homogeneous surface which exhibits a constant heat almost to an adsorbate monolayer. Experiments with ethane, propylene, nitrogen and helium showed that surface diffusion proceeds more rapidly on Graphon surfaces.

Gilliland et al. (1974) presented data on the flow of CO_2, SO_2 and NH_3 in porous glass. They describe surface transport in terms of the hopping of adsorbed molecules between adjacent sites of different adsorption strength. The change in surface diffusivity with surface concentration attributed to a change in the strength of adsorption, as evidenced by a change in the differential heat of adsorption q, with concentration. The correlating equation predicts that the surface diffusivity varies as exp (-aq/RT) where a is an experimental constant. In a second part (Sladek et al., 1974), surface diffusion of hydrogen on platinum was detected. Using these data and literature values of D_S three classes of behavior were found. Differences were attributed to differences in the type of gas-surface bonding. Numbers m were assigned to each bond type and a general correlation was produced, $D_S = 1.6 \cdot 10^{-6} \exp(-0.45\, q/m\, RT)$, m^2/s.

The quasi-steady flux of $CHCL_3$ in a porous bed of Graphon particles was measured under various conditions by Lee and O´Connell (1975). A correlation was made with a statistical mechanical model developed by the authors.

Ponce et al. (1977) measured the flux of Freon 12 through Carbon Regal 660. Surface permeabilities calculated with a new hopping mechanistic model were compared with the experimental data.

An extended hopping model was derived by Okazaki et al. (1981 a,b) by separately taking into account the hopping behaviors of monolayer and multilayer molecules. A good agreement was obtained with experimental surface flow rates of C_2H_4, C_3H_6, iC_4H_{10} and SO_2 through porous Vycor glass in a wide range of surface concentrations.

Surface diffusion from a gas phase has also been studied experimentally on numerous heterogeneous solid catalysts (Barrer and Barrie, 1952; Barrer and Gabor, 1960; Gelbin, 1968; Sterret and Brown, 1968; Satterfield, 1970; Reed and Butt, 1971).

In physicochemical context experimental work on surface migration has been done by Boddenberg et al. (1972) and Fripiat (1977). A review was done by Haul and Hübner (1975).

Boddenberg et al. (1972) and Fripiat (1977) both used the NMR-technique in their investigations. Boddenberg et al. made a study of the surface diffusion of benzene adsorbed on modified silica surfaces. Within the range below monolayer coverage the diffusion coefficients of benzene adsorbed on a hydroxylated surface increase with increasing coverage, whereas on a methylated surface the opposite dependence was observed. This difference is due to the specific interaction of the benzene molecules with OH groups. This explains why the diffusion coefficients for the methylated surface are distinctly larger than for the hydroxylated sample. The decrease of D_s in the case of the energetically more homogeneous methylated surface is attributed to increasing mutual hindrance of the adsorbed molecules with rising density of adsorption layer. In the case of the hydroxylated adsorbent, the increase of the diffusion coefficient is attributed to the influence of OH groups, which are preferential adsorption sites for benzene molecules. As the coverage becomes larger, more and more weaker adsorption sites will come into play. Also, adsorption of molecules in higher layers may be appreciable even below the completed monolayer.

In Fripiat (1977) the mobility of physically adsorbed hydroxylic molecules on surfaces made from oxygen atoms is investigated. The correlation times were primarily measured through the longitudinal spin-lattice relaxation rate $T_1{}^{-1}$. The surface diffusion coefficient was approximated by:

$$D = \lambda^2/6\tau_m \qquad (11)$$

where the quadratic jump distance λ^2 was taken as the molecular area of methanol. τ_m is the average correlation time.

Clays

Ion diffusion in clay-water systems is receiving increasing attention because of the role of diffusion in nutrient uptake by plants. Accordingly, the bulk of the literature on the subject is found in Soil Science journals. Gast (1962) determined the diffusivities of Na, Ba, Ce, K, Ca, Sr, Cs, Y in bentonite clay pastes. Evidence is presented which points toward the diffusivity of cations in the clay pastes as being a multiple rate process. Results suggested that contributions of 1) the diffuse layer and true solution ions and 2) the Stern layer ions (physically adsorbed) dominate the diffusion process.

Schaik et al. (1966) measured self-diffusion of sodium and calcium ions in bentonites containing various amounts of water and the respective chlorides. The contribution of mobile exchangeable cations to diffusion was calculated from the data by subtracting measured rates of free electrolyte diffusion from the total rate of self-diffusion measured in these systems. Mobile exchangeable cations accounted for from 3 to over 500 times as much diffusive movement as was accounted for by free electrolyte cations.

Kemper and Quirk (1972) placed compacted bentonite, illite and kaolinite clays between chloride solutions of the respective cations of different concentrations. Rates of osmotic flow, electric potentials in the solutions and streaming potentials were measured across these compacted clay membranes. The portion of adsorbed cations participating in the diffuse portion of the double layer was calculated from the ζ potential. This mobile fraction of the adsorbed cations appears to decrease for multivalent cations as the equilibrium solution concentration decreases.

Dufey and Laudelout (1975) studied the surface self-diffusion of sodium in mixed Na-Li and Na-Rb-clay suspensions. The Rb^+ ions were found to increase the surface mobility of sodium while the Li^+ ions produced a very slight opposite effect. This was attributed to a modification of the relative distribution of the Na^+ ions between the

Stern and Gouy layers when another cation was introduced on the clay surface. The surface self-diffusion of a cation was calculated from measured quantities by:

$$D_\sigma^{Na} = \frac{D_g^{Na} F - D_s^{Na} (1-X_\sigma^{Na})}{X_\sigma^{Na}} \qquad (12)$$

where

D_g^{Na}	self-diffusion coefficient of Na^+ measured in the clay suspension
D_s^{Na}	self-diffusion coefficient of Na^+ in the solution
F	formation factor that accounts for tortuosity effects in the clay-water system
X_σ^{Na}	fraction of the total amount of Na^+ ions present in the suspension which is contained in the surface phase.

Eriksen et al. (1981) and Eriksen and Jacobsson (1982) recently determined the diffusivities of Cs^+, Sr^{2+}, I^- and Cl^- in compacted Na- and Ca-bentonites. The experimental results indicate that the diffusion through compacted bentonite is governed by complex mechanisms and cannot be accomodated by a simple pore diffusion model. It seems reasonable to assume that non-sorbing ions migrate in the pore water, while cations also move through smectic crystal lattices, preferably through interlamellar spacings according to an ion-exchange-type model.

Rocks

Diffusion experiments on uncrushed rock samples are being performed by Skagius and Neretnieks (1982). The experiments are being done on both

Stripa and Finnsjoe granite with Sr and Cs as diffusing and sorbing components. In a series of experiments the electrical conductivity of saturated (1M Na Cl) rock samples are also measured. The diffusivities and resistivities are related by the equation:

$$\frac{D_p \varepsilon_p}{D_v} = \varepsilon_p \frac{\delta_D}{\tau_p^2} = \frac{R_o}{R_s} \qquad (13)$$

where

D_v = diffusivity in water
D_p = diffusivity in water in pores
ε_p = porosity
δ_D/τ_p^2 = geometric factor
R_o = resistivity of electrolyte
R_s = resistivity of rock sample saturated with electrolyte

The experiments are not yet finished. However, for Finnsjoe granite there are some preliminary results. The resistivity measurements indicate a value of

$$\varepsilon_p \frac{\delta_D}{\tau_p^2} \quad \text{of } 7.0 \cdot 10^{-5} - 1.0 \cdot 10^{-4}$$

For Sr, using the relation above and $D_v = 2 \cdot 10^{-9}$. we get

$$D_p \varepsilon_p \leq 2 \cdot 10^{-13} \text{ m}^2/\text{s}$$

However, the diffusion experiments with Sr gave

$D_p \varepsilon_p = 2.2 \cdot 10^{-12}$ m^2/s, i.e. a diffusivity an order of magnitude higher.

This points to additional transport mechanisms (surface diffusion ?) for Sr.

THEORY

Retention time

An important factor in surface migration is the average time molecules remain on the surface. Frenkel (see de Boer, 1968) derived the following theoretical expression for the retention time:

$$t_R = t_{R0} e^{q/RT} \qquad (14)$$

where

q is the molar heat of adsorption

t_{R0} is the period of oscillation of the molecules in the adsorbed state (vibrations normal to the surface)

Equation (14) which has been experimentally verified for many pairs of adsorbent-adsorbate, predicts an increase of the retention time on going from physical adsorption to chemisorption, for this transition corresponds to an increase in q.

The period of oscillation t_{R0} is usually between 10^{-12} and 10^{-14} sec. It can be calculated using statistical mechanics, since the period of oscillation is related to the entropy lost by the adsorbed molecule. When the sorbed molecule can migrate on the surface, only one degree of freedom (corresponding to linear translation perpendicular to the surface) is lost and t_{R0} is given by:

$$t_{R0} = h/kT = 1.6 \cdot 10^{-13} \text{ sec.} \qquad (15)$$

at room temperature. The period of oscillation is greater than $1.6 \cdot 10^{-13}$ sec when a fraction of the lost entropy is transformed into vibrational entropy (thus giving rise to an excited vibration in the direction normal to the surface). If there is no surface migration, in which case the three translational degrees of freedom are lost, t_{R0} can be as small as 10^{-16} sec.

Values of retention times as a function of the molar heat of adsorption at room temperature are given in Table 4.

q (kJ/mol)	t_R (sec)
1	$2.4 \cdot 10^{-13}$
3	$5.5 \cdot 10^{-13}$
10	$9.7 \cdot 10^{-12}$
30	$3.5 \cdot 10^{-8}$
100	$1.0 \cdot 10^{5}$ (1.2 days)
300	$4.5 \cdot 10^{40}$ (= $1.4 \cdot 10^{31}$ centuries)

Table 4: Retention times for different heats of adsorption at 20° C and $t_{R0} = 1.6 \cdot 10^{-13}$ sec.

Gibbs´ adsorption isotherm - spreading pressure

In one class of models for surface migration the flux of molecules is assumed to be the result of a gradient in spreading pressure or two-dimensional pressure. The concept of spreading pressure was introduced by Gibbs in his treatment of thermodynamics of surfaces.

As shown by Gibbs, the solution-solid interfacial region can be considered as a separate two-dimensional phase. If the solid is assumed to be inert and to possess a specific surface area identical for all adsorbates, then the differential of the Helmholtz´ energy of the adsorbed phase, designated by superscript a, is given by:

$$dF^a = - S^a\, dT + \gamma dA + \sum_i \mu_i^a\, dn_i^a + \mu_s^a\, dn_s^a \qquad (16)$$

where

F	Helmholtz´ free energy, J
S	entropy, J/°K
A	surface area. m²
γ	surface tension. N/m
μ	chemical potential. J/mol
n	moles of solute or solvent. mol
i	solute
s	solvent

The amount of solid adsorbed does not appear in equation (16) because the Gibbs´ dividing surface is chosen in such a manner that the adsorption of solid is zero.

By Euler´s theorem, equation (16) can be integrated to give:

$$F^a = \gamma A + \sum_i \mu_i^a\, n_i^a + \mu_s^a\, n_s^a \qquad (17)$$

Differentiation of equation (17) and comparison with equation (16) lead to the Gibbs´ isothermal adsorption equation:

$$- A d\gamma = \sum_i n_i^a\, d\mu_i^a + n_s^a\, d\mu_s^a \qquad \text{(constant T)} \qquad (18)$$

At equilibrium the chemical potentials of the adsorbed and liquid phases are identical. Hence the isothermal Gibbs-Duhem equation can be written as

$$\sum_i C_i\, d\mu_i^a + C_s\, d\mu_s^a = 0 \qquad \text{(constant T)} \qquad (19)$$

where C_i and C_s are the bulk liquid concentration of solute i and solvent s in moles per unit volume.

Substitution of equation (19) into equation (18) gives

$$- A d\gamma = A d\pi = \sum_i n_i^m \, d\mu_i^a \qquad \text{(constant T)} \qquad (20)$$

where the summation is over solute species only.

The spreading pressure π is defined as the difference between the interfacial tension of the pure solvent-solid interface and that of the solution-solid interface at the same temperature:

$$\pi = \gamma_{\text{pure solvent-solid}} - \gamma_{\text{solution-solid}} \qquad (21)$$

The quantity n_i^m is an "invariant" adsorption of solute i defined by:

$$n_i^m = n_i^a - \frac{C_i}{C_s} n_s^a \qquad (22)$$

Moles of solute and solvent adsorbed n_i^a and n_s^a are defined as Gibbs' surface excess quantities. relative to that dividing surface which makes the adsorption of solid zero. The invariant adsorption n_i^m, being independent of the location of the Gibbs dividing surface, is measurable without experimentally specifying the position of that dividing surface.

For a dilute solution $n_i^m \approx n_i^a$ and for a single solute we get:

$$d\pi = n_1^a \, d\mu_1 \qquad (23)$$

where n_1^a is the number of adsorbed moles. The potential may be written in terms of activity as:

$$\mu_1 = \mu_1^0 + RT \ \ell n \ a_1 \qquad (24)$$

Combining (23) and (24) we get

$$\pi = \frac{RT}{S_w} \int n_1^a \ d\ell n a_1 \qquad (25)$$

For a dilute solution $a_1 \alpha C_1$ and

$$\pi = \frac{RT}{S_w} \int_0^{C_1} n_1^a \ d\ell n C_1 \qquad (26)$$

The situation is slightly more complicated for electrolytes. For example the activity for a single salt ($C_{\nu+} A_{\nu-}$) is given by (Moore, 1962 p. 346)

$$a_1 = \gamma_\pm^{\ \nu} \ \nu_+^{\ \nu+} \ \nu_-^{\ \nu-} \ m_1^{\ \nu} \qquad (27)$$

where $\nu = \nu_+ + \nu_-$.

For CsCl at low concentrations we get $a_1 \alpha C_1$ giving the spreading pressure as

$$\pi = \frac{RT}{S_w} \int_0^{C_1} n_1^a \ d\ell n C_1^2$$

It is obvious from equation (26) that there exists a relation between the spreading pressure π and the concentration C_1 of the adsorbed component in the solution. Using the adsorption isotherm $n_1^a = n_1^a \ (C_1)$ this relation may be explicitly obtained.

The Langmuir isotherm is defined as:

$$n_l^a = n^a \, b \, C_l/(1 + b \, C_l) \qquad (28)$$

where n^a is the number of moles of adsorption sites per mass unit. From (26) we get:

$$\pi = \frac{RTn^a}{S_w} \ln(1+bC_l) = \frac{RTn^a}{S_w} \ln \frac{n^a}{n^a-n_l^a} \qquad (29)$$

The Freundlich isotherm may be written:

$$n_l^a = n^a \, a \, C_l^{\frac{1}{n}} \qquad (30)$$

We now obtain:

$$\pi = \frac{RTn^a an}{S_w} C_l^{\frac{1}{n}} = \frac{RTn}{S_w} n_l^a \qquad (31)$$

For a linear isotherm (n=1) this reduces to:

$$\pi = \frac{RTn^a a}{S_w} C_l = \frac{RT}{S_w} n_l^a \qquad (32)$$

The relations (29), (31) and (32) may be written as $\pi = \pi(C_S)$ using $C_s = C_l^a = \rho_p n_l^a$.

Models of surface flux

Fluid dynamic models

By analogy with volumetric flux, a constitutive equation for surface flux is written in terms of the spreading pressure gradient. This idea was originally applied by Babbit (1950) to the diffusion of gases in nonporous solids, was extended by Gilliland et al. (1958) and applied independently by Flood et al. (1952). The idea seems not to have been applied before to liquid systems.

The equation for surface flux may be arrived at by assuming there is a balance of the viscous forces f_V and the pressure forces $-\nabla\pi$ in the adsorbed layer, i.e.:

$$f_V = -\nabla\pi \tag{33}$$

Assuming that the viscous forces are directly proportional to the surface velocity V_S of the adsorbed molecules, we have:

$$R_S V_S = -\nabla\pi \tag{34}$$

where R_S is a proportionality constant. Using $N_S = C_S V_S$ in equation (34) leads to:

$$N_S = -\frac{C_S}{R_S}\nabla\pi \tag{35}$$

The proportionality constant R_S may be evaluated using simple hydrodynamic models.

Using the relations $\pi = \pi(C_S)$ developed in the preceding chapter the spreading pressure gradient may be transformed into a gradient in surface concentration. It is interesting to note that for a Freundlich isotherm (including the special case of a linear isotherm) the gradients are directly proportional.

Diffusion models

In these models the surface flux is defined in terms of a Fick´s-type law:

$$N_S = - D_S \nabla C_S \tag{36}$$

where D_S is the surface diffusivity. In general D_S may vary with concentration.

The proportionality constant D_S includes the factor τ_S, the surface tortuosity. In general, $\tau_S > \tau_p$ (τ_p tortuosity for pore diffusion). Using a model of randomly placed, freely overlapping spheres of the same radius, Ho and Strieder (1981) derived a relation between the surface tortuosity and void fraction. Furthermore, they derived a variational upper bound on the effective diffusion coefficient for a porous slab of arbitrary pore geometry for liquid or gas phase Fickian bulk diffusion in the void and Fickian surface diffusion on the pore walls.

A word of caution. According to Ehrlich and Stolt (1980), in dealing with systems more complicated than Langmuir layers, it becomes important to recognize explicitly that the net transport of material occurs as a response to a gradient in the chemical potential of the atoms in the adsorbed layer, not to a gradient in the concentration as assumed in Fick´s law.

To evaluate D_S different random walk or hopping mechanisms have been proposed (Hill, 1956; Higashi et al., 1963; Smith and Metzner, 1964; Weaver and Metzner, 1966; Gilliland et al., 1974; Ponzi et al., 1977; Thakur et al., 1980; Okazaki et al., 1981).

One group of models is sometimes called mechanistic. They are based on kinetic studies of the hopping movement of adsorbed gas molecules along the solid surface. They were principally developed by Smith and Metzner (1964) and Weaver and Metzner (1966). A modification was suggested by Ponzi et al. (1977). The calculation of surface flux is based on the following assumptions

1. The gaseous and adsorbed phases, both composed of a single gas, are in thermodynamical equilibrium characterized by adsorption isotherms.

2. Adsorbed molecules migrate along the adsorbent surface by means of small hops. For a molecule to hop it is necessary to make a transition from an adsorbed state to a partially desorbed state by obtaining an activation energy.

3. Although hops are in random directions, a concentration gradient in the adsorbed phase yields a net flux in a given direction.

Under these assumptions D_S in equation (36) may be expressed as (Weaver and Metzner, 1966):

$$D_s = \frac{S_w \rho_p}{2 \pi \tau_s^2} \left[r \frac{d\lambda^2}{dC_s} + \frac{\pi}{2} \lambda^2 \frac{dr}{dC_s} \right] \qquad (37)$$

where

λ is mean hopping distance, m

r is mean hopping rate, $mol/m^2 . s$

In general λ and r depend on C_S. To use the equation, particular forms must be chosen for λ and r.

Gilliland et al. (1974) simply assume that the hopping distance λ is independent of surface concentration. The first term in equation (37) is then equal to zero.

Smith and Metzner (1964) propose the equation:

$$\lambda = C\Theta^{\frac{1}{2}} \qquad (38)$$

where Θ is the surface coverage.

This equation cannot be valid at low surface coverage because it predicts that $\lambda \to 0$ when $\Theta \to 0$.

Weaver and Metzner (1966) obtain an expression for $\lambda(\Theta)$ as the result of a dynamic study which takes into account the forces acting on the hopping molecule describing a ballistic-like trajectory. However, the result is of limited practical use because the expression $\lambda(\Theta)$ is quite involved and depends on several parameters. Using some simplifying assumptions Ponzi et al. (1977) arrive at:

$$\lambda^2 = \frac{d^2}{g(1-\Theta)} \qquad (39)$$

where

d is a solid structure constant
g is adsorption probability

Customarily the hopping rate is estimated using the transition state theory of chemical kinetics (Glasstone et al. 1941). The adsorbed molecule undergoes an energy exchange with the surface and with other adsorbed molecules. If in the process it attains sufficient energy it is capable of leaving its adsorption position and either desorbing into the gas phase or hopping to another position on the surface. The nonactivated molecules are assumed to be in chemical equilibrium with the activated species. According to the transition state theory, the rate of hopping r is equal to the rate at which the activated molecules cross the activation energy barrier. The following rate expression is obtained:

$$r = C_a \frac{Q^*}{Q} \frac{kT}{h} \exp\left(-\frac{E}{RT}\right) \qquad (40)$$

where

C_a surface concentration, mol/m^2
Q^* partition function of activated species
Q partition function of adsorbed species

Accordingly, we have transformed the problem of estimating the hopping rate to the problem of estimating the activation energy. A simple approximation is to assume that the ratio of the activition energy E to the differential heat of adsorption q is constant, i.e.:

$$E = aq \tag{41}$$

where a depends on both adsorbent and adsorbate. Ponzi et al. (1977) suggest the form:

$$E = a'e^{-b'\Theta} \tag{42}$$

where Θ is the surface coverage and a' and b' are fitting parameters.

Okazaki et al. (1981) derive a modified hopping model by separately taking into account the hopping behaviors of monolayer and multilayer molecules. The model is an extension of a previous model by Higashi (1963). Two experimental constants are needed. Thakur et al. (1980) introduce methods for incorporating gas-adsorbate momentum transfer in calculating surface fluxes. A criterion is developed for predicting when gas-adsorbate collisional effects will change the calculated value of the surface flux significantly.

Brenner and Leal (1977) developed a theoretical model for surface diffusion of adsorbed spherically symmetric molecules along a locally planar solid surface. The model is based upon the assumption of short-range attractive and repulsive forces exerted by the surface on a molecule proximate to it. This results in the existence of a large number of molecules at that distance h_m from the surface at which these opposing forces offset each other. This position corresponds to the minimum point in the potential energy-distance curve. It is demonstrated that the surface diffusivity D_s is numerically equal to the value, at h_m, of that component of the position-specific bulk diffusion tensor lying parallel to the surface:

$$D_s = D_{\parallel}(h_m) \tag{43}$$

The analysis applies only for low surface coverages, where molecule/wall interactions predominate over molecule/molecule interactions. The result holds for all regimes - including the viscous-continuum regime and the Knudsen regime. The relation between $D_{\parallel}$ and h_m is, however, obtained explicitly only for Brownian particles, where existing low-Reynolds-number hydrodynamic theory provides the requisite wall-effect correction to the Stokes´ law particle mobility.

The same distance parameter h_m entering into the surface diffusivity also enters into the computation of both the equilibrium adsorption coefficient K_A (in the linear "Henry´s law" region) and the corresponding molar heat of adsorption q. By eliminating the microscopic molecular parameter h_m between these quantities Brenner and Leal obtained:

$$D_s/D_v = \text{function } (q/\alpha RT) \tag{44}$$

where α depends upon the so-called Hamaker constant, whose magnitude to some extent depends upon the nature of the adsorbent-adsorbate bond.

For liquid systems the theories above may not be appropriate since, unlike gaseous systems, the adsorbed molecule is closely surrounded by solvent or other adsorbate molecules. Therefore, force fields are involved between adsorbed and solvent molecules as well as those between adsorbate molecules and adsorbent surface. Surface diffusion in this situation seems more analogous to diffusion in bulk liquids than to surface diffusion in gas-filled pores.

Accordingly, Komiyama and Smith (1974) presented a theory for liquid-filled pores based upon a modification of one of the hole theories for molecular diffusion in liquids (McLaughlin, 1959). In this theory the diffusivity is expressed as:

$$D_V = \nu P_h a^2 \tag{45}$$

where

ν frequency with which a molecule attains sufficient energy to surmount the potential barrier restricting it to a given location or cell.

P_h probability of a hole being available for migration of an activated molecule.

a distance between adjacent cells.

Following Eyring's rate theory (Glasstone et al., 1941), the frequency ν is given by:

$$\nu = \frac{kT}{h} \exp\ (- \Delta F_b/RT) \tag{46}$$

The probability of a hole being available for the activated molecule to move is postulated to be:

$$P_h = \exp\ (- \Delta F_h/RT) \tag{47}$$

Combining these equations gives:

$$D_v = a^2 \frac{kT}{h} \exp\ (- \frac{\Delta F_h + \Delta F_b}{RT}) \tag{48}$$

An analogous mechanism is proposed for surface diffusion. The process is visualized to occur in two steps: the formation of a hole on the surface followed by movement of the activated, adsorbed molecule into the hole. The total Gibbs free energy of activation may be written as:

$$\Delta F = \Delta F_h + \Delta F_b \tag{49}$$

where ΔF_h represents the contribution of the hole-making step so that exp $(- \Delta F_h/RT)$ is the probability that a vacant site is adjacent to the activated molecule. Then ΔF_b represents the contribution associated with breaking the bond between the adsorbed molecule and the surface. It may be expressed as $\Delta F_b = \Delta H_b - T\ \Delta S_b$. Then the intrinsic surface diffusivity, following Equation (48) may be written:

$$D_s = A \exp(- \Delta F_h/RT) \exp(- \Delta H_b/RT) \qquad (50)$$

where A includes the entropy of activation for the bond-breaking step. Comparison with Equation (48) indicates that A will also be a function of the distance between two adsorption sites.

Empirical relationships for calculating surface diffusivities

Using data given in the literature and his own results Sladek et al. (1974) proposed the following relation:

$$D_s = 1.6 \cdot 10^{-6} \exp(- 0.45\ q/mRT),\ m^2/s \qquad (51)$$

where m is a coefficient that depends on the type of sorbent-sorbate bond, as shown in Table 5. The table shows that values of $m > 1$ correspond to surface migration on conductors (except for the nonpolar adsorbates) where electronic delocalization decreases the activation energy.

The relation (51) is based on values of D_s that range over 11 orders of magnitude, values of the activation energy that range from 0.3 up to 200 kcal/mole, and temperatures that range from -230 to 600 ° C. However, the estimation has an error margin of ±75 %.

Horiguchi et al. (1974) have proposed the following empirical relationship, which is valid for physical adsorption on some solids:

$$D_s = D_{so} \cdot 10^{-4} \exp(-0.57\ q/RT)\ (1-\theta)^{-1},\ m^2/s \qquad (52)$$

where D_{so} = 0.8 for Graphon, 0.08 for Vycor glass, and 0.008 for Carbolac and silica-alumina. Equation (52) with these constants gives estimates of surface fluxes with an error margin of ±50 %.

Table 5. Different types of gas solid bonds (from Sladek et al. (1974)).

Bond	Nature of solid	*m*	Example
van der Waals			
polar adsorbate	Conductor	2	Sulfur dioxide–carbon
	Insulator	1	Sulfur dioxide–glass Ammonia–glass
nonpolar adsorbate	Conductor	1	Argon–tungsten Nitrogen–carbon
	Insulator	1	Krypton–glass Ethylene–glass
Ionic	Conductor	2	Cesium–tungsten
	Insulator	1	Barium–tungsten
Covalent	Conductor	3	Hydrogen–metals Oxygen–tungsten
	Insulator	1	—

It should be noted that D_{so} is a function of surface area per unit volume and of the tortuosity.

MATHEMATICAL MODELING CONSIDERATIONS

In the following we assume Fickian pore and surface migration acting in parallel. Note that both for the flow and the diffusion mechanism of surface migration the flux may be written as

$$N_s = - D(C_s) \frac{\partial C_s}{\partial x} .$$

In one dimension and rectangular coordinates, we have

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \frac{\partial C_s}{\partial t} = D_p \varepsilon_p \frac{\partial^2 C_p}{\partial x^2} + \frac{\partial}{\partial x} [D_s(C_s) \frac{\partial C_s}{\partial x}] \qquad (53)$$

where

C_p = concentration in fluid in intrapores, mol/m^3

C_s = concentration in solid material (per unit particle volume), mol/m^3

ε_p = void fraction

D_p = diffusivity in fluid in intrapores, m^2/s

$D_s(C_s)$ = surface transport coefficient, in general dependent on surface concentration, m^2/s

The concentration in the solid C_s is related to the concentration in the fluid C_p through the equilibrium relationship:

$$C_s = f(C_p) \qquad (54)$$

where f in general is a nonlinear function of C_p.

Using

$$\frac{\partial C_s}{\partial t} = f' \frac{\partial C_p}{\partial t}$$

$$\frac{\partial C_s}{\partial x} = f' \frac{\partial C_p}{\partial x} \qquad \text{where} \quad f' = \frac{df}{dC_p}$$

equation (53) may be written with C_p as the single dependent variable:

$$(\varepsilon_p + f')\frac{\partial C_p}{\partial t} = \frac{\partial}{\partial x}\{D_p\varepsilon_p + D_s\,[f(C_p)]f'\}\frac{\partial C_p}{\partial x} \qquad (55)$$

For D_s concentration-dependent but f linear, i.e. $C_s = K_A C_p$, we get (55) as the ordinary diffusion equation:

$$\frac{\partial C_p}{\partial t} = \frac{\partial}{\partial x}\{D_a(C_p)\frac{\partial C_p}{\partial x}\} \qquad (56)$$

with the apparent diffusivity:

$$D_a = (D_p\varepsilon_p + D_s(C_p)K_A)/(\varepsilon_p + K_A)$$

For D_s constant we can put D_a = constant in front of the spatial derivative.

Equation (55) may be written in general form:

$$K(C_p)\frac{\partial C_p}{\partial t} = \frac{\partial}{\partial x}\{D(C_p)\frac{\partial C_p}{\partial x}\} \qquad (57)$$

This is a nonlinear diffusion equation with a concentration-dependent capacity term.

In fact, by making the transformation (Carslaw and Jaeger, 1959, p. 89):

$$\alpha = \int_0^{C_p} D(C_p')/D_o dC_p' \qquad (58)$$

equation (57) is reduced to:

$$K(\alpha)\frac{\partial \alpha}{\partial t} = \frac{\partial^2 \alpha}{\partial x^2} \qquad (59)$$

Equation (57) can be solved analytically only for special forms of $K(C_p)$ and $D(C_p)$ (see e.g. Crank, 1975). Although some progress has been made in the analytical treatment of nonlinear partial differential equations (Ames, 1972) numerical methods must be used in more general situations. Various numerical methods may be employed. Neretnieks (1976) used orthogonal collocation to solve (57) with D exponential and a Freundlich isotherm. Using the TRUMP code (Edwards, 1969; Rasmuson et al. 1982) the case with D constant (but K variable) has been solved with a Freundlich isotherm in the evaluation of Skagius´ diffusion experiments (Skagius and Neretnieks, 1982). The solution of equation (57) may be steep. Finlayson (1980, p. 263) made a comparison of different numerical methods on a typical problem. The results show that the finite difference method is best by a small margin. Global orthogonal collocation might be too expensive.

It may be pertinent at this point to investigate the relative importance of surface migration to pore volume diffusion.

The total mass flux is given by:

$$N_T = N_p + N_s = -D_p \varepsilon_p \frac{\partial C_p}{\partial x} - D_s[f(C_p)]f' \frac{\partial C_p}{\partial x}$$

$$= -(D_p \varepsilon_p + D_s[f(C_p)]f') \frac{\partial C_p}{\partial x} \qquad (60)$$

Accordingly, the relative importance of surface migration is given by:

$$\frac{N_s}{N_p} = \frac{D_s[f(C_p)]f'}{D_p \varepsilon_p} \qquad (61)$$

We consider three common equilibrium relationships:

linear	$C_s = K_A C_p$	$f' = K_A$
Langmuir	$C_s = \frac{aC_p}{1+bC_p}$	$f' = \frac{a}{(1+bC_p)^2}$
Freundlich	$C_s = K_F C_p^W$	$f' = K_F W C_p^{W-1}$ $(0 < W \leqslant 1)$

In general the surface transport coefficient is dependent on surface coverage or concentration. In the literature the following functional forms have been proposed:

constant	$D_S = D_O$	Schneider and Smith (1968)
exponential	$D_S = D_O \exp(\alpha C_S)$	Neretnieks (1976)
quadratic	$D_S = D_O C_S^2$	Gelbin (1968)
power	$D_s = D_o C_s^n$	Suzuki and Fujii (1982)

In the cases treated by Schneider and Smith (1968) the surface coverages were very low and it was assumed that the surface "diffusivity" was constant.

Gilliland et al. (1974) have shown that the coefficient of surface migration in certain circumstances is:

$$D_S = D_O \exp(-\,aq/RT) \qquad (62)$$

where q in general is dependent on concentration. Assuming a linear dependence of the heat of adsorption with concentration, Neretnieks (1976) obtained:

$$D_S = D_O \exp(\alpha C_S) \qquad (63)$$

Gelbin (1968) proposed that surface flux for hydrocarbons adsorbed on platinum-alumina should be proportional to the gradient of C_S^3, i.e.:

$$N_s = -D_o' \frac{\partial}{\partial x} (C_s)^3 \qquad (64)$$

Equation (64) may be rewritten with a concentration-dependent surface "diffusivity" as:

$$N_s = -3D_0' \, C_s^2 \, \frac{\partial C_s}{\partial x} = -D_s(C_s) \, \frac{\partial C_s}{\partial x} \qquad (65)$$

where

$$D_s(C_s) = D_0 \, C_s^2$$

In the investigation the adsorption was governed by Henry´s law (linear equilibrium).

Suzuki and Fujii (1982) performed Wicke Kallenbach type steady state diffusion experiments for varying concentrations of propionic acid solutions through activated carbon pellets. Independent adsorption equilibrium experiments showed that the apparent isosteric heat of adsorption $q_{st,a}$ determined from van´t Hoff plotting of the experimental data, decreases with the amount adsorbed s(mol/kg) as:

$$q_{st,a} = -q_0 \ell n(a \cdot s) \qquad (66)$$

This relation is consistent with the fact that when $s > 0.1$ mol/kg, each isotherm can be correlated by a Freundlich type equation $s = KC_p^{\frac{1}{n}}$ and n is related to the value of q_0 by $n = q_0/RT$. If the activation energy of surface diffusion is assumed to be of the same order of magnitude as q_{st}, using equation (66) in an Arrhenius type equation gives:

$$D_s = D_{so}(as)^n = D_0 C_s^{\frac{1}{w}} \qquad (67)$$

where w is the Freundlich isotherm power.

In Table 6 the relative importance of surface migration to pore volume diffusion (equation 61) is given for various combinations of isotherms and concentration-dependent surface transport coefficients.

Isotherm type	Functional form of surface transport coefficient	Relative importance of surface migration
linear	constant	$\frac{D_s K_A}{D_p \varepsilon_p}$
Langmuir	constant	$\frac{D_s a}{D_p \varepsilon_p (1+bC_p)^2}$
Freundlich	constant	$\frac{D_s K_F W C_p^{w-1}}{D_p \varepsilon_p}$
linear	exponential	$\frac{D_o \exp(\alpha K_A C_p) K_A}{D_p \varepsilon_p}$
Langmuir	exponential	$\frac{D_o \exp[\alpha a C_p/(1+bC_p)] a}{D_p \varepsilon_p (1+bC_p)^2}$
Freundlich	exponential	$\frac{D_o \exp[\alpha K_F C_p^w] K_F W C_p^{w-1}}{D_p \varepsilon_p}$
linear	quadratic	$\frac{D_o K_A^3 C_p^2}{D_p \varepsilon_p}$
Freundlich	power	$\frac{D_o K_F^{\frac{1}{w}+1} W C_p^{W}}{D_p \varepsilon_p}$

Table 6. Relative importance of surface migration to pore volume diffusion for different isotherms and surface transport coefficients.

To evaluate N_s/N_p as a function of the pore fluid concentration C_p we need to consider the product $D_s f'$. In general D_s increases with C_p while f' decreases. The latter is due to the fact that, except in the linear case, the isotherms are concave (i.e. $f'' < 0$). The driving force for surface migration is the gradient in surface concentration. However, in order to compare pore fluid and surface migration, we use the gradient in pore fluid concentration (equation (60)). For surface flux, $\frac{\partial C_p}{\partial x}$ has to be multiplied by f'. Hence, f' may be interpreted as a gradient scaling factor. At low concentrations a large difference in C_s corresponds to a small difference in C_p. Accordingly, f' must be large. At higher concentrations the situation is reversed and we get a small scaling factor. In accordance with this, for D_s constant the importance of surface migration will decrease with increasing concentration (except for a linear isotherm). For D_s concentration-dependent we get a product of two factors, one increasing with concentration and one decreasing. The overall dependence will then be a function of isotherm type and $D_s(C_s)$. In some instances, one might expect a relatively constant value of N_s/N_p. In real mass transfer situations the overall importance of surface migration will depend on the concentration level (and on the temperature).

DISCUSSION

In the description of the transport in a microporous material two fundamental problems arise. One is concerned with the partition of molecules between the solid (sorbed) and fluid phases. The other is involved with the rate of transport within the material.

The transport is usually interpreted as molecular diffusion in the fluid phase. At steady state the transport rate is then independent of the equilibrium relationship. In the instationary phase the rate of front advance is also a function of the equilibrium. For example, for linear equilibrium, we may define an apparent diffusivity as $D_a = D_p \varepsilon_p / K$.

On the other hand, if the surface phase is mobile, the transport rate is dependent on the partition between the phases (and accordingly the equilibrium relationship) both at steady state and unsteady state.

Three different transport mechanisms may be distinguished:

(i) pore diffusion only
(ii) pore diffusion and surface diffusion acting in parallel
(iii) pore diffusion and surface flow acting in parallel.

A summary of the different transport mechanisms is given in Table 7.

A key question is then how to discriminate between the different transport mechanisms. Since most of the models contain fitting parameters, absolute values on transport rates are difficult to predict. However, the change in transport rate due to a variation in a parameter can be utilized. We may then consider the dependence on temperature and the dependence on concentration.

Mechanism	Flux	Transport coefficient
Pore diffusion	$N_p = -D_p \varepsilon_p \frac{\partial C_p}{\partial x}$	$D_p = D_v \frac{\delta_D}{\tau_p^2}$
Surface diffusion	$N_s = -D_s \frac{\partial C_s}{\partial x} =$ $-D_s f' \frac{\partial C_p}{\partial x}$	$D_s = \frac{S_w \rho_p}{2\pi\tau_s^2} \left[r \frac{d\lambda^2}{dC_s} + \frac{\pi}{2} \lambda^2 \frac{dr}{dC_s} \right]$
Surface flow	$N_s = -\frac{C_s}{R_s} \frac{\partial \pi}{\partial x} =$ $-D_s \frac{\partial C_s}{\partial x} =$ $-D_s f' \frac{\partial C_p}{\partial x}$	$D_s = \frac{RT}{S_w \rho_p R_s} \frac{C_s^2}{C_p f'}$

Table 7. Transport mechanisms in microporous materials.

Temperature-dependence

(i) The diffusivity of non-electrolytes in liquids is roughly governed by (Perry and Chilton p. 3-234):

$$\frac{D_v \eta}{T} = \text{const.}$$

where η varies with temperature as A exp (B/T) (Perry and Chilton p. 3-246).

Diffusion coefficients of electrolytes can be predicted at infinite dilution using (Perry and Chilton p. 3-235):

$$D_v = 8.931 \cdot 10^{-14}\, T \left(\frac{\ell_+^0 \, \ell_-^0}{\Lambda^0} \right) \left(\frac{z_+ + z_-}{z_+ z_-} \right)$$

where

ℓ_+^0, ℓ_-^0	cationic and anionic conductances at infinite dilution
$\Lambda^0 = \ell_+^0 + \ell_-^0$	
z_+, z_-	valences of cation and anion.

Observe that ℓ_+^0 and ℓ_-^0 vary with temperature.

(ii) In general D_s will increase with temperature but C_s will decrease. The temperature-dependence of the equilibrium constant is given approximately by van´t Hoff´s relation (equation (2)):

$$K_a = C_1 \exp (q/RT) \qquad (68)$$

If the adsorption is exothermic (q positive) the equilibrium constant decreases as the temperature is raised.

The mean hopping distance is considered to be independent of temperature. The hopping rate, however, is a complicated, probably increasing, function of temperature (equation (40)).

(iii) In this case the change in flux with temperature is also a product of two functions, one increasing and one decreasing with temperature. The flow resistance R_s is proportional to the dynamic viscosity η_s. The dependence of η_s with temperature is roughly A exp (B/T), i.e. an exponential decrease (Perry and Chilton, p. 3-246). Accordingly, the flux (for a linear equilibrium for example) will change with temperature as $\text{const.}\cdot T\cdot \exp\left(\frac{2q}{RT} - \frac{B}{T}\right)$.

In conclusion it seems difficult to use the temperature-dependence to say which mechanism is active, since, the temperature-dependence of the flux is complicated. In order to distinguish between the surface transport mechanisms, the equilibrium relationship $C_s = f(C_p)$ must be experimentally determined at different temperatures. If this is done it should be possible to say something about the likelihood of the mechanism of surface flow.

Concentration-dependence

(i) D_v is independent of concentration at moderate concentrations

(ii) D_s increases with concentration while f' decreases.

The mean hopping distance will in general increase with concentration according to the relations given in the section on "Diffusion models". The jump rate r will also increase with concentration according to equation (40).

(iii) For this mechanism the concentration-dependence is rather well-defined. The viscosity η_s is a rather weak (decreasing) function of concentration for inorganic salts. (Weast, 1979-1980, p. D-229)

Experimental determination of the flux at different concentration levels should give a strong indication whether mechanism (i) is the only active mechanism. Again, an independent measurement of the equilibrium relationship (and thus of f') should give a fair chance to discriminate between mechanisms (ii) and (iii).

The most straightforward way to distinguish between pore diffusion on the one hand and coupled pore diffusion and solid migration on the other is to run two separate measurements on the same material. In one experiment a non-sorbing species is utilized to obtain $\varepsilon_p \delta_D / \tau^2$. In the second experiment the sorbing component is used. Using the proper values of D_v and $\varepsilon_p \delta_D / \tau^2$ from the first run, the results from the second run should compare favorably. If the transport rate is significantly higher some other mechanism than pore diffusion must be active. Komiyama and Smith (1974) used a different technique, having the same species in both runs, but changing the solvent. In one solvent the adsorption capacity was very low, in the other it was high.

To compare mechanisms (ii) and (iii) on an order-of-magnitude basis it is of interest to determine the "intrinsic" diffusivity. Consider a system with a surface phase characterized by porosity ε_s and a fluid phase with porosity ε_p. The mass flow is generally given by:

$$Q = -(\text{diffusivity})(\text{concentration gradient})(\text{area}) = -D(\nabla C)A \quad (\text{mol/s}) \tag{69}$$

The mass flow in the fluid phase is then :

$$Q_p = -D_p \nabla C_p \, (A\varepsilon_p) \tag{70}$$

The mass flow in the surface phase, with the driving force taken as the gradient in concentration (C_s') per unit volume of surface phase, is:

$$Q_s = -D_s \nabla C_s' \, (A\varepsilon_s) \tag{71}$$

The relation between C_s' and C_s (concentration per unit particle volume) is:

$$C_s' = \frac{C_s}{\varepsilon_s} = \frac{f(C_p)}{\varepsilon_s} \tag{72}$$

Accordingly:

$$Q_s = -D_s \nabla C_s A = -D_s f' \, \nabla C_p A \tag{73}$$

The proper quantities to compare then are the "pure fluid" diffusivities D_v and D_v' obtained from D_p and D_s above respectively. That is, the geometrical parts like tortuosities etc. are removed. If $D_v' > D_v$, i.e. diffusion is more rapid in the surface than in the fluid phase, this is a strong indication in favor of mechanism (iii), i.e. surface flow. This is due to the fact that molecular diffusion in the surface phase should be less effective (due to energy barriers) than diffusion in the fluid phase. Unfortunately it seems that D_V' obtained in this way is generally less than D_V.

Actually the two mechanisms of surface flux may be superimposed. Their relative importance will then depend upon the physical situation.

ACKNOWLEDGEMENT

Several stimulating discussions with Professor Jan Christer Eriksson at the Dept. of Physical Chemistry, Royal Institute of Technology, Stockholm, are gratefully acknowledged.

NOTATION

A	surface area of adsorbent	m^2
C	concentration in fluid	mol/m^3
C_a	surface concentration	mol/m^2
C_p	concentration in fluid in intrapores	mol/m^3
C_s	concentration in solid material (per unit particle volume)	mol/m^3
D	diffusivity	m^2/s
D_a	apparent diffusivity, equal to $(D_p\varepsilon_p+D_sK_A)/(\varepsilon_p+K_A)$	m^2/s
D_p	diffusivity in fluid in intrapores	m^2/s
D_s	surface transport coefficient	m^2/s
D_v	diffusivity in pure fluid	m^2/s
D_{ll}	component of position-specific bulk tensor lying parallel to the surface	m^2/s
E	activation energy for surface diffusion	J/mol
h	Planck´s constant	Js
h_m	distance from the surface at which attractive and repulsive forces offset each other	m
K	volume equilibrium constant	m^3/m^3
K_A	adsorption equilibrium constant	m^3/m^3
k	Boltzmann´s constant	J/ °K
N_p	mass flux in fluid in intrapores	$mol/m^2,s$
N_s	mass flux on surfaces in intrapores	$mol/m^2,s$
N_T	total mass flux in intrapores	$mol/m^2,s$
n_i^a	moles of species i adsorbed	mol
Q,Q*	partition functions of adsorbed and activated molecules	
q	differential heat of adsorption	J/mol
q_{st}	isosteric heat of adsorption equal to q+RT	J/mol
q_v	heat of vaporization	J/mol
R	gas constant	J/mol, °K
R_s	resistance coefficient defined in equation (34)	Ns/m^3
r	mean hopping rate	$mol/m^2,s$

S	entropy (of adsorbed phase)	J/°K
S_w	specific surface area of adsorbent	m^2/kg
s	concentration in solid material	mol/kg
T	temperature	°K
T_b	boiling point of adsorbate	°K
t	time	s
t_R	retention time	s
t_{RO}	period of oscillation of the molecules in the adsorbed state	s
V_s	surface velocity of adsorbed molecules	m/s
x	distance into porous material	m

γ	surface tension	N/m
δ_D	constrictivity for diffusion	
ε_p	porosity	
η	viscosity	Ns/m^2
η_s	viscosity of surface phase	Ns/m^2
Θ	surface coverage	
λ	mean hopping distance	m
μ_i	chemical potential of component i	J/mol
π	spreading pressure	N/m
ρ_p	bulk density of adsorbent	kg/m^3
τ_p	tortuosity factor for pore diffusion	
τ_s	tortuosity factor for surface diffusion	

REFERENCES

Adamson, A.W.: Physical Chemistry of Surfaces 3rd ed., Wiley 1976.

Ames, W.F.: Nonlinear Partial Differential Equations in Engineering, Vol II, Academic Press 1972.

Babbit, J.D.: On the differential equations of diffusion, Can. J. Res. 28A, 449 (1950).

Barrer, R.M. and J.A. Barrie: Proc. Roy. Soc. (London) A219, 250 (1952)

Barrer, R.M. and T. Gabor: Proc. Roy. Soc. (London) A256, 267 (1960).

Bauer, E. and H. Poppa: Thin Solid Films 12, 167 (1972).

Belfort, G.: Adsorption on carbon: Theoretical considerations. Environ. Sci. Technol. 14, 911 (1980).

Blakely, J.M.: Surface diffusion, Prog. Mater. Sci. 10 (1963).

Boddenberg, B.; R. Haul and G. Opperman: NMR-spin echo studies on mobility and diffusion of benzene adsorbed on silica. J. Colloid Interface Sci. 38, 210 (1972).

Bonzel, H.P. and N.A. Gjostein: In situ measurements of surface self-diffusion of metals. In "Molecular Processes on Solid Surfaces" (E. Drauglis, R.G. Gretz and R.I. Jaffee eds.) pp. 533-568, McGraw-Hill (1969).

Bonzel, H.P.: Transport of matter at surfaces. In "Surface Physics of Materials" (J.M. Blakely ed.) Vol. II pp. 279-338, Academic Press (1975).

Brenner, H. and L.G. Leal: A model of surface diffusion on solids, J. Colloid Interface Sci. 62, 238 (1977).

Brunauer, S.; P.H. Emmett and E. Teller, J. Amer. Chem. Soc. 60, 309 (1938).

Chen, T.-R. and R. Gomer: Surface Sci. 79, 413 (1979).

Crank, J.C.: The Mathematics of Diffusion, 2nd ed. Oxford University Press (1975).

Cunningham, R.E., and R.J.J. Williams: Diffusion in Gases and Porous Media, Plenum Press (1980).

Dacey, J.R.: Surface diffusion of adsorbed molecules. Ind. Eng. Chem. 57, 26 (1965).

de Boer, J.H.: The Dynamical Character of Adsorption, 2nd ed., Oxford University Press (1968).

Dufey, J.E. and H.G. Laudelout: Self-diffusion of sodium on clay surfaces as influenced by two other alkali cations. J. Colloid Interface Sci. 52, 340 (1975).

Edwards, A.L.: TRUMP: A computer program for transient and steady state temperature distributions in multi-dimensional systems. National Technical Information Service, National Bureau of Standards, Springfield Va. 1969.

Ehrlich, G. and K. Stolt: Surface diffusion. Ann. Rev. Phys. Chem. 31, 603 (1980).

Eriksen, T.; A. Jacobsson and R. Pusch: Ion diffusion through highly compacted bentonite, KBS TR 81-06 (1981).

Eriksen, T. and A. Jacobsson: Ion diffusion in compacted sodium and calcium bentonites, KBS TR 81-12 (1982).

Finlayson, B.A.: Nonlinear Analysis in Chemical Engineering, McGraw-Hill (1980).

Flood, E.A.; R.H. Tomlinson and A.E. Leger: The flow of fluids through activated carbon rods. Can. J. Chem. 30, 389 (1952).

Fripiat, J.J.: Mobility of physically adsorbed hydroxylic molecules on surfaces made from oxygen atoms. J. Colloid Interface Sci. 58, 511 (1977).

Fuerstenau, D.W.:
Chem. Biosurfaces 1, 143 (1971).

Furusawa, T. and J.M. Smith: Fluid particle and intraparticle mass transport rates in slurries. Ind. Eng. Chem.Fundam. 12, 197 (1973).

Gal, V.V. and V.T. Borisov: Regularities of surface diffusion. Fiz. Metal. Metalloved 30, 950 (1971).

Gast, R.G.: An interpretation of self-diffusion measurements of cations in clay-water systems. J. Colloid Sci. 17, 192 (1962).

Geguzin, Ya. E.: Diffusion along a real crystal surface. In "Poverkhnostnayi Diffuziya in Rastekaniye" (Ya.E. Geguzin ed.) pp. 11-77, Izd. Nauke Moscow (1969).

Geguzin, Ya. E.; Yu. S. Kaganovsky and V.V. Slyozov:
J. Phys. Chem. Solids 30, 1173 (1969).

Gelbin, D.: The surface transport of various gases on a platinum-alumina-catalyst. Chem. Eng. Sci. 23, 41 (1968).

Geuss, J.W.: Mobility of atoms and molecules over solid surfaces. Ned. Tijdschr. Vacuum Technol. 10, 59 (1972).

Gibbs, J.W.: Scientific papers. Langman and Green and Co, New York (1906).

Gilliland, E.R.; R.F. Baddour and J.L. Russell: Rates of flow through microporous solids. AIChE. J. 4, 90 (1958).

Gilliland, E.R.: R.F. Baddour; G.P. Perkinson and K.J. Sladek: Diffusion on surfaces I. Effect of concentration on diffusivity of physically adsorbed gases. 13, 95 (1974).

Gilmer, G.H. and P. Bennema:
J. Appl. Phys. 34, 1347 (1972).

Gjostein, N.A.: Surface self-diffusion. In "Metal Surfaces: Structure, Energetics and Kinetics" Amer. Soc. Metals, Metals Park Ohio (1963).

Gjostein, N.A.: Surface, grain boundary, and dislocation pipe diffusion. In "Techniques of Metals Research" (R.F. Bunshah ed.) Vol IV, Part 2, Wiley (1970).

Gjostein N.A.: Short circuit diffusion. In "Diffusion" ASM Seminar Proc., Metals Park, Ohio (1973).

Glasstone, S.; K.J. Laidler and H. Eyring: "The Theory of Rate Processes" McGraw-Hill (1941).

Gomer, R.: Surface structure and diffusion Discuss. Faraday Soc. 28, 23 (1959).

Gomer, R.: Surface diffusion. Scientific American, Aug., 92 (1982).

Haul, R. and K. Hübner: Molekularer Transport an Porenoberflächen, Berichte der Deutsche Bunsengesellschaft für Physikalische Chemie 79, 777 (1975).

Hayek, K. and U. Schwabe:
J. Vac. Sci. Technol. 9, 507 (1972).

Higashi, K.; H. Ito and J. Oishi: Surface diffusion phenomena in gaseous diffusion. J. Japan Atom. Energy, Soc. 5, 846 (1963).

Hill, T.L.: Surface diffusion and thermal transpiration in fine tubes and pores. J. Chem. Phys. 25, 730 (1956).

Hirano, K. and R. Tanaka: Surface self-diffusion on metals, Nippon Kinzoku Gakkai Kaiho 9, 341 (1970).

Hirth, J.P. and G.M. Pound:
Progr. Mater. Sci. 11 (1963).

Ho, F.-G. and W. Strieder: A variational calculation of the effective surface diffusion coefficient and tortuosity. Chem. Eng. Sci. 36, 253 (1981).

Horiguchi, Y.; R.R. Hudgins and P.L. Silveston: Effect of surface heterogeneity on surface diffusion in microporous solids. Can. J. Chem. Eng. 49, 76 (1971).

Johansson, R. and I. Neretnieks: Adsorption on activated carbon in countercurrent flow. An experimental study. Chem. Eng. Sci. 35, 979 (1980).

Jossens, L.; J.M. Prausnitz; W. Fritz; E.U. Schlünder and A.L. Myers: Thermodynamics of multi-solute adsorption from dilute aqueous solutions. Chem. Eng. Sci. 33, 1097 (1978).

Kemper, W.D. and J.P. Quirk: Ion mobilities and electric charge of external clay surfaces inferred from potential differences and osmotic flow. Soil Sci. Amer. Proc. 36, 426 (1972).

King, D.A.: Surface diffusion of adsorbed species: A review. J. Vac. Sci. Technol. 17, 241 (1980).

Knoblauch, K.; H. Jüntgen and W. Peters:
Chem. Ing. Techn. 41, 798 (1969).

Komiyama, H. and J.M. Smith: Intraparticle mass transport in liquid-filled pores, AIChE J. 20, 728 (1974).

Komiyama, H. and J.M. Smith: Surface diffusion in liquid-filled pores AIChE J. 20, 1110 (1974).

Kuczynski, G.C.: "Powder Metallurgy" p. 11, Wiley (1961).

Langmuir, I:
J. Amer. Chem. Soc. 40, 1361 (1918).

Lee, C.S. and J.P. O'Connell: Measurement of adsorption and surface diffusion on homogeneous solid surfaces. J. Phys. Chem. 79, 885 (1975).

McLaughlin, E.: Viscosity and self-diffusion in liquids. Trans. Faraday Soc. 55, 28 (1959).

Meyer, H.J.: Zur Oberflächendiffusion und oberflächennahen Diffusion auf Kristallen. Nova Acta Leopoldina Suppl. 1, 34, 155 (1968).

Milchev, A. and M. Paunov: A unified model description of mobile and localized adsorption II. Surface Sci. 108, 38 (1981).

Moore, W.J.: Physical Chemistry 4th ed.. Prentice Hall (1962).

Myers, A.L. and J.M. Prausnitz: Thermodynamics of mixed-gas adsorption. AIChE J. 11, 121 (1965).

Neretnieks, I.: Adsorption in finite bath and countercurrent flow with systems having a nonlinear isotherm. Chem. Eng. Sci. 31, 107 (1976).

Neretnieks, I.: Adsorption in finite bath and countercurrent flow with systems having a concentration dependent coefficient of diffusion. Chem. Eng. Sci. 31, 465 (1976).

Neretnieks, I.: Analysis of some adsorption experiments with activated carbon. Chem. Eng. Sci. 31, 1029 (1976).

Neumann, G. and G.M. Neumann: Surface self-diffusion of metals. Diffusion Monograph Series. (F.H. Wohlbier ed.) Diffusion Inform. Center, Bay Village, Ohio (1972).

Okazaki, M.; H. Tamon and R. Toei: Interpretation of surface flow phenomenon of adsorbed gases by hopping model. AIChE J. 27, 262 (1981).

Okazaki, M.; H. Tamon, T. Hyodo and R. Toei: Measurement of surface self-diffusion of sulfur dioxide on porous Vycor glass by radioisotope tracer method. AIChE J. 27, 1035 (1981).

Perry, R.H. and C.H. Chilton (eds.) Chemical Engineers' Handbook, 5th ed., McGraw-Hill.

Polanyi, M.: Über die Adsorption vom Standpunkt des dritten Värmesatzes. Deut. Physik. Ges. Verhand. 16, 1012 (1914).

Ponzi, M.; J. Papa; J.B.P. Rivarola and G. Zgrablich: On the surface diffusion of adsorbable gases through porous media. AIChE J. 23, 347 (1977).

Radke, C.J. and J.M. Prausnitz: Thermodynamics of multi-solute adsorption from dilute liquid solutions. AIChE J. 18, 761 (1972).

Rasmuson A.; T.N. Narasimhan and I. Neretnieks: Chemical transport in fissured rock: Verification of a numerical model. Water Resour. Res. 18, 1479 (1982).

Reed, E.M. jr. and J.B. Butt:
J. Phys. Chem. 75, 133 (1971).

Rhead, G.E.:
Scripta Met. 6, 47 (1972).

Robertson, W.M.: Surface diffusion of oxides. J. Nucl. Mater. 30, 36 (1969).

Rosenberg, R.:
J. Vac. Sci. Technol. 9, 263 (1972).

Satterfield, C.N.: Mass Transfer in Heterogeneous Catalysis. MIT Press, Cambridge, Mass. 1970.

Schaik, J.C. van; W.D. Kemper and S.R. Olsen: Contribution of adsorbed cations to diffusion in clay-water systems. Soil Sci. Soc. Amer. Proc. 30, 17 (1966).

Schneider, P. and J.M. Smith: Chromatographic study of surface diffusion. AIChE J. 14, 886 (1968).

Skagius, C. and I. Neretnieks: Diffusion in crystalline rocks of some sorbing and non-sorbing species. Final report 82-03-01.

Sladek, K.J.; E.R. Gilliland and R.F. Baddour: Diffusion on surfaces II. Correlation of diffusivities of physically and chemically adsorbed species. Ind. Eng. Chem. Fundam. 13, 100 (1974).

Smith, R.K. and A.B. Metzner: Rate of surface migration of physically adsorbed gases. J. Phys. Chem. 68, 2741 (1964).

Sterret, J.S. and L.F. Brown: The application of theoretical diffusion models in the presence of a catalytic reaction. AIChE J. 14, 696 (1968).

Sudo, Y.; D.M. Misic and M. Suzuki: Concentration dependence of effective surface diffusion coefficients in aqueous phase adsorption on activated carbon. Chem. Eng. Sci. 33, 1287 (1978).

Suzuki, M. and T. Fujii: Concentration dependence of surface diffusion coefficient of propionic acid in activated carbon particles. AIChE J. 28, 380 (1982).

Suzuki, M. and K. Kawazoe: Effective surface diffusion coefficients of volatile organics on activated carbon during adsorption from aqueous solution. J. Chem. Eng. Japan 8 , 379 (1975).

Suzuki M.; T. Kawai and K. Kawazoe: Adsorption of poly (oxyethylene) of various molecular weights from aqueous solutions on activated carbon. J. Chem. Eng. Japan 9, 203 (1976).

Thakur, S.C.; L.F. Brown and G.L. Haller: Gas-adsorbate collisional effects and surface diffusion in porous materials. AIChE J. 26, 355 (1980).

Weast, R.C. (ed.): Handbook of Chemistry and Physics, 60th ed. CRC Press, Boca Raton, Fla. 1979-1980.

Weaver, J.A. and A.B. Metzner: The surface transport of adsorbed molecules. AIChE J. 12, 655 (1966).

Willertz, L.E. and P.G. Shewman:
Metall. Trans. 1, 2217 (1970).

Wynblatt, P. and N.A. Gjostein:
Progr. Solid State Chem. 9, (1974).

Zsigmondy, R.:
Z. Anorg. Chem. 71, 356 (1911).

LIST OF KBS's TECHNICAL REPORTS

1977-78

TR 121	KBS Technical Reports 1 - 120. Summaries. Stockholm, May 1979.

1979

TR 79-28	The KBS Annual Report 1979. KBS Technical Reports 79-01--79-27. Summaries. Stockholm, March 1980.

1980

TR 80-26	The KBS Annual Report 1980. KBS Technical Reports 80-01--80-25. Summaries. Stockholm, March 1981.

1981

TR 81-17	The KBS Annual Report 1981. KBS Technical Reports 81-01--81-16 Summaries. Stockholm, April 1982.

1983

TR 83-01	Radionuclide transport in a single fissure A laboratory study Trygve E Eriksen Department of Nuclear Chemistry The Royal Institute of Technology Stockholm, Sweden 1983-01-19
TR 83-02	The possible effects of alfa and beta radiolysis on the matrix dissolution of spent nuclear fuel I Grenthe I Puigdomènech J Bruno Department of Inorganic Chemistry Royal Institute of Technology Stockholm, Sweden January 1983

TR 83-03 Smectite alteration
Proceedings of a colloquium at State University of New York at Buffalo, May 26-27, 1982
Compiled by Duwayne M Anderson
State University of New York at Buffalo
February 15, 1983

TR 83-04 Stability of bentonite gels in crystalline rock - Physical aspects
Roland Pusch
Division Soil Mechanics, University of Luleå
Luleå, Sweden, 1983-02-20

TR 83-05 Studies in pitting corrosion on archeological bronzes - Copper
Åke Bresle
Jozef Saers
Birgit Arrhenius
Archaeological Research Laboratory
University of Stockholm
Stockholm, Sweden 1983-01-02

TR 83-06 Investigation of the stress corrosion cracking of pure copper
L A Benjamin
D Hardie
R N Parkins
University of Newcastle upon Tyne
Department of Metallurgy and Engineering Materials
Newcastle upon Tyne, Great Britain, April 1983

TR 83-07 Sorption of radionuclides on geologic media - A literature survey. I: Fission Products
K Andersson
B Allard
Department of Nuclear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-01-31

TR 83-08 Formation and properties of actinide colloids
U Olofsson
B Allard
M Bengtsson
B Torstenfelt
K Andersson
Department of Nuclear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-01-30

TR 83-09 Complexes of actinides with naturally occurring organic substances - Literature survey
U Olofsson
B Allard
Department of Nucluear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-02-15

TR 83-10 Radiolysis in nature:
Evidence from the Oklo natural reactors
David B Curtis
Alexander J Gancarz
New Mexico, USA February 1983

TR 83-11 Description of recipient areas related to final storage of unreprocessed spent nuclear fuel
Björn Sundblad
Ulla Bergström
Studsvik Energiteknik AB
Nyköping, Sweden 1983-02-07

TR 83-12 Calculation of activity content and related properties in PWR and BWR fuel using ORIGEN 2
Ove Edlund
Studsvik Energiteknik AB
Nyköping, Sweden 1983-03-07

TR 83-13 Sorption and diffusion studies of Cs and I in concrete
K Andersson
B Torstenfelt
B Allard
Department of Nuclear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-01-15

TR 83-14 The complexation of Eu(III) by fulvic acid
J A Marinsky
State University of New York at Buffalo, Buffalo,NY
1983-03-31

TR 83-15 Diffusion measurements in crystalline rocks
Kristina Skagius
Ivars Neretnieks
Royal Institute of Technology
Stockholm, Sweden 1983-03-11

TR 83-16 Stability of deep-sited smectite minerals in crystalline rock - chemical aspects
Roland Pusch
Division of Soil Mechanics, University of Luleå
1983-03-30

TR 83-17 Analysis of groundwater from deep boreholes in Gideå
Sif Laurent
Swedish Environmental Research Institute
Stockholm, Sweden 1983-03-09

TR 83-18 Migration experiments in Studsvik
O Landström
Studsvik Energiteknik AB
C-E Klockars
O Persson
E-L Tullborg
S Å Larson
Swedish Geological
K Andersson
B Allard
B Torstenfelt
Chalmers University of Technology
1983-01-31

TR 83-19 Analysis of groundwater from deep boreholes in Fjällveden
Sif Laurent
Swedish Environmental Research Institute
Stockholm, Sweden 1983-03-29

TR 83-20 Encapsulation and handling of spent nuclear fuel for final disposal
1 Welded copper canisters
2 Pressed copper canisters (HIPOW)
3 BWR Channels in Concrete
B Lönnerberg, ASEA-ATOM
H Larker, ASEA
L Ageskog, VBB
May 1983

TR 83-21 An analysis of the conditions of gas migration from a low-level radioactive waste repository
C Braester
Israel Institute of Technology, Haifa, Israel
R Thunvik
Royal Institute of Technology
November 1982

TR 83-22 Calculated temperature field in and around a repository for spent nuclear fuel
Taivo Tarandi
VBB
Stockholm, Sweden April 1983

TR 83-23

TR 83-24 Corrosion resistance of a copper canister for spent nuclear fuel
The Swedish Corrosion Research Institute and its reference group
Stockholm, Sweden April 1983

TR 83-25 Feasibility study of EB welding of spent nuclear fuel canisters
A Sanderson
T F Szluha
J Turner
Welding Institute
Cambridge, United Kingdom April 1983

TR 83-26 The KBS UO_2 leaching program
Summary Report 1983-02-01
Ronald Forsyth
Studsvik Energiteknik AB
Nyköping, Sweden February 1983

TR 83-27 Radiation effects on the chemical environment in a radioactive waste repository
Trygve Eriksen
Royal Institute of Technology
Stockholm, Sweden April 1983

TR 83-28 An analysis of selected parameters for the BIOPATH-program
U Bergström
A-B Wilkens
Studsvik Energiteknik AB
Nyköping, Sweden April 1983

TR 83-29 On the environmental impact of a repository for spent nuclear fuel
Otto Brotzen
Stockholm, Sweden April 1983

TR 83-30 Encapsulation of spent nuclear fuel -
Safety Analysis
ES-konsult AB
Stockholm, Sweden April 1983

TR 83-31 Final disposal of spent nuclear fuel -
Standard programme for site investigations
Compiled by
Ulf Thoregren
Swedish Geological
April 1983

TR 83-32 Feasibility study of detection of defects in thick welded copper
Tekniska Röntgencentralen AB
Stockholm, Sweden April 1983

TR 83-33 The interaction of bentonite and glass with aqueous media
M Mosslehi
A Lambrosa
J A Marinsky
State University of New York
Buffalo, NY, USA April 1983

TR 83-34 Radionuclide diffusion and mobilities in compacted bentonite
B Torstenfelt
B Allard
K Andersson
H Kipatsi
L Eliasson
U Olofsson
H Persson
Chalmers University of Technology
Göteborg, Sweden April 1983

TR 83-35 Actinide solution equilibria and solubilities in geologic systems
B Allard
Chalmers University of Technology
Göteborg, Sweden 1983-04-10

TR 83-36 Iron content and reducing capacity of granites and bentonite
B Torstenfelt
B Allard
W Johansson
T Ittner
Chalmers University of Technology
Göteborg, Sweden April 1983

TR 83-37 Surface migration in sorption processes
A Rasmuson
I Neretnieks
Royal Institute of Technology
Stockholm, Sweden March 1983

TR 83-38 Evaluation of some tracer tests in the granitic rock at Finnsjön
L Moreno
I Neretnieks
Royal Institute of Technology, Stockholm
C-E Klockars
Swedish Geological, Uppsala
April 1983

TR 83-39 Diffusion in the matrix of granitic rock
Field test in the Stripa mine. Part 2
L Birgersson
I Neretnieks
Royal Institute of Technology
Stockholm, Sweden March 1983

TR 83-40 Redox conditions in groundwaters from Svartboberget, Gideå, Fjällveden and Kamlunge
P Wikberg
I Grenthe
K Axelsen
Royal Institute of Technology
Stockholm, Sweden 1983-05-10

TR 83-41 Analysis of groundwater from deep boreholes in Svartboberget
Sif Laurent
Swedish Environmental Research Institute
Stockholm, Sweden April 1983

TR 83-42 Final disposal of high-level waste and spent nuclear fuel - foreign activities
R Gelin
Studsvik Energiteknik AB
Nyköping, Sweden May 1983

TR 83-43 Final disposal of spent nuclear fuel - geological, hydrological and geophysical methods for site characterization
K Ahlbom
L Carlsson
O Olsson
Swddish Geological
Sweden May 1983

TR 83-44 Final disposal of spent nuclear fuel - equipment for site characterization
K Almén, K Hansson, B-E Johansson, G Nilsson
Swedish Geological
O Andersson, IPA-Konsult
P Wikberg, Royal Institute of Technology
H Åhagen, SKBF/KBS
May 1983