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The Random-Spheres Model for Porous Materials

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In the "random spheres model" for porous materials the porous substance is assumed to consist of a large number of randomly overlapping solid microspheres, the void being constituted by the remaining space between the microspheres. For most porous materials this model is more realistic than the usual tubular pore models. The properties of the model are described, and some applications are presented, the most important being the calculation of the lifetime of a porous catalyst which is clogged by deposits.

1. INTRODUCTION

In a porous material, the pore space is often the residual volume between a large number of microscopic solid bodies. This type of material is simulated by the "random spheres model" (RSM) introduced by Weissberg (*1*). In its simplest form, the RSM is constructed by placing $n\Omega$ identical solid microspheres of radius r in a volume Ω (n is the number of microspheres per unit volume), without any correlation between the positions of the spheres, so that in the end some will remain isolated and others will overlap. The pore space is constituted by the interstices between the microspheres. The values of n and r are chosen in such a way that the correct specific void volume Ψ and specific surface area Σ are obtained. The RSM, unlike the more common tubular pore models, gives a truly three-dimensional pore space, thus affording a more realistic description of the porous material itself, and of processes which occur inside these materials. As far as we know, up till now the RSM has only been used by Weissberg (*1*) and Strieder and Prager (*2, 3*) to compute upper bounds for the coefficient of diffusion through porous materials (see Sect. 3), and by Haller (*4*) to explain the phase continuity and the rearrangement kinetics in melts of immiscible alkali borosilicates.

In this paper we summarize the basic formulae which one needs in applying the RSM, including the generalized case in which the microspheres are not all identical, but have their radii distributed according to some distribution $f(r)$. We will define a pore radius distribution and an average pore radius in the model, based on the partial void volume which is accessible to spherical particles with a finite radius a. In Sect. 3 we treat diffusion through the RSM, and in Sect. 4 we give a few applications, the most important being the calculation of the lifetime of a porous catalyst which is being clogged by deposits. In this last case we will present the results, relative values of the lifetimes under different circumstances (different space velocities, different catalyst particle radii), in one simple figure which is ready for use.

2. GEOMETRICAL PROPERTIES OF THE RANDOM SPHERES MODEL

Consider a porous material with void volume Ψ and surface area Σ, both per unit volume (interpellet voids excluded). The RSM of the material is generated by placing a large number of solid microspheres in randomly overlapping positions. In the simplest version of the RSM the microspheres all have the same radius r_0; this radius r_0 and the number of microspheres per unit volume of material are then determined uniquely by Ψ and Σ. In general, however, we take the total volume, overlap counted double, of microspheres with radius r to be some function $f(r)$ of r, with

$$\int_0^\infty f(r)\,dr = 1.$$

The n-th inverse moment of the distribution $f(r)$,

$$\int_0^\infty \frac{f(r)}{r^n}\,dr,$$

will be called L_n; thus $L_0 = 1$, and we define r_0 by $L_1 = 1/r_0$. If we denote by V the total volume of the spheres used in generating unit volume of porous material, Ψ and Σ determine V and r_0 by the following fundamental equations of the random spheres model:

$$V = -\log\Psi, \qquad (1)$$

$$r_0 = -(3\,\Psi/\Sigma)\log\Psi. \qquad (2)$$

For a porous material with void fraction Ψ, we define the reduced void fraction $\Psi'(a)$ as the volume accessible to a point particle which has to stay at least a distance a away from the solid surface. Thus, $\Psi'(a)$ is the volume accessible to the centre of a spherical particle of radius a, and it is found from (1):

$$\frac{\log\Psi'(a)}{\log\Psi} = \int_0^\infty f(r)\left(\frac{r+a}{r}\right)^3 dr$$
$$= 1 + 3aL_1 + 3a^2L_2 + a^3L_3. \qquad (3a)$$

Formula (3a) also gives the reduced void fraction that is obtained by allowing the radius of all microspheres to increase by a; this added layer may for instance represent a layer of deposits. The reduced specific surface area $\Sigma'(a)$ is obtained from the relation $\Sigma'(a) = -\,d\Psi'(a)/da$; if all microspheres have the same radius r_0, this reduces to the obvious generalization of (2):

$$r_0 + a = -\frac{3\Psi'(a)}{\Sigma'(a)}\log\Psi'(a) \qquad (3b)$$

The concept of a reduced void fraction $\Psi'(a)$ for particles of radius a may be used to define a pore radius distribution $g(\rho)$ in the RSM. First consider a "random pores model" with the same void fraction Ψ, in which the pore volume consists of randomly overlapping pores. Let the pore radius distribution in the random pores model be $g(\rho)$, by which we mean that the total volume, overlap counted double, of pores with radius ρ is a function $g(\rho)$ of ρ, with

$$\int_0^\infty g(\rho)\,d\rho = 1.$$

If we require that the reduced void fraction in this random pores model is the same function $\Psi'(a)$ of a as in the RSM, we obtain an equation which uniquely determines $g(\rho)$:

$$(1-\Psi)^{\int_a^\infty g(\rho)\left(\frac{\rho-a}{\rho}\right)^2 d\rho}$$
$$= 1-\Psi^{\int_0^\infty f(r)\left(\frac{r+a}{r}\right)^3 dr} \quad \text{for all } a. \qquad (4)$$

We have used the fact that for the "random pores model" the equations analogous to (1) and (3a) are: $V = -\log(1-\Psi)$ and

$$\log(1-\Psi'(a))$$
$$= \log(1-\Psi)\int_a^\infty g(\rho)[(\rho-a)/\rho]^2\,d\rho.$$

For any given $f(r)$ and Ψ, this equation for $g(\rho)$ is easily solved by taking the logarithm of both sides and differentiating three times with respect to a. The function $g(\rho)$ obtained in this way will be called the pore radius distribution in the RSM with void fraction Ψ and sphere-radius distribution $f(r)$. For any sphere-radius distribution $f(r)$, we thus find a corresponding pore radius distribution $g(\rho)$. The inverse is not true: we cannot find a distribution $f(r)$ for every conceivable $g(\rho)$; that is we cannot construct random spheres models with every conceivable "pore radius distribution." From (4) we find that the function $g(\rho)$ is determined by Ψ and the first three moments of $f(r)$: if we define the parameters α and β by $\alpha = L_2/L_1^2$ and $\beta = L_1L_3/L_2^2$, we have

$$r_0 g(\rho) = Z_{\alpha,\beta,\Psi}\left(\frac{\rho}{r_0}\right), \qquad (5$$

with

$$Z_{\alpha,\beta,\Psi}(x) = \frac{x^2 G}{-2\log(1-\Psi)} \times \left[\frac{1+G}{(1-G)^3}\dot{Q}^3 - \frac{3}{(1-G)^2}\dot{Q}\ddot{Q} + \frac{1}{1-G}\dddot{Q}\right],$$

where $G = e^{-Q}$,

$Q = (1 + 3x + 3\alpha x^2 + \alpha^2\beta x^3) \log(1/\Psi)$,

and $\dot{Q} = dQ/dx$ etc.

The average pore radius $\bar{\rho}$ is defined by

$$\int_0^{\bar{\rho}} g(\rho)\, d\rho = \tfrac{1}{2}$$

From (5) and (2) one can derive that $\bar{\rho}/\rho_{hd}$, with ρ_{hd} the "hydrodynamic pore radius," $2\Psi/\Sigma$, is a unique function of α, β and Ψ.

From (3a) and (5) we see that higher inverse moments of $f(r)$ than the third have no practical importance. In other words, for a porous material with given Ψ and Σ, the RSM is essentially a two-parameter model, the two parameters being α and β. If all microspheres have the same radius r_0, then $\alpha = \beta = 1$; for this case we have drawn $\bar{\rho}/\rho_{hd}$ as a function of Ψ in Fig. 1. For $0.3 < \Psi < 0.8$, the results are rather well approximated by the simple formula $\bar{\rho}/\rho_{hd} = 1.32 - \Psi$. The circles in Fig. 1 represent data for two silica gels, for which independent measurements of Ψ, Σ and $\bar{\rho}$ have been performed in our laboratory (*5*). Again for $\alpha = \beta = 1$ the pore radius distribution $g(\rho)$ is almost Gaussian, as is shown in Fig. 2.

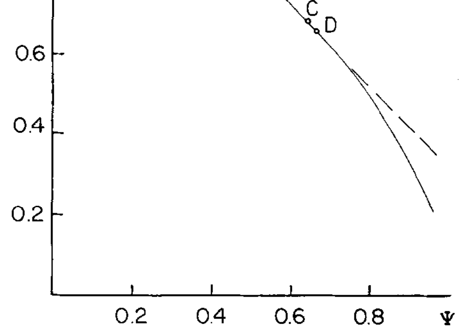


FIG. 1. Average pore radius in the RSM with $f(r) = \delta(r - r_0)$. Points C and D represent data for the silica gels porasil C and D. The dashed line is a plot of the approximate relation $\bar{\rho}(\Sigma/2\Psi) = 1.32 - \Psi$.

If the spheres are not all identical, that is, if $f(r)$ is not a delta function, α and β differ from one; actually, it can be shown that they may, independently, take on all values from one to infinity. In Fig. 3a we have drawn three distributions $f(r)$ (not normalized), and inserted the appropriate values of α, β and $\bar{\rho}/\rho_{hd}$. Figure 3b gives the corresponding pore radius distributions. It is to be noted that for these "reasonable" distributions $f(r)$ the pore radius distribution deviates relatively little from that for $f(r) = \delta(r - r_0)$, while the value of $\bar{\rho}$ has decreased by less than 10%.

Finally, the length distribution $F(x)$ of the free paths (unobstructed straight lines) in the void space can be shown to be $F(x) = (1/\lambda)e^{-x/\lambda}$ with $\lambda = 2\rho_{hd} = 4\Psi/\Sigma$. From this one can derive that the average interface area which can be "seen" from a point on the void/solid interface is $8\pi\lambda^2$, while the average void volume visible from an interface point is $4\pi\lambda^3$. For a point in the void this average visible interface area and void volume is twice as large as for a point on the interface. These facts may possibly be of use in, e.g., the interpretation of Auger signal strengths.

3. PHYSICAL PROPERTIES OF THE RANDOM SPHERES MODEL

The coefficients for diffusion through a RSM with identical microspheres $[f(r) = \delta(r - r_0)]$ are relatively easy to calculate, at least to a first approximation, because the length distribution of the free paths is simple, and also because the diffusing molecule never undergoes two successive collisions with the surface of one and the same microsphere. In a system with intersecting cylindrical pores successive collisions are

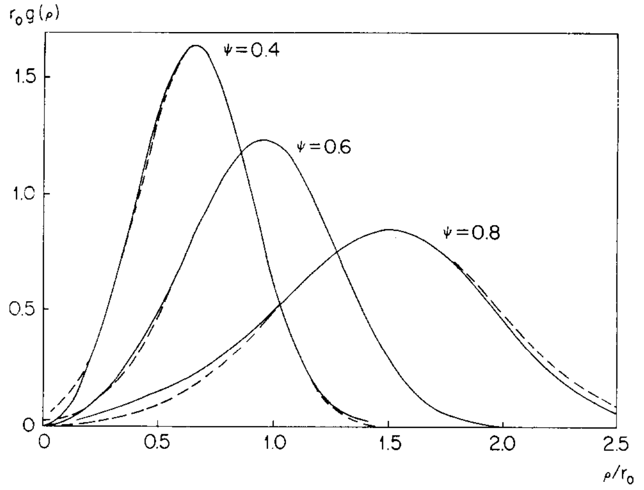


FIG. 2. The effective pore radius distribution $g(\rho)$ in the RSM with $f(r) = \delta(r - r_0)$. The dashed lines are the best fitting Gaussians. ψ is the dimensionless porosity, r_0 is the radius of the microspheres.

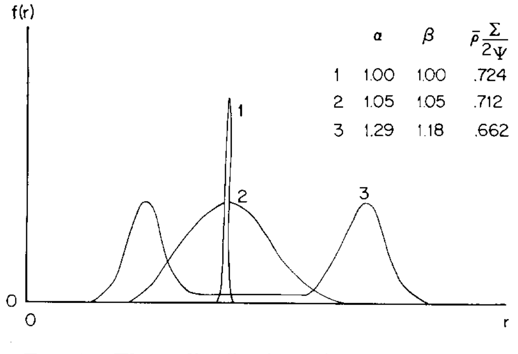
often with the wall of the same pore; this gives rise to correlations which would have to be taken into account in any statistical calculation of the diffusion coefficients.

When the porous structure is permeated by a liquid, molecules in the liquid will (except in the case of extremely narrow pores) hit other molecules much more often than they hit the wall. Consequently, collisions of the diffusing molecules with the wall may be neglected, except for the fact that the molecules have to proceed along a tortuous route. For the RSM Weissberg (*1*) proved that

$$D'/D \equiv \tau \geq 1 - \tfrac{1}{2} \log \Psi, \qquad (6)$$

where D is the diffusion coefficient in the porous material, and D' is the diffusion coefficient in the free fluid; τ is called the tortuosity. We will use Eq. (6) with the equality sign, which means that the effect of cavities and blind pores (which do not occur in practice, at least not in clean catalysts) is neglected. Equation (6) also gives the variation of τ with Ψ when the porous structure is clogged by deposits. Experimental values of τ, though very uncertain, tend to be higher than the value found from (6). An alternative to using Eq. (6) is to use the engineering formula $\tau = 1/\Psi$.

When the porous structure is permeated by a gas, the diffusing molecules will, in general, hit the wall much more often than they hit other molecules. Consequently, intermolecular collisions may be neglected (Knudsen diffusion), and a lowest-order approximation to the diffusion coefficient is



	α	β	$\bar{\rho}\frac{\Sigma}{2\Psi}$
1	1.00	1.00	.724
2	1.05	1.05	.712
3	1.29	1.18	.662

FIG. 3a. Three distributions $f(r)$, not normalized, with the corresponding values of α, β and $\bar{\rho}(\Sigma/2\Psi)$.

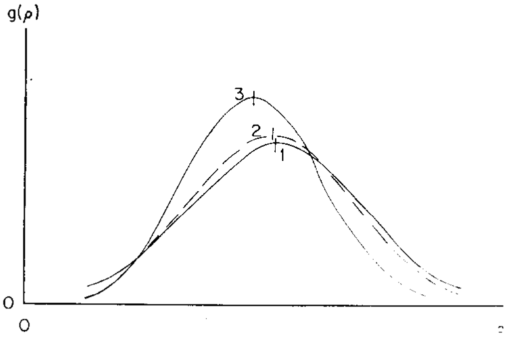


FIG. 3b. Pore radius distribution $g(\rho)$ in the RSM for the sphere radius distributions $f(r)$ drawn in Fig. 3a. The vertical bars give the values of $\bar{\rho}$.

easily calculated using simple statistics (*6*). The result depends on the nature of the collisions with the solid surface. If one assumes specular reflection (classical hard sphere bouncing) the result is $D = \lambda\bar{v}/3$, where again $\lambda = 4\Psi/\Sigma$, and where $\bar{v} = (8kT/\pi m)^{1/2}$, the thermal mean velocity of the gas particles. If, on the contrary, one assumes diffuse reflection (particles which hit the wall re-evaporate with a Maxwellian velocity distribution and with an angular distribution given by the cosine law), the first-order diffusion coefficient is somewhat smaller: $D = 3\lambda\bar{v}/13$.

However, one can do better than this. Van Leeuwen and Weijland (7) have recently given an exact theory for diffusion in a Lorentz gas. It so happens that the problem of Knudsen diffusion through a RSM, with specular reflection from the solid surfaces, can be treated as a special case of diffusion in a Lorentz gas.[1] The result is

$$D = \tfrac{1}{3}\lambda\bar{v}(1 + 2.02\,Y + 0.068\,Y^2 \log Y)^{-1},$$

with $Y = (3/4\pi)\ \log(1/\Psi)$. For $\Psi = 0.6$ this gives for instance $D = (1/3.732)\ \lambda\bar{v}$. For the case of diffuse reflection it is not unreasonable to assume that the first-order formula $D = 3\lambda\bar{v}/13$ is improved by applying the same correction factor $(1 + 2.02\,Y + 0.068\,Y^2 \log Y)^{-1}$.

We finally note that the diffusion coefficients in this section have been defined using the transport per unit void cross-section. If one assumes the ideal gas law $dp/d\rho = kT$, with p the pressure and ρ the number density of the gas, the permeability is $\pi = \Psi D/kT$.

4. Applications of the Random Spheres Model

A. Gel Permeation Chromatography

In Sect. 2 we mentioned the fact that for certain porous silica gels, the measured values of $\bar{p}\Sigma/2\Psi$ agree almost exactly with those predicted by the RSM with identical microspheres (see Fig. 1). These porous silica gels are used in our laboratory for separating polymers by gel permeation chromatography. Van Kreveld *et al.* (*5*) described the separation mechanism in terms of the accessible volume $\Psi'(a)$ for a molecule of radius *a*, as defined in Sect. 2 of this paper. They found excellent agreement between the values of $\Psi'(a)$ deduced from the measured retention times, and the theoretical curve derived from Eq. (3a). For further details see Ref. 5. It is obvious, however, that the structure of these porous silica gels is adequately represented by the random spheres model.

B. The Lifetime of a Porous Catalyst

The RSM with identical microspheres may be used to describe the clogging of porous catalysts by deposits, the layer of deposits being represented by an increase in the radius of the microspheres. We have made a general calculation of the lifetime of a catalyst on the following assumptions:

(*a*) The reactor is a stirred reactor, or a fixed-bed recycle reactor with a sufficiently high recycle ratio.

(*b*) The catalyst particles are homogeneous spheres, all with the same radius *R*.

(*c*) The feed contains an unpleasant component *X*, a fraction γ of which is converted into deposits and other reaction products. The conversion obeys first-order kinetics, and is not inhibited by the deposits, except for the fact that it is slowed down owing to the increasing diffusional resistance and the decreasing surface area.

(*d*) The deposits gradually clog the pores and so put an end to the useful catalyst life. The end has come when the

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[1] The Lorentz gas is a mixture of light and heavy hard-sphere particles with zero mass ratio of light to heavy, so that the motion of the heavy particles can be neglected as long as we take a random average over their positions. The interaction between the light particles is omitted. If in the Lorentz gas we take the radius of the light particles equal to r_0 and that of the heavy particles equal to zero, the system also describes Knudsen diffusion of light particles of radius zero through a RSM of heavy microspheres of radius r_0. The zero radius of the heavy particles in the Lorentz gas guarantees the "random overlap" of the corresponding microspheres of radius r_0 in the RSM.

effectiveness factor[2] for conversion of the component X has decreased to some fraction α of its original value.

The relative values of the lifetime of the catalyst under different circumstances, e.g., different space velocities or different values of the catalyst particle radius R, turned out to be virtually independent of the choice of α. In the present calculation we have taken $\alpha = 25\%$; increasing α to 40% did not cause changes of more than a few percent in the calculated relative values of the lifetime.

The computational procedure is rather straightforward. Starting at time zero, we compute the conversion γ, and the total amount of deposits and their distribution over the catalyst particle, at successive instants of time. This is done by solving the mass-balance equation (see Appendix), using the appropriate reduced void fraction Ψ' and reduced surface area Σ'; these are functions of time and of position in the catalyst particle, and are determined by the amount and distribution of deposits that have already been laid down. From these "simulated runs" we compute the lifetime[3] of the catalyst under different circumstances. Further details of the computation are given in the Appendix.

There are three dimensionless parameters in the calculation: the void fraction Ψ, the Thiele modulus $h = R(\Sigma K/\Psi D)^{1/2}$, and the parameter $g = s/\Sigma K$. Here Ψ, Σ, D and K (the intrinsic rate constant) are for the clean catalyst; s is the space velocity. For a number of values of these parameters Ψ, h, and g, we computed the initial conversion γ_0 and the lifetime t. Plotting γ_0 against log t, we obtained two families of curves for each value of Ψ, one for constant values of h, the other for constant values of g. For each of the two families all curves could be made to coincide by applying appropriate shifts along the log t axis. The two resulting master curves, one for constant h and varying g, the other for constant g and varying h, showed only a slight dependence on the value of Ψ. They have been plotted in Fig. 4 for $\Psi = 0.60$; the inserted intervals are for $0.45 < \Psi < 0.75$. Curve B is for $h > 4$; for $h < 2$ the variation of t with h is larger by $\sim 5\%$.

We also looked into the influence of our assumption for the tortuosity, Eq. (6). Replacing (6) by the more common engineering formula $\tau = 1/\Psi$ did not cause the plotted relative lifetimes to change by more than 2%, but the deviation from curve B for small values of h was somewhat larger than with formula (6): approximately 10%. Of course, the absolute values of the lifetime do depend very much on the choice of α (the survival criterion, see above), on Ψ, and on the formula for the tortuosity; but for the relative values of t this dependence is negligible.

Our results may be summarized as follows.

(*a*) If we vary g at a constant value of the Thiele modulus h, the lifetime t depends in a unique way on γ_0; see curve A in Fig. 4.

(*b*) If we vary h at a constant value of g, the lifetime again depends in a unique way on the initial conversion γ_0; see curve B in Fig. 4.

We give an example of the use of these curves. In our laboratory, three runs have been carried out on one and the same desulfurization catalyst, at space velocities 1, 2, and 4.35 kg kg^{-1} h^{-1}. The initial conversions of the component X (in this case metal-bearing asphaltenes) were $\gamma_0 = 73\%$, 62%, and 44%. From curve A we find that the lifetimes should be in the ratio 1:1.24:1.91; the experimental ratio was 1:1.5:2.0. Curve B is used in an analogous way, when s is kept constant and R is varied. If one

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[2] The effectiveness factor is defined as the actual reaction rate divided by the rate which would be obtained if internal transport effects were absent.

[3] In actual fact, we computed values of a reduced lifetime t', which is directly proportional to $t{:}t' = t\ a/b$, where t is the lifetime in kg feed processed per kg catalyst, b the pore volume per unit weight of catalyst, and a the volume of deposits which would be laid down per unit weight of feed processed if all X were converted, i.e., if γ were equal to one. As we will only use the relative values of the computed lifetimes, the distinction between t' and t is not relevant, as long as a and b are kept constant.

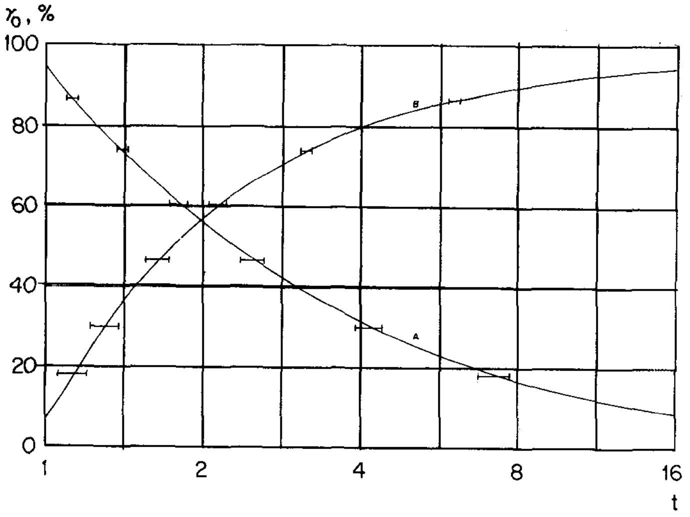

FIGURE 4

FIG. 4. Variation of the lifetime t with the initial conversion γ_0 of the fouling component X. Curve A relates to constant Thiele modulus, curve B to constant space velocity. $\Psi = 0.60$; the intervals are for $0.45 < \Psi < 0.75$, the largest variation of t corresponding to $\Psi = 0.75$.

does not measure γ_0 at all relevant values of R or s, one may use the following formula [see Eq. (4.148) in Ref. 8].

$$\frac{1}{\gamma_0} - 1 = g\frac{h}{3}\left(\frac{1}{\tanh h} - \frac{1}{h}\right)^{-1}. \tag{7}$$

Note that h and g are dimensionless; for instance, $g = s/\Sigma K$, with s the volume of fluid processed per unit volume of catalyst (interpellet voids excluded) per unit time, Σ the surface area per unit catalyst volume, and K the amount of X which reacts per unit time per unit surface area, divided by the amount of X per unit volume of fluid. The values of γ_0 which we mentioned in the above example are reasonably consistent with (7). If one wants to use (7) in cases where R is varied, one needs the value of the Thiele modulus h which is often not known.

5. DISCUSSION

We have given a short review of the theory and applications of the random spheres model (RSM) for porous materials. The model has a number of advantages over the classical tubular pore models, the main advantage being that it is more realistic. The RSM can give very precise predictions of the properties of some porous materials, like silica gels. It may also be used to compute the lifetime of porous catalysts on which deposits are laid down. In the latter case, the RSM is in principle only applicable if the catalyst has a more or less Gaussian pore radius distribution; however, if a porous catalyst has macropores as well as micropores, with radii which differ by an order of magnitude or more, the RSM may still be applicable, provided the "unpleasant" component X which lays down the deposits does not really notice the micropores. This will often be the case, for instance when the component X consists of large and very reactive molecules.

APPENDIX

For a porous sphere in which deposits have been laid down inhomogeneously, but with radial symmetry, Ψ, Σ and D are functions of Q, the distance to the centre of the sphere. The mass-balance equation for the conversion of the component X is

$$4\pi\Delta Q \frac{d}{dQ}\left(Q^2\Psi(Q)\,D(Q)\,\frac{dX(Q)}{dQ}\right) = 4\pi Q^2\Delta Q K\Sigma(Q)\,X(Q) \tag{A.1}$$

$X(Q)$ is the concentration of the component X in the fluid at Q, and K is the intrinsic rate constant for the conversion (the amount of X which reacts per unit time, per unit area, divided by the amount of X per unit volume of fluid at Q). The right-hand member of (A.1) is the amount of X which reacts in the slice between Q and $Q + \Delta Q$, while the left-hand member contains the net amount of X which enters the slice. We introduce the reduced functions $\psi(q)$, $\sigma(q)$ and $d(q)$, which are equal to $\Psi(qR)$, $\Sigma(qR)$ and $D(qR)$ divided by the values of Ψ, Σ and D for the clean catalyst. $X(qR)$ divided by the concentration of X in the fluid outside the catalyst pellets will be called $x(q)$. (A.1) may then be written as

$$x''(q) + \alpha(q)\,x'(q) = \beta(q)\,x(q), \qquad \text{(A.2)}$$

where

$$\alpha(q) = (2/q) + (d/dx)\log[\psi(q)\,d(q)],$$

and

$$\beta(q) = [\sigma(q)/\psi(q)\,d(q)]\,h^2,$$

with h the Thiele modulus $R(\Sigma K/\Psi D)^{1/2}$ for the clean catalyst. In (A.2), a prime means differentiation with respect to q; the boundary conditions are $x(1) = 1$ and $x'(0) = 0$. The volume of deposits already laid down at Q immediately gives us $\psi(q)$; $\sigma(q)$ then follows from (3a) and (3b), and $d(q)$ from (6) or another formula for the tortuosity as a function of Ψ, for instance $\tau = 1/\Psi$. Once we know $\psi(q)$, $\sigma(q)$ and $d(q)$, Eq. (A.2) may be solved numerically, using the method of finite differences.

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