

# 21

## Gas Permeation

The movement of gases through porous structures is fairly well understood. The theory is used in heterogeneous catalysis and adsorption. In this chapter we consider the transport coefficients of gases in structures consisting of either parallel cylindrical pores, or a random packing of equal-sized spheres.

### 21.1 Transport in Cylindrical Pores

We begin with a matrix consisting of parallel cylindrical pores. The matrix is regarded as a separate phase. There are two permeating gases, but we can easily extend the reasoning to more components. Figure 21.1 shows the transport equations. First of all, if there is a pressure gradient, there will be viscous flow. We can calculate the viscous velocity with the Poiseuille equation; in not-too-narrow pores, with no adsorption, the viscous velocities are equal for all species. Viscous flow is small in narrow pores, but it increases rapidly with increasing pore sizes.

Secondly, there are two diffusion equations. Each contains two friction terms: one covering the interaction between the two gases, and the other friction between the gas and the matrix. If we omit either of the two, we obtain one of the two classical diffusion equations:

- If we omit friction with the matrix, we recover the equation for free binary diffusion.
- If we omit the free diffusion term the result is the Knudsen equation. This describes diffusion in solids where the pores are smaller than the mean free path of the gas.

The Maxwell-Stefan equations used here describe both phenomena and the transition from one mechanism to the other.

Of course, the total or whole velocity is the sum of the viscous and diffusive velocities. We use the whole velocity to calculate fluxes of the species.

### 21.2 The Diffusion Coefficients

Before looking at the diffusivities in the matrix, we repeat the formula for the diffusivity in free space, according to the kinetic gas theory (Figure 21.2). We will be referring to this several times. For molecules of greatly different size, the larger of the two diameters dominates. However, the smaller of the two molar masses is the most important.

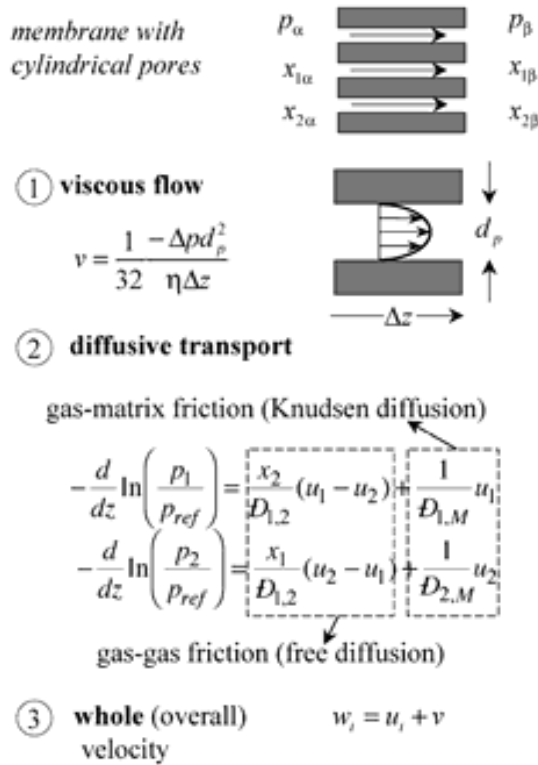


Fig. 21.1 Transport of gases in a porous matrix

$$D_{1,2}^0 = \sqrt{\frac{2}{\pi^3}} \frac{(RT)^{3/2}}{\mathcal{A} p d_{1,2}^2} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{1/2} \quad d_{1,2} = \frac{d_1 + d_2}{2}$$

Fig. 21.2 (Free space) binary diffusivity from the kinetic gas theory

Figure 21.3 gives the formulae for the three diffusivities in the matrix. These formulae are valid when

- there is no adsorption at the pore walls, and
- the pores have a diameter considerably larger than the gas molecules.

The gas-gas diffusivity is then equal to the value in free space. The gas-wall diffusivity can be derived from momentum transfer arguments; here we only show the final result (Figure 21.3). Gas-wall friction becomes more important for smaller pores and heavier gases. As usual the mass transfer coefficients are equal to the ratio of the diffusivity and the thickness of the porous layer.

We will discuss the effects of adsorption and ‘surface diffusion’ in Chapter 23.

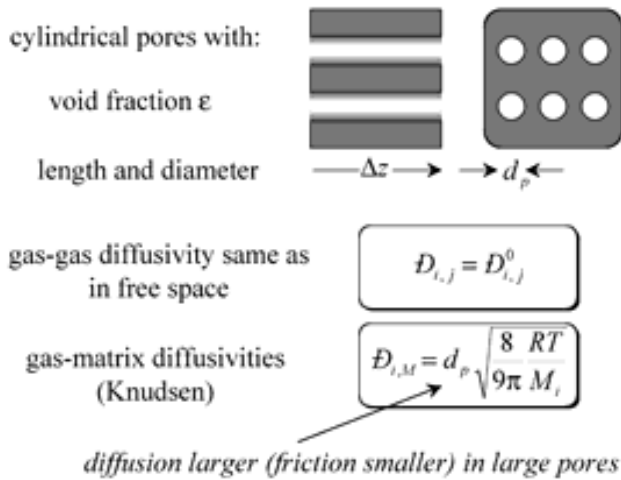


Fig. 21.3 Diffusivities in cylindrical pores

Figure 21.4 shows the results of experiments on a membrane with cylindrical pores. There is only diffusive transport in these experiments. Can you distinguish the two regimes of our diffusion equation?

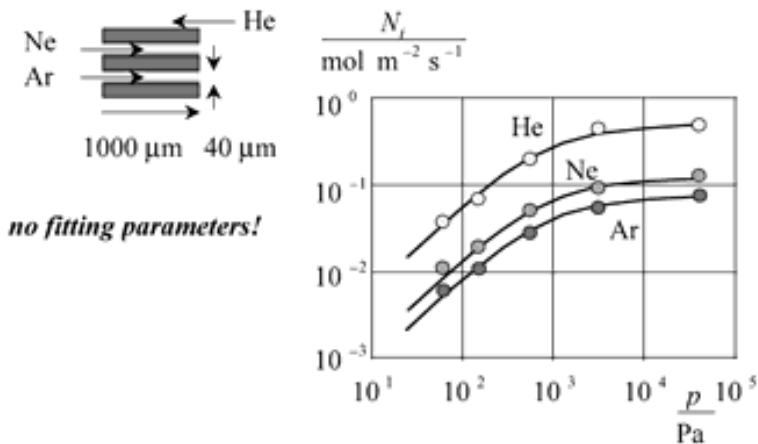


Fig. 21.4 Diffusion of three gases in cylindrical pores

### 21.3 Looking Back

Playing a bit with the cylindrical pore model will give you more understanding of two examples in Chapter 2: the ‘three gases’ (Figure 2.4) and the ‘two gases with a porous plug’ (Figure 2.7).

A fairly fundamental way of describing the ‘three gases’ example is to consider it a problem with four components:

- the three gases, and

- the capillary wall.

If the volume of the bulbs is large compared with that of the capillary, you may regard the flow at any instant as stationary. You can then set up the transport equations for the three gases, including wall friction and a pressure gradient. This of course causes viscous flow. The geometry also indicates that the net flow must be close to zero. If you solve the set of equations you will find an extremely small pressure difference because the hydrogen migrates more rapidly than the other gases. It is this difference which balances the flows. A simpler way of describing the problem is to regard it as free diffusion of three gases with a ‘no net flow’ bootstrap relation. For not-too-narrow capillaries you will find that the results of the two approaches are almost identical.

The cylindrical pore model also gives a good description of the experiment with ‘two gases and a porous plug’. If there is no pressure difference over the plug, the mole fraction differences of the two gases are equal but opposite. It is then easy to show that the gas-matrix friction terms determine the ratio of the fluxes. These in turn contain the square root of the molar masses of the two gases, as we had already noted in Chapter 2.

## 21.4 Transport in a Bed of Spheres

Many porous media are more realistically described as aggregates of spherical particles. Models for such systems have also been developed. Also here, we consider a matrix with two gases (Figure 21.5)

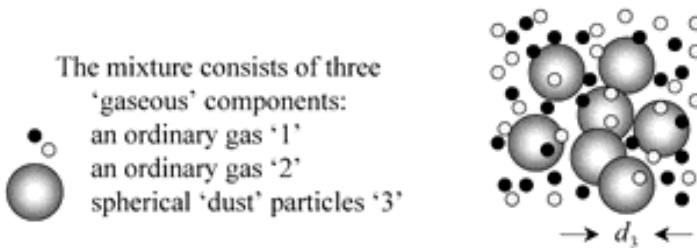


Fig. 21.5 A bed of spheres: large ‘dust’ molecules

We first look at the gas-matrix (Knudsen) diffusivity. Possibly to your surprise there is a simple theory which describes the behaviour of this coefficient quite well. In the following you may think your leg is being pulled. But really it works. The idea is that the matrix particles are giant gas molecules (‘dust’) in an ideal gas mixture (!). Because they are so large their thermal motion is negligible and that is just what happens in a sintered matrix. We can now use the kinetic gas theory to obtain the gas-‘dust’ diffusivity (step (1) in Figure 21.6). However, we are not so much interested in this parameter as in the gas-matrix diffusivity. This is the ratio of the

gas-dust diffusivity over the mole fraction of dust. We obtain this mole fraction using the ideal gas law (step (2)).

The gas-matrix diffusivity, which is derived in step (3) is seen to increase

- linearly with the coarseness (particle size) of the membrane,
- with the square root of the absolute temperature, and
- inversely with the square root of the molar mass of the diffusing species.

① gas-dust diffusivity

$$M_3 \gg M_1 \quad d_3 \gg d_1 \quad \rightarrow \quad D_{1,3} = \frac{2^{5/2} (RT)^{3/2}}{\pi^{3/2} \mathcal{A} p d_3^2} \frac{1}{M_1^{1/2}}$$

② mole fraction of dust:  $x_3 = \frac{n_3}{n_1 + n_2 + n_3}$

$$p = \frac{n_1 + n_2 + n_3}{\mathcal{A}} RT \quad n_3 = \frac{1 - \epsilon}{\frac{\pi}{6} d_3^3} \quad \rightarrow \quad x_3 = \frac{(1 - \epsilon) RT}{\frac{\pi}{6} d_3^3 p \mathcal{A}}$$

③ matrix diffusivity:  $D_{1,M} = \frac{D_{1,3}}{x_3} = \frac{2^{3/2} (RT)^{1/2} d_3}{3\pi^{1/2} (1 - \epsilon) M_1^{1/2}} = \frac{d_3}{1 - \epsilon} \sqrt{\frac{8 RT}{9\pi M_1}}$

$D_{2,M}$  similar

this is only valid for a 'gas':  $\epsilon \rightarrow 1$

Fig. 21.6 Deriving an expression for the gas-matrix diffusivity

The derivation above is only valid for a 'gas', so for low concentrations of the dust particles. We come back to this in a moment.

Figure 21.7 shows a few aspects of the gas-gas diffusivity. The idea is that we are dealing with tortuous pores with wide parts and narrow parts (constrictions). The tortuosity has two effects: it increases the pore length and reduces the effective pore width. So the effect on the diffusivities is quadratic. The constrictions also reduce the effective diffusivity: the extra friction in the narrow parts is not balanced by the reduced friction in the wide parts. Together the effect is to reduce the gas-gas diffusivity by roughly one order of magnitude (less in very open structures, more in compressed structures).

In many references you will find the ratio of tortuosity squared over constriction factor designated as the 'tortuosity'. We have kept the two things separate. Note that the gas-gas coefficient does not depend on the size of the channels or the particles of the matrix.

For dense structures, we need to apply a tortuosity-constrictivity correction to the gas-matrix diffusivity just as we have done for the gas-gas diffusivity. This correction depends on details of the structure of the matrix. However, the formula in

Figure 21.8 roughly describes the correction for many structures. This yields our final formulae for the diffusivities in a bed of spherical particles.

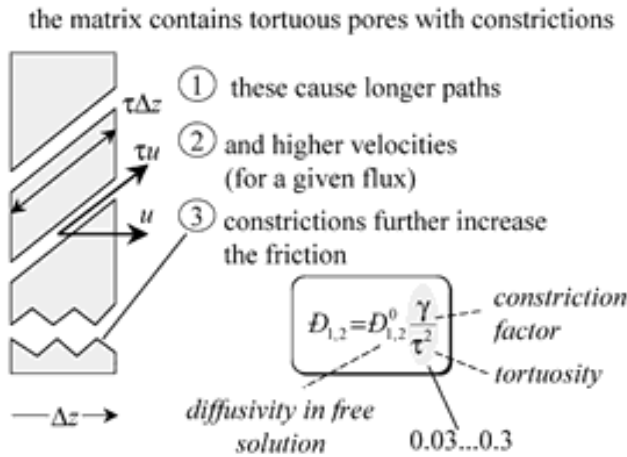


Fig. 21.7 Gas-gas diffusivity in a porous medium – tortuosity and constriction factor

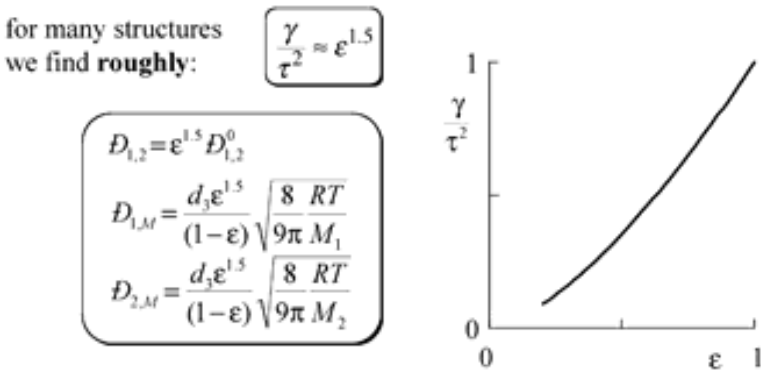


Fig. 21.8 Diffusivities in a bed of spheres

We calculate the viscous flow in a matrix of spherical particles with relations for packed beds (such as the Carman-Kozeny equation, Figure 21.9). The viscous flow increases with the pressure gradient and the square of the diameter of the matrix particles. The velocity we need is not the superficial velocity, but the average velocity in the pores. That is why the exponent in the void fraction is one less than in packed bed relations.

## 21.5 The Dusty Gas Model

The results of the bed-of-spheres model are very similar to those of the model with cylindrical pores. You will note that the effects of temperature, pressure, molar mass,

diameters of the permeants and dimensions of the matrix are identical. The two models are examples of a more general model known as the ‘dusty gas model’ (Figure 21.10). The constants in the transport coefficients are usually determined experimentally.

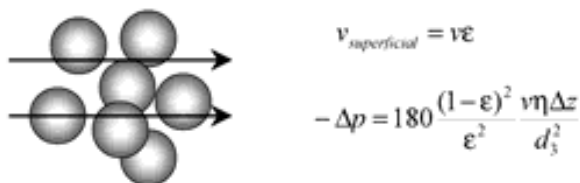


Fig. 21.9 Viscous flow in a bed of spheres

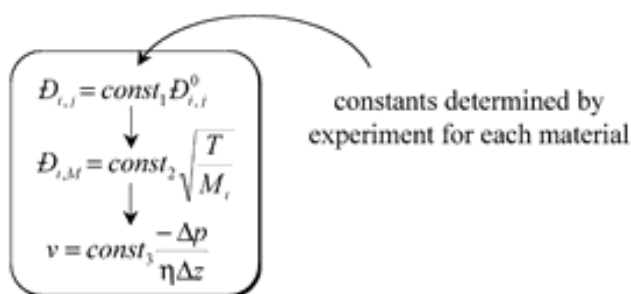


Fig. 21.10 Practical Dusty Gas Model

The Dusty Gas Model is one of those parts of science that has been discovered many times (Figure 21.11).

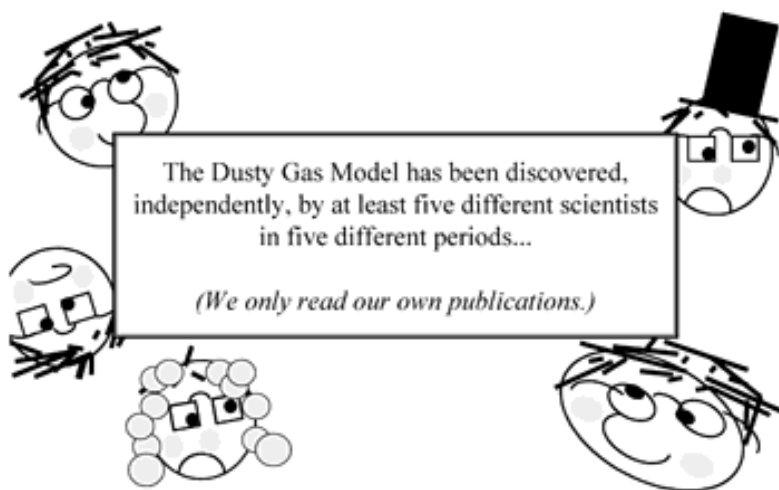


Fig. 21.11 Science

## 21.6 Summary

This chapter has introduced two heterogeneous models for transport of gases through a porous medium:

- a model with parallel cylindrical pores, and
- a model consisting of a packed bed of equal spheres.

Both models are similar. They contain terms for

- gas-gas interactions,
- gas-wall interactions and
- viscous flow.

They require a dimension: a pore size or particle diameter. In addition the bed-of-spheres model requires the void fraction, and tortuosity and constriction factor of the membrane.

The two models can be regarded as special cases of a more general model. This is known as the 'dusty gas model'. If we know the structure of the matrix, we can estimate the coefficients of the model. However, they are usually determined via diffusion and permeation experiments.

## 21.7 Further Reading

Remick, R.R. and Geankoplis, C.J. (1974) Ternary diffusion of gases in capillaries in the transition region between Knudsen and molecular diffusion. *Chem. Eng. Sci.*, **29**, 1447-1455.

The source of the experimental data used in Figure 21.4 to verify the dusty gas model.

Jackson, R., *Transport in Porous Catalysts*. Elsevier, Amsterdam, 1977  
*An excellent book about the dusty gas model. Written for the chemical engineer.*

Cunningham, R.E. and Williams, R.J.J., 1980, *Diffusion in gases and porous media*. Plenum Press, New York.  
*Provides a very good historical perspective of diffusion inside porous media.*

Mason, E.A. and Malinauskas, A.P., 1983, *Gas transport in porous media: The dusty gas model*. Elsevier, Amsterdam.  
*The first author is considered to be one of the fathers of the dusty gas model. The book is very readable.*

Epstein, N. (1989) On the tortuosity and the tortuosity factor in flow and diffusion through porous media. *Chem. Eng. Sci.*, **44**, 777-779.  
*A clear exposition of the proper interpretation of the tortuosity factor.*

## 21.8 Exercises

21.1 Modifying the Knudsen Relation. A diffusivity can often be regarded as the product of a jump velocity, a jump distance and a coefficient which is a little smaller than unity. For gases, the velocity is obviously the thermal velocity  $v_i^T \approx \sqrt{RT/M_i}$ .

(a) What would the jump distance be in the Knudsen regime in the parallel pores of Figure 21.3?

(b) You would expect the jump distance to actually be smaller by one molecule diameter, because the molecule can only approach the wall up to its radius. Modify the Knudsen relation for the gas-solid diffusivity to take this into account.

(c) For which pore diameter does the gas-solid diffusivity now become zero?

21.2★ Three Gases with the Wall (Mathcad). We go back to the three gases problem of Figures 2.4 and 2.5. You are to include the effect of friction with the tube wall and to find how small it is. This is a good exercise for getting hold of all main effects of the Dusty Gas Model.

21.3 Helium, Neon and Argon in a Capillary (Mathcad). In this file you are to analyse the experimental data of Remick and Geankoplis leading to Figure 21.4. This is quite a challenge.

21.4 Different Models for Tortuosity (Mathcad). If you want to know how we came to choosing the tortuosity - constriction factor in Figure 21.8, have a look at this file. If you still find this a baffling subject, do have a look in the article of Epstein.

21.5 Diffusivities of Nitrogen, Hydrogen and Ammonia in a Catalyst (Mathcad). This is a four component system (the fourth is the matrix). So you need the following set of diffusivities:

$$\begin{array}{ccc} \mathcal{D}_{1,2} & \mathcal{D}_{1,3} & \mathcal{D}_{1,M} \\ & \mathcal{D}_{2,3} & \mathcal{D}_{2,M} \\ & & \mathcal{D}_{3,M} \end{array}$$

This file shows how to calculate these for non-adsorbing species in an array of spherical particles. This is lengthy but straightforward; only use this file if you need it.

21.6 A Novel Process for Gas Separation (Mathcad). A student having followed a course by Wesselingh and Krishna on the Maxwell-Stefan approach to mass transfer has come up with an idea for selective removal of styrene (1) from a mixture with ethyl benzene (2) and hydrogen (3). You are required to examine this invention and comment on its feasibility. This requires carefully reading and thinking about a file.