GAS DIFFUSION IN MICROPOROUS MEDIA IN KNUDSEN'S REGIME

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A diffusion equation for gas permeation through microporous media in the Knudsen regime was obtained theoretically, considering the potential energy between a gas molecule and the solid surface of pores. The equation as a function of temperature contains four parameters, all of which have physical meanings. The most significant of these parameters is the effective potential energy ε^*, by which the gas diffusion equation as a function of temperature is characterized. Permeabilities of He, H_2, CO, N_2, O_2, Ar, and CO_2 through a microporous Vycor glass membrane were measured in the temperature range from 300 K to 950 K. The validity of the diffusion equation obtained was verified experimentally and was shown to express well the previous data.

For helium in particular, diffusion is almost gas-phase flow, with no adsorbed flow except at very low temperature. However, the diffusion is affected by the interaction energy between the gas molecules and the solid surface in the pores.

Introduction

Mass transport phenomena through porous media are important in the fields of gas separation with porous membranes, gas diffusion on catalytic reactions, and the like.

Permeability of gas through a porous medium is usually taken as the sum of gas-phase flow and surface flow. A problem of engineering interest is the accurate measurement and description of surface permeability. Most of the reported work is based on the concept that helium can be used as a calibration gas for the estimation of surface flow, because it is considered that helium exhibits no surface flow or at most a negligible amount.

However, in a series of papers by Hwang and Kammermeyer[8,9] it was reported that helium as well as nitrogen, oxygen, argon and carbon dioxide has significant surface flow and shows a temperature minimum of the adjusted permeability corrected for temperature and molecular weight. They obtained Eq. (1) to express the adjusted permeability $Q\sqrt{MT}$ as a function of temperature.

$$Q\sqrt{MT} = A + BT\exp(\varDelta/T) \qquad (1)$$

The first term on the right-hand side indicates Knudsen flow (gas-phase flow), which is independent of gas species and temperature. The second term indicates surface flow, which depends on temperature and shows a temperature minimum. Their conclusion has been introduced widely.[10,13,19] However, some

reports[1,6,22] have been critical or have had questions about their conclusion.

There have been two main ideas opposing one another. One[7,11] is that helium has surface flow being adsorbed on a surface, the other is that helium has no surface flow except at very low temperatures, but only gas-phase flow which is influenced by the surface attractive energy. Sandler[21] and Nicholson[15-17] obtained diffusion equations for gas permeation through porous media in view of the molecule-surface interaction model. However, their theories have not been examined experimentally, but have merely been used to explain qualitatively the results of Hwang and Kammermeyer.

The purpose of this paper is to derive theoretically a new equation of gas diffusion through a porous medium with consideration of the molecule-surface interaction force and to examine the equation experimentally.

1. Theory

In a gas diffusion of the Knudsen[14] regime, the gas molecules collide with the walls, not with other molecules. If the pores in which gas molecules diffuse are very small, the collisions, rebounds and flights of the molecules are always under the influence of a force field due to the potential energy between the molecules and the surface of a pore.

A new diffusion equation, in which the interforce energy is taken into account as a function of temperature, was derived on the basis of a few assumptions as follows.

1.1 Basic assumptions

(I) There are force fields on the surface in a porous medium. The magnitude of the force, which affects a gas molecule, depends upon the interaction energy between the molecule and the solid surface. This interaction energy is called surface potential energy ε_s.

(II) After each collision, a gas molecule rebounds with a fresh direction of motion and a fresh kinetic energy, regardless of those it had before collision. This means that the molecules rebound diffusively, not specularly.[20]

(III) The gas molecules which rebound from the surface are divided into two groups according to the ratio of translational kinetic energy ε_v in the direction vertical to the surface with surface potential energy ε_s. (See **Fig. 1**.)

When $\varepsilon_v < \varepsilon_s$: Such a molecule cannot pass through the force field, and it collides with the surface again. It hops along the surface, being attracted by the surface potential energy. The flow of such molecules is called surface flow in this paper.

When $\varepsilon_v > \varepsilon_s$: Such a molecule may pass through the force field, i.e., the potential well depth. It travels in the pore to another surface. However, the gas molecule is affected by the potential energy during passage through the force field. (See **Fig. 2**.) The flow of such molecules is called gas-phase flow.

1.2 Derivation of a gas diffusion equation

In either of the two cases mentioned above, a gas molecule in a pore moves wall to wall at random. We can apply the random-walk model to both gas-phase and surface[3] flows. Designating λ and u for the mean free path wall-to-wall and the mean velocity of the molecules in three-dimensional space respectively, the molar flux f (mol per unit time and area) in the direction of l is represented according to the random-walk theory as follows.

$$f = -gu\lambda \frac{dC}{dl} \qquad (2)$$

where g is a numerical constant, (geometrical factor), and C is the concentration of gas. In terms of Eq. (2), the molar flux of the surface flow can be written as

$$f_s = -g_s u_s \lambda_s \frac{dC_s}{dl} \qquad (3)$$

where the subscript s means the molecules of surface flow and g_s is a geometrical factor which depends on the physical structure of the pores. By assumption (III), the relationship between the concentration of surface flow molecules C_s and the concentration of gas-phase flow molecules C_g may be written as follows. (See **Fig. 3**.)
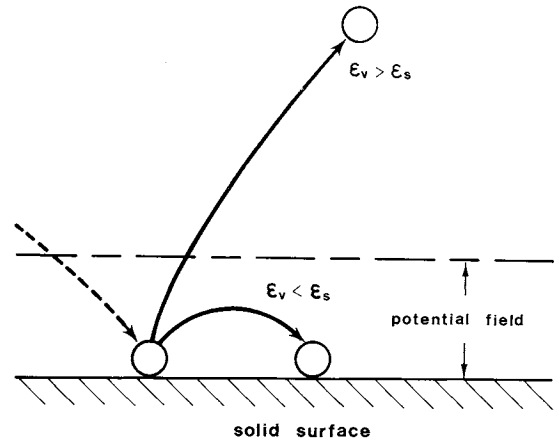

Fig. 1. Schematic view of rebounds of gas molecules on solid surface.
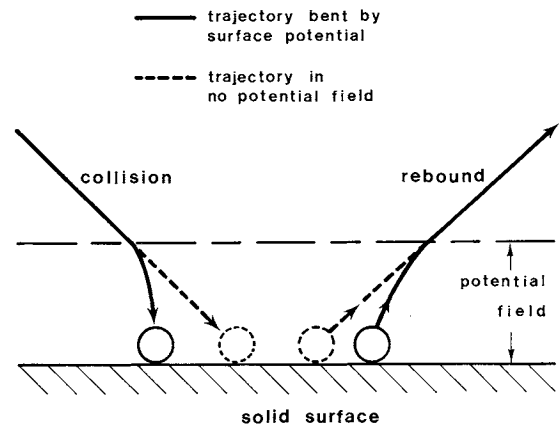

Fig. 2. Schematic view of collision and rebound for molecules in gas-phase flow influenced by surface potential energy.

$$\frac{C_s}{C_g} = \frac{\text{number of surface flow molecules in a certain volume}}{\text{number of gas-phase flow molecules in a certain volume}} \qquad (4)$$

$$= \frac{\tau_s \times \text{probability of being surface flow molecules}}{\tau_g \times \text{probability of being gas-phase flow molecules}} \qquad (5)$$

$$= \frac{\tau_s \displaystyle\int_0^{\varepsilon_s} \Psi(\varepsilon_v)\,d\varepsilon_v}{\tau_g \displaystyle\int_{\varepsilon_s}^{\infty} \Psi(\varepsilon_v)\,d\varepsilon_v} \qquad (6)$$

where $\Psi(\varepsilon_v)$ is a distribution function of the translational kinetic energy in the direction vertical to the surface for the molecules after rebounding from the wall. Here, the distribution function is assumed to take the form:

$$\Psi(\varepsilon_v) = \frac{1}{\bar{\varepsilon}_v} \exp\left(\frac{-\varepsilon_v}{\bar{\varepsilon}_v}\right) \qquad (7)$$

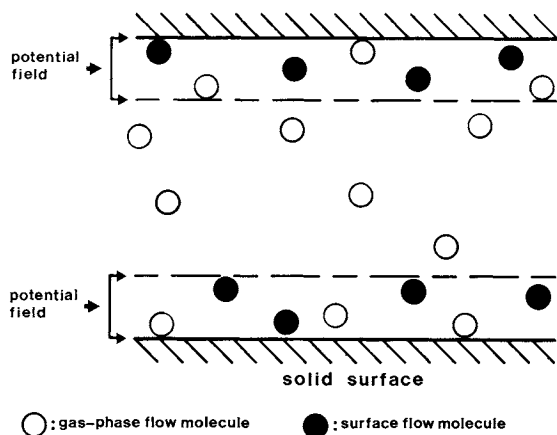○ : gas-phase flow molecule   ● : surface flow molecule

Fig. 3. Schematic view of gas molecules in pore.

where $\bar{\varepsilon}_v$ is the mean translational kinetic energy in the direction vertical to the surface.

We cannot obtain exactly the value of $\bar{\varepsilon}$. It may be assumed that $\bar{\varepsilon}_v$ depends on temperature and is expressed as

$$\bar{\varepsilon}_v = \gamma kT \tag{8}$$

in which γ is constant and k is the Boltzmann constant. Inserting Eq. (8) into Eq. (7), one obtains

$$\Psi(\varepsilon_v) = \frac{1}{\gamma kT} \exp\left(\frac{-\varepsilon_v}{\gamma kT}\right) \tag{9}$$

Equation (6) can be calculated by use of Eq. (9), the result being

$$\frac{C_s}{C_g} = \frac{\tau_s}{\tau_g} \left\{ \exp\left(\frac{\varepsilon_s}{\gamma kT}\right) - 1 \right\} \tag{10}$$

Here, defining the effective potential energy as

$$\varepsilon^* = \frac{\varepsilon_s}{\gamma} \tag{11}$$

the relationship between C_s and C_g is given by

$$C_s = \frac{\tau_s}{\tau_g} \left\{ \exp\left(\frac{\varepsilon^*}{kT}\right) - 1 \right\} C_g \tag{12}$$

Inserting Eq. (12) into Eq. (3), the molar flux of the surface flow f_s is represented as

$$f_s = -g_s u_s \lambda_s \frac{\tau_s}{\tau_g} \left\{ \exp\left(\frac{\varepsilon^*}{kT}\right) - 1 \right\} \frac{dC_g}{dl} \tag{13}$$

The molecules in gas-phase flow can pass through the force field, but within that field they are attracted by the solid surfaces. The attractive force will bend the trajectories of the gas-phase molecules. (See Fig. 2.) It may be considered that the mean free path is shortened by the attractive force. Consequently, the gas-phase flow rate becomes smaller than the ideal gas flow rate, which is not affected by the potential energy. With increasing temperature, the kinetic energy of a gas molecule increases. It follows that the

influence of potential energy on molecules becomes relatively small.

We take a Sutherland[2,23] type equation to express the relation between temperature and mean free path λ_g, as Eq. (14). Sutherland's equation is a semi-empirical equation, used in estimation of transport coefficients, i.e., viscosity, diffusion coefficient and thermal conductivity. It expresses well the relation between mean free path and temperature when the attractive interforce is applied to a gas molecule.

$$\lambda_g = \lambda_0 \frac{1}{1 + \frac{\beta \varepsilon^*}{kT}} \tag{14}$$

where β is a constant and λ_0 is the mean free path of the molecules not affected by the potential energy or at very high temperature $(T \to \infty)$. The relation between temperature and mean free path for each gas is characterized by the magnitude of the effective potential energy ε^*. With Eqs. (2) and (14), we obtain

$$f_g = -g_g u_g \lambda_0 \frac{1}{1 + \frac{\beta \varepsilon^*}{kT}} \frac{dC_g}{dl} \tag{15}$$

where the subscript g means the molecules in gas-phase flow and g_g is the geometrical factor for gas-phase flow. The total molar flux f_t is given by a combination of Eqs. (13) and (15).

$$f_t = f_g + f_s \tag{16}$$

$$= -g_g u_g \lambda_0 \frac{1}{1 + \frac{\beta \varepsilon^*}{kT}} \frac{dC_g}{dl}$$
$$\quad -g_s u_s \lambda_s \frac{\tau_s}{\tau_g} \left\{ \exp\left(\frac{\varepsilon^*}{kT}\right) - 1 \right\} \frac{dC_g}{dl} \tag{17}$$

$$= -g_g u_g \lambda_0 \left[\frac{1}{1 + \frac{\beta \varepsilon^*}{kT}} \right.$$
$$\left. + \frac{g_s u_s \lambda_s \tau_s}{g_g u_g \lambda_0 \tau_g} \left\{ \exp\left(\frac{\varepsilon^*}{kT}\right) - 1 \right\} \right] \frac{dC_g}{dl} \tag{18}$$

Defining the parameter α as

$$\alpha \equiv \frac{g_s u_s \lambda_s \tau_s}{g_g u_g \lambda_0 \tau_g} \tag{19}$$

and using the ideal gas relation and kinetic molecular theory,

$$p = C_g RT \tag{20}$$

$$u_g = \sqrt{\frac{8RT}{\pi M}} \tag{21}$$

then one obtains

$$f_t = -g_g \lambda_0 \sqrt{\frac{8}{\pi MRT}} \left[\frac{1}{1+\frac{\beta \varepsilon^*}{kT}} + \alpha \left\{ \exp\left(\frac{\varepsilon^*}{kT}\right) - 1 \right\} \right] \frac{dp}{dl}$$

(22)

Defining K as

$$K \equiv g_g \lambda_0 \sqrt{\frac{8}{\pi R}}$$

(23)

Then the total molar flux becomes

$$f_t = -\frac{K}{\sqrt{MT}} \left[\frac{1}{1+\frac{\beta \varepsilon^*}{kT}} + \alpha \left\{ \exp\left(\frac{\varepsilon^*}{kT}\right) - 1 \right\} \right] \frac{dp}{dl}$$ (24)

The permeability Q is defined by the equation

$$f_t = -Q \frac{dp}{dl}$$

(25)

Combining Eqs. (24) and (25) gives

$$Q = \frac{K}{\sqrt{MT}} \left[\frac{1}{1+\frac{\beta \varepsilon^*}{kT}} + \alpha \left\{ \exp\left(\frac{\varepsilon^*}{kT}\right) - 1 \right\} \right]$$ (26)

and finally we obtain

$$Q\sqrt{MT} = K \left[\frac{1}{1+\frac{\beta \varepsilon^*}{kT}} + \alpha \left\{ \exp\left(\frac{\varepsilon^*}{kT}\right) - 1 \right\} \right]$$ (27)

The first term on the right-hand side of Eq. (27) shows gas-phase flow, and the second term shows surface flow. When the temperature rises, the effect of the potential energy on the molecules in gas-phase flow decreases and the number of surface flow molecules diminishes. Hence, the first term progressively decreases to unity and the second term decreases to zero with increasing temperature. The total flow is expressed by the sum of gas-phase flow and surface flow. Therefore, the total flow shows a temperature minimum for the adjusted permeability $Q\sqrt{MT}$. Figure 4 shows a schematic view of this relation.

1.3 Consideration of parameters K, α and β

The parameter K is considered to be constant, regardless of gas species and temperature. Because the mean free path λ_0 in zero potential field depends on pore diameter, so the factor $g_g \lambda_0$ in Eq. (23) is determined by the geometrical structure of the pore. The paramerer α is defined by Eq. (19). It can be rewritten as below, with the relations $\lambda_s = u_s \tau_s$ and $\lambda_g = u_g \tau_g$.

$$\alpha = \frac{g_s \lambda_s^2}{g_g \lambda_g \lambda_0}$$ (28)

The mean free path λ_s may be considered to depend on the thickness of the potential field on the surface. As a simple approximation, it is assumed that the mean free path λ_s is independent of gas species, and that λ_0 is nearly equal to λ_g. Furthermore, it may
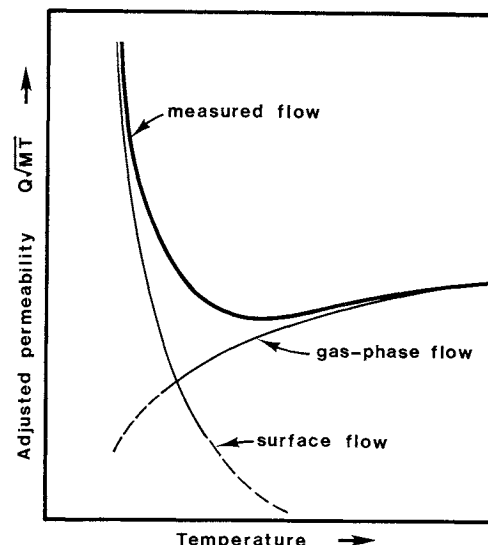

Fig. 4. Schematic view of total flow as sum of gas-phase and surface flows.

be supposed that the effects of temperature on λ_g and λ_s can be neglected in comparison with the effect of temperature on the exponential term of $\{\exp(\varepsilon^*/kT) - 1\}$ in Eq. (27). The parameter β is defined as a constant in Eq. (14).

Therefore, the parameters K, α and β can be considered to be constants, in the form of the simple approximations mentioned above.

2. Experimental

Hwang and Kammermeyer[8,9] measured permeabilities for several gases through a microporous Vycor glass membrane in the range of temperature from 77 K to 600 K. It may be considered important to measure the permeabilities at temperatures far above 600 K. Permeabilities were measured in the temperature range from 300 K to 950 K in this work.

2.1 Experimental apparatus

A schematic diagram of the apparatus for flow measurement is shown in Fig. 5. The gas was fed into the high-pressure side of the diffusion cell. It permeated through the membrane into the low-pressure side and the flow rate was measured by a soap-film flowmeter. The diffusion cell was made of microporous Vycor glass and quartz so that sealing problems at high temperatures were avoided.

2.2 Physical properties of the membrane

Porous Vycor glass, produced by the Corning Glass Works, was employed as the permeable membrane. The void fraction, specific surface area, average pore diameter and apparent density are reported as: 0.28, 250 m^2/g, 4 nm (40 Å) and 1.45–1.50 g/cm^3 respectively. The porous glass had the shape of a cylinder of 1.4 mm in thickness. The logarithmic mean of the outside and inside surface areas was 151 cm^2. It is
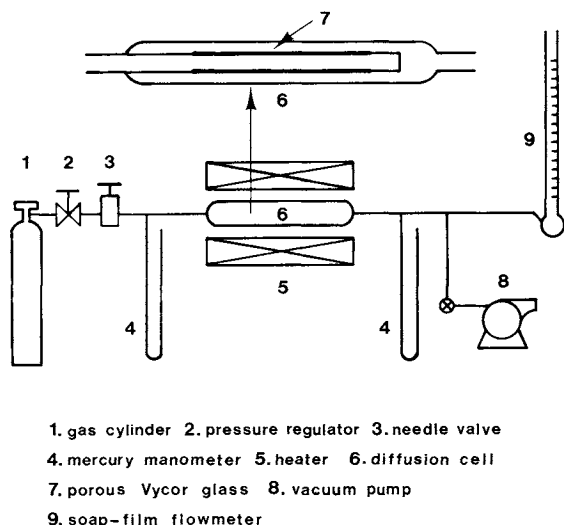
1. gas cylinder 2. pressure regulator 3. needle valve
4. mercury manometer 5. heater 6. diffusion cell
7. porous Vycor glass 8. vacuum pump
9. soap-film flowmeter

Fig. 5. Schematic diagram of experimental apparatus.

reported[18] that porous Vycor glass may contract after being heated for a long time and that its contractibility is 2% at a temperature of 700°C (973 K). The permeabilities of gases were measured at temperatures lower than 700°C to prevent shrinking of the membrane. No effects of contraction of the membrane on the permeabilities were found in the present experiments.

3. Results and Discussion

The downstream pressure was fixed at atmospheric pressure. Upstream pressures of up to 200 kPa could be used, in order to obtain various pressure drops across the membrane. Still, the observed permeabilities were pretty much constant at any one temperature. There was no indication of a pressure effect. This proves that the gases permeate according to Eq. (27), which includes no pressure factors. The permeabilities were measured usually by fixing upstream and downstream pressures at about 160 kPa and atmospheric pressure respectively.

3.1 Experimental results

The adjusted permeabilities for gases through the porous Vycor glass membrane are shown in **Fig. 6.** The temperature minima of $Q\sqrt{MT}$ for CO, N_2, O_2 and Ar were determined. It was predicted by Hwang and Kammermeyer that $Q\sqrt{MT}$ would drop again at very high temperatures. However, $Q\sqrt{MT}$ did not drop within the temperature region of our experiments. Equation (27) was applied to these experimental results. The values of K, ε^*, α and β were calculated by the least squares method. The best-fitting values of α and β for all gases are 0.246 and 0.606 respectively. The values of K and ε^* for each gas are shown in **Table 1.** It may be said that the values of K derived for the gases are almost the same. Figure 6 shows the curves calculated from Eq. (27) with the values of the
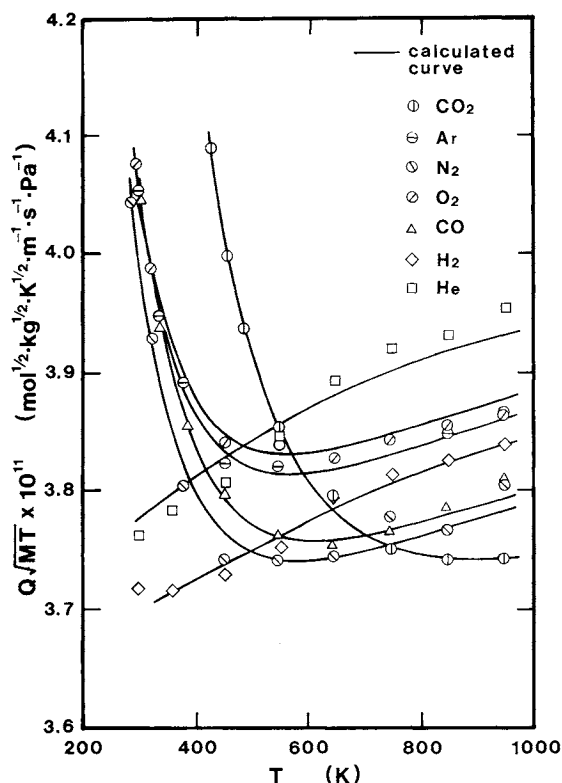

Fig. 6. Adjusted permeabilities for several gases through microporous Vycor glass membrane.

parameters given in Table 1. Close agreement between observed and calculated values was obtained.

3.2 Application to the previous data

Equation (27) was applied to Hwang and Kammermeyer's data.[8] The values $\alpha = 0.246$ and $\beta = 0.606$ were used in this application, because the porous Vycor glass membrane used by them has almost the same physical properties as the one we used. **Figure 7** shows that their permeabilities data are well expressed by Eq. (27), and the values of the two parameters are given in **Table 2.** The average value of K for their data is a little different from that for our data. It may be estimated that the disparity is due to slight differences in the method of measurement or in the physical structures of the porous glass membranes, such as pore size distribution, for example.

3.3 Consideration of the effective potential energy

The effective potential energy ε^* is the most important parameter in Eq. (27). It is supposed that there should be a relation between effective potential energy and intermolecular potential enegy, ε, which is defined as the potential energy between two identical gas molecules.[4,5] **Figure 8** gives the relation between ε and ε^*. The effective potential energy ε^* is approximately proportional to ε as

$$\varepsilon^*/k = 2.26\varepsilon/k \qquad (29)$$

We may predict ε^* for any unknown gas from its intermolecular potential energy ε by use of Eq. (29).

Table 1. Calculation results of parameters in this work and physical properties of gases[12]

		He	Ne	H_2	N_2	CO	O_2	Ar	CO_2
$K \times 10^{11}$	$[\mathrm{mol}^{1/2} \cdot \mathrm{kg}^{1/2} \cdot \mathrm{K}^{1/2}/\mathrm{s} \cdot \mathrm{m} \cdot \mathrm{Pa}]$	4.07	—	4.01	4.04	4.06	4.14	4.12	4.04
ε^*/k	[K]	108	—	142	253	266	247	249	390
M	[g/mol]	4.0	20.2	2.0	28.0	28.0	32.0	39.9	44.0
ε/k	[K]	10.2	35.7	37.0	91.5	110	88.0	124	190

M, molecular weight; ε, intermolecular potential energy; k, Boltzmann constant.

Table 2. Calculation results of parameters for the data of Hwang and Kammermeyer

		He	Ne	H_2	N_2	O_2	Ar	CO_2
$K \times 10^{11}$	$[\mathrm{mol}^{1/2} \cdot \mathrm{kg}^{1/2} \cdot \mathrm{K}^{1/2}/\mathrm{s} \cdot \mathrm{m} \cdot \mathrm{Pa}]$	5.44	5.52	5.47	5.67	5.71	5.69	5.80
ε^*/k	[K]	39	82	104	228	211	208	439
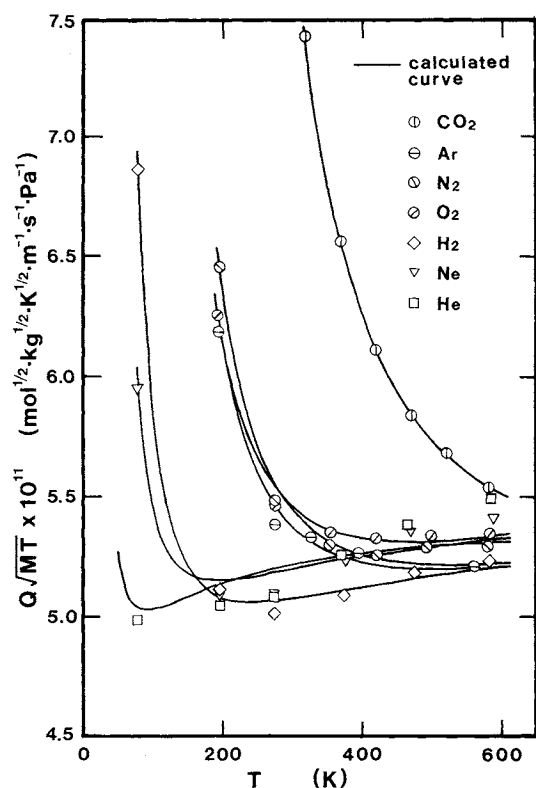
Fig. 7. Adjusted permeabilities for several gases by Hwang and Kammermeyer.

Fig. 8. Relationship between ε^*/k and ε/k.

Conclusion

A diffusion equation was derived for gas permeation through microporous media in the Knudsen regime on the concept of the effect of the potential energy between a gas molecule and the solid surface in a porous medium. The equation includes four parameters, all of which have physical meanings. The most significant of these parameters is the effective potential energy ε^*, by which the gas diffusion equation as a function of temperature is characterized. The validity of this equation was experimentally verified and it
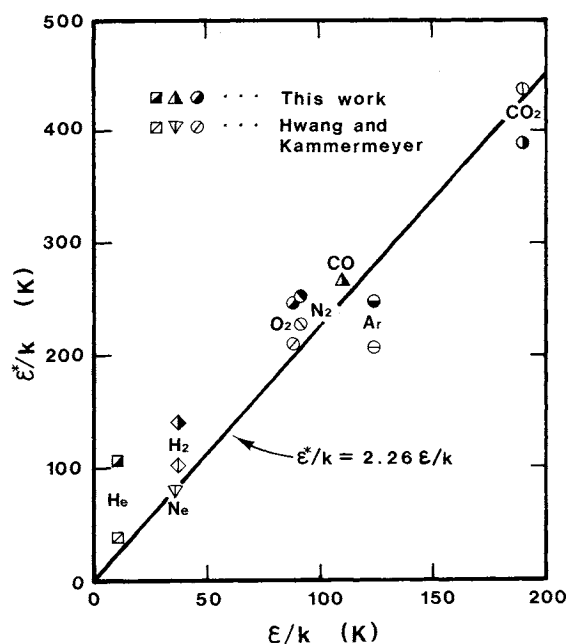
agrees well with the previous data. A proportional relation between the effective potential energy ε^* and the intermolecular energy ε of each gas was also derived. With respect to the diffusion of helium through microporous media, the diffusion is almost gas-phase flow, but it is influenced by the surface potential energy. The increase of $Q\sqrt{MT}$ for helium above room temperature is caused by the relative decrease of interaction energy between the molecule and the solid surface corresponding to the kinetic energy of the gas molecule.

Nomenclature

A = gas-phase flow coefficient

$$[\mathrm{mol}^{1/2} \cdot \mathrm{kg}^{1/2} \cdot \mathrm{K}^{1/2}/\mathrm{s} \cdot \mathrm{m} \cdot \mathrm{Pa}]$$

B	= surface flow coefficient	
		$[\text{mol}^{1/2} \cdot \text{kg}^{1/2} \cdot \text{K}^{1/2}/\text{s} \cdot \text{m} \cdot \text{Pa}]$
C	= concentration	$[\text{mol}/\text{m}^3]$
f	= molar flux	$[\text{mol}/\text{s} \cdot \text{m}^2]$
f_t	= total molar flux	$[\text{mol}/\text{s} \cdot \text{m}^2]$
g	= geometrical factor	$[—]$
K	= diffusion coefficient defined by Eq. (23)	
		$[\text{mol}^{1/2} \cdot \text{kg}^{1/2} \cdot \text{K}^{1/2}/\text{s} \cdot \text{m} \cdot \text{Pa}]$
k	= Boltzmann constant	$[\text{J}/\text{K}]$
l	= distance along diffusion	$[\text{m}]$
M	= molecular weight	$[\text{kg}/\text{mol}]$ or $[\text{g}/\text{mol}]$
p	= pressure	$[\text{Pa}]$
Q	= gas permeability	$[\text{mol}/\text{s} \cdot \text{m} \cdot \text{Pa}]$
R	= gas constant	$[\text{J}/\text{K} \cdot \text{mol}]$
T	= temperature	$[\text{K}]$
u	= mean velocity of gas molecules	$[\text{m}/\text{s}]$
α	= constant defined by Eq. (19)	$[—]$
β	= constant defined by Eq. (14)	$[—]$
γ	= constant defined by Eq. (8)	$[—]$
Δ	= quantity depending on gas species	$[\text{K}]$
ε	= intermolecular potential energy of two identical gas molecules	$[\text{J}]$
ε_s	= surface potential energy	$[\text{J}]$
ε_v	= translational kinetic energy of gas molecule in the direction vertical to the surface	$[\text{J}]$
$\overline{\varepsilon_v}$	= average value of ε_v	$[\text{J}]$
ε^*	= effective potential energy between a gas molecule and the solid surface	$[\text{J}]$
λ	= mean free path of molecules between successive collisions with the pore walls	$[\text{m}]$
τ	= mean holding time of molecules in pores between successive collisions	$[\text{s}]$

⟨Subscripts⟩

g	= gas-phase flow	
s	= surface flow	
0	= zero potential field	

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