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Sun-Tak Hwang[a]
[a] DIVISION OF MATERIALS ENGINEERING, THE UNIVERSITY OF IOWA, IOWA CITY, IOWA

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Surface Diffusion Parallel with Knudsen Flow*

SUN-TAK HWANG

DIVISION OF MATERIALS ENGINEERING
THE UNIVERSITY OF IOWA
IOWA CITY, IOWA 52242

Abstract

A phenomenological theory is derived for surface diffusion of noncondensible gases (also in the absence of capillary condensation) parallel with Knudsen flow. This theory does not require any specific model for adsorption and diffusion. The only assumption needed is the local equilibrium condition between gas phase and adsorbed phase along the flow axis. Numerous data both published in the literature and in the present paper can be explained by the theory.

INTRODUCTION

When a gas flows through a microporous medium, it is well known that there exists a transport of adsorbed molecules in addition to the gas-phase flow. In some cases the magnitude of surface flow exceeds that of gas-phase flow. The importance of this surface transport has been stressed in many fields of study, such as catalysis, membrane separation, and surface science. Many theories have been proposed and studied to explain the observed experimental data. Most of these theories are based on particular models or mechanisms of surface diffusion. However, perhaps, due to the diversity of adsorption isotherms and complexity of the surface transport mechanisms, no single theory can explain all experimental data.

Since the surface diffusion is caused by the adsorbed molecules, it occurs at all temperatures and pressures to various degrees. However, when the

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operating temperature is below the critical temperature of the diffusing vapor, capillary condensation may take place on top of the adsorption if the pressure is right. This phenomenon further complicates the transport process of vapor through microporous media. Even though it is very difficult to make a clear distinction between the adsorbate and the capillary condensate, the flow characteristics of these two phases are entirely different. Almost always, the capillary condensate forms either a lens or a plug within a pore so that the transport of these can not be treated as a parallel flow to the gas-phase flow.

On the other hand, the surface diffusion is always in parallel with the gas-phase flow. It is generally agreed that a local equilibrium can be assumed between the gas and adsorbate in a steady-state flow system. Most of the existing theories of surface diffusion are based on Fick's equation for the two-dimensional case:

$$F_s = -D_s \frac{dC_s}{dx} \tag{1}$$

The concentration of the adsorbed phase can be calculated from the adsorption isotherm if local equilibrium is assumed. The most difficult part is to calculate the two-dimensional diffusion coefficient, and this requires a specific model of flow mechanism. Depending on the type of diffusion mechanism, the final results vary greatly from model to model.

Therefore, it is a general consensus among investigators that the surface flow rate should be a function of the surface concentration because it is caused by the adsorbed molecules. Thus the surface flow rate is believed to be dependent upon the gas-phase pressure.

However, the experimental results (*1–6*) show the contrary. When the permeating gas is above the critical temperature, the total permeability is always independent of the pressure. Since the gas-phase flow is considered as Knudsen flow which is pressure independent, the surface flow is also pressure independent, but the adsorption isotherms for the same systems show that they are well beyond the Henry's law region (*1*, *2*), and some of them even look like the BET type.

For a low surface coverage or a low pressure range when Henry's law can be applied, it has been shown that the surface diffusion is independent of pressure (*7–10*). However, in some cases the pressure ranges were extended tremendously, yet the surface flow rate changed very little (*3–6*). In other words, experimental evidence is mounting convincingly to indicate that the surface flow rate is independent of the adsorption isotherm as long as there is no capillary condensation.

This conflict between the experimental results and various theories must be resolved. In the following discussion a phenomenological theory which is model independent will be derived. The most important concept is the assumption of local equilibrium between gas phase and adsorbed phase.

THEORY

Most investigators are using the concept of parallel flow in that total flow is equal to the sum of surface flow and gas-phase flow. Nevertheless, there have not been many arguments in the literature whether or not this assumption is correct for a system of flow through porous media. The continuous adsorption and desorption processes along the pores, where nonequilibrium flow takes place, prohibit the simple formalism of parallel flow in general. This question, however, can be analyzed rather easily if the analogy of an electric circuit is employed.

Consider a parallel connection of two different resistors R_1 and R_2 between points A and B. If two equipotential points C and D are joined by an arbitrary resistor R_3 as shown in Fig. 1, the current through resistor R_3 will be zero regardless of the magnitude of the resistance. Therefore, the currents through R_1 and R_2 will not be affected by the presence of R_3, maintaining parallel flow. Likewise, any other equipotential points E and F can be connected by any arbitrary resistance without disturbing the parallel flow.

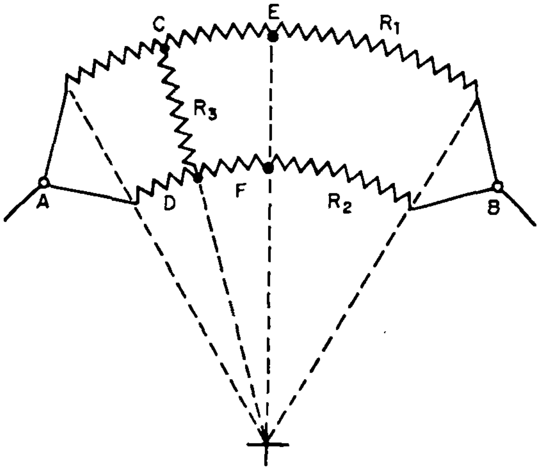

FIG. 1. Parallel circuit.

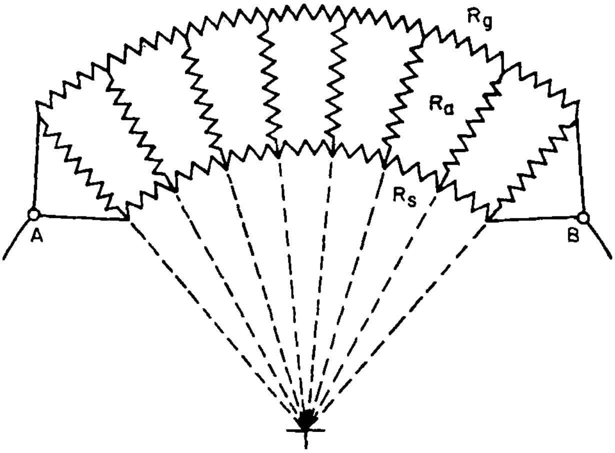

FIG. 2. Electric analogy of surface diffusion.

Now, if the gas flow through a pore can be simulated by a lumped parameter circuit (a more realistic simulation would be a model with distributed parameter), the combined resistance will be the one shown in Fig. 2. Here, R_g, R_s, and R_a denote the gas phase, surface, and adsorption resistances, respectively. However, this representation will be true only if local equilibrium is assumed. The assumption of local equilibrium means that, at every point along the pore, the surface phase is in equilibrium with the gas phase; in other words, equipotential prevails along the pore. This type of equilibrium does not have to be the genuine thermodynamic equilibrium, instead, it can be a pseudoequilibrium (steady state) in general. Using the same argument developed with Fig. 1, the following conclusion may be drawn regarding the circuit in Fig. 2: The total current is independent of R_a and is the same as the sum of two parallel currents through R_g and R_s, disregarding R_a entirely. Consequently, at steady state the gas-phase flow and the surface flow are in parallel and they are constant. The important point is that both of these flows are not a function of position along the pore. Thus the total flow rate can be expressed as

$$F = F_g + F_s \tag{2}$$

where both F_g and F_s are constant along the pore.

If the gas-phase flow obeys the Knudsen equation, F_g is linear with respect to the pressure gradient:

$$F_g = -Q_g \frac{dP}{dx} \tag{3}$$

where

$$Q_g = \frac{SG_1}{\sqrt{2\pi MRT}} \tag{4}$$

where S is the macroscopic cross-sectional area of a microporous medium and G_1 is a geometric factor which includes the porosity, tortuosity, etc. The coefficient Q_g is independent of pressure. At steady state the gas-phase flow rate F_g is constant along the.axis of pore. Therefore, the pressure distribution along the axis becomes linear.

If local equilibrium prevails, the surface concentration C_s can be calculated from the adsorption isotherm:

$$C_s = f(P) \tag{5}$$

Hence

$$\frac{dC_s}{dx} = \frac{df}{dP}\frac{dP}{dx} \tag{6}$$

Equation (1) can be rewritten as

$$F_s = -D_s \frac{dC_s}{dx} = -D_s \frac{df}{dP}\frac{dP}{dx} \tag{7}$$

Furthermore

$$-D_s \frac{df}{dP} = \frac{F_s}{dP/dx} = -\frac{F_s}{F_g} Q_g \tag{8}$$

At steady state both F_g and F_s are constant and are not functions of position x. Therefore Eq. (8) is not a function of x, and thus it is independent of pressure. Let us denote this pressure-independent quantity by

$$Q_s = D_s \frac{df}{dP} \tag{9}$$

The surface flow rate then becomes

$$F_s = -Q_s \frac{dP}{dx} \tag{10}$$

The most important point in the above expression is the fact that Q_s is independent of pressure regardless of the type of adsorption isotherm as long as the gas-phase flow obeys the Knudsen equation.

However, if the gas phase becomes the transition flow, Q_g will be slightly pressure-dependent. From Eqs. (8) and (9) it is apparent that Q_s should behave just like Q_g as pressure changes.

In conclusion, so long as local equilibrium is assumed between gas phase and surface phase in parallel flow, the pressure dependency of surface flow will be the same as that of gas-phase flow.

EXPERIMENTAL EVIDENCES

There are numerous experimental data published in the literature which support the above theory. Instead of reproducing those results here, some significant conclusive remarks will be quoted.

Aylmore and Barrer (*1*) studied the surface diffusion of Ar, N_2, Kr, and CO_2 through a microporous carbon membrane for the temperature range of 273 to 323°K and pressures between zero and 40 cmHg. They concluded: "The permeability coefficients for combined surface and gas-phase transport in the ranges investigated are independent of pressure and amount sorbed. These coefficients are not changed when the isotherms become curved." They further stated: "The surface permeability coefficient K for any one gas has been shown over the range investigated here to be characteristic for each gas; independent of the amount sorbed and therefore of whether the isotherm obeys Henry's law or is curved; and unaltered when there is a second flowing, adsorbed species competing for the same surface."

Reed and Butt (*2*) reported their experimental results of surface diffusion for propane and 2,2-dimethyl propane through a porous molybdenum sulfide for temperatures between 20 and 90°C and surface coverage of 0.3 to 15% of monolayer. They concluded: "A notable feature of these measurements is the linear relationship between the total flux and the gas-phase concentration drop across the pellet in the concentration range investigated." They also stated: "It follows, then, that the adsorbed flux, which is the difference between total flux and gas-phase flux, is also linear in gas-phase concentration drop. Consequently, the product of the surface diffusion coefficient and the adsorption coefficient, $D_{s,p}'K$, must be independent of gas-phase concentration."

Kammermeyer and Rutz (*3*) were perhaps the earliest to report the constancy of the surface diffusion with respect to pressure. They observed the permeability of H_2, He, CO_2, N_2, and O_2 through a porous Vycor glass at 25°C, but their pressure range covered was very wide, the high pressure side being up to 100 psig. They said, "A rather remarkable feature is the constancy of the total permeability over the pressure range covered . . . , one would expect that the amount of the condensed flow would increase with increasing pressure. Obviously, this is not the case. . . ."

A recent French article by Lallemand and Eyraud (*4*) contains permeability data of O_2, Ar, and N_2 through an unspecified microporous membrane (average pore radius 73 Å). Below the critical temperatures the gas permeabilities are strong functions of the relative pressures. However, above the critical temperatures all three gases show constant total permeability over the range of pressures covered.

In addition to the above literature data, the following two sets of experimental results will demonstrate how the total permeabilities stay constant over wide pressure ranges.

The first system (*5*) is a VF-Millipore membrane with seven different gases. The deviations from Knudsen flow, $Q\sqrt{MT}$, are plotted against the mean pressure in Fig. 3. The slight upward trend with increase of pressure is believed due to the transitional behavior of gas-phase flow. The pore size

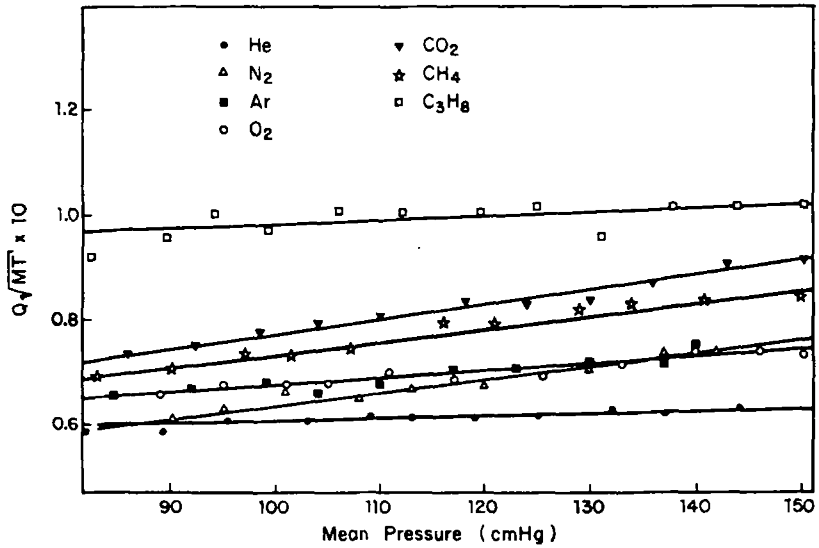

FIG. 3. Pressure effect on surface diffusion of gases through VF-Millipore at 0°C.

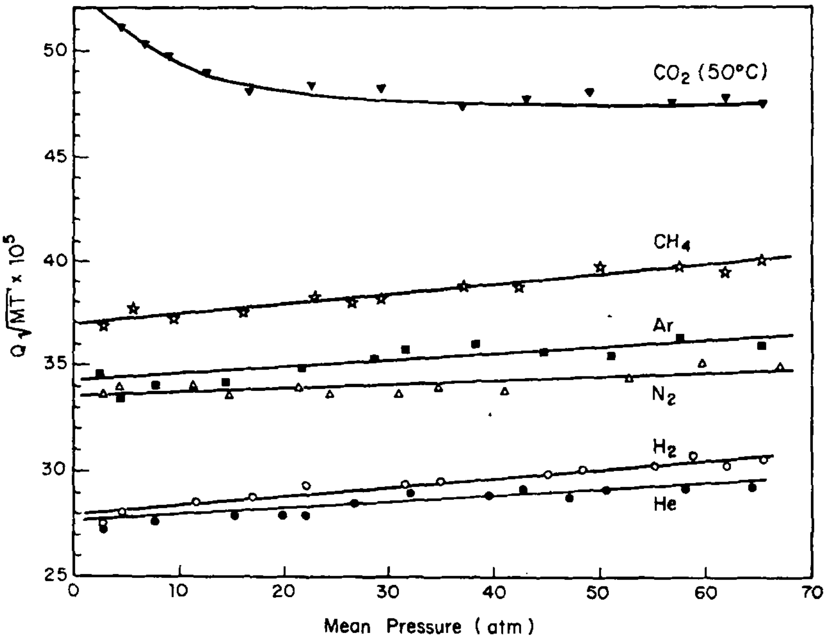

FIG. 4. Pressure effect on surface diffusion of gases through porous Vycor glass at 25 °C.

(~ 0.02 to 0.03 μ) and pressures are such that the flow regime is in between the Knudsen and laminar flow.

The second system (*6*) is a porous Vycor glass membrane and six noncondensible gases. Again the deviations from Knudsen flow, $Q\sqrt{MT}$, are plotted as functions of mean pressure in Fig. 4. This type of wide pressure range study of permeability has never been carried out before. The surprising fact is that the permeabilities change very little over such a wide pressure range. This small increase in permeability can also be attributed to the transition flow of the gas phase.

DISCUSSION

Since the phenomenological theory developed above does not require any specific model, the explanation of the surface diffusion as a function of pressure is valid for every type of adsorption isotherm and diffusion mechanism. Nevertheless, the very advantage becomes a disadvantage when a calculation (or prediction) of surface diffusion is attempted, because there is no model to use as a base.

When the gas-phase flow obeys the Knudsen law, the surface diffusion becomes pressure-independent. In that case, the surface diffusion term can be evaluated at low pressure (in Henry's law region) using a particular model. For example, a pressure-independent equation was derived and successfully tested for a number of systems (*7*, *11–13*). Since the total permeability is

$$Q = Q_g + Q_s \tag{11}$$

the surface permeability, which is pressure independent, can be expressed as

$$Q_s = B\sqrt{\frac{T}{M}}e^{\Delta/T} \tag{12}$$

because it was shown (*7*) that

$$Q\sqrt{MT} = A + BTe^{\Delta/T} \tag{13}$$

Thus once the constants B and Δ are determined for a given system at low pressure, the same equation will hold at higher pressures. The above constants can also be correlated very well with the critical properties (*11*). As an example, the data of the VF-Millipore system are correlated in Fig. 5. Here the surface flow is expressed as a function of critical properties:

$$Q\sqrt{MT} - A = BTe^{\Delta/T} = a(V_c\sqrt{T_c})^b \tag{14}$$

The results are very good except for CO_2, which is to be expected based on previous experience with porous Vycor glass (*7*).

In summary, a model-independent phenomenological theory of surface diffusion is derived when pressures and temperatures are such that no capillary condensation occurs. It is proven that the surface permeability, Q_s, is independent of pressure as long as local equilibrium prevails between the adsorbed phase and a gas phase which obeys Knudsen's law. Also presented are experimental evidences obtained by various laboratories in a wide pressure range for a number of different porous materials, all of which show pressure-independent surface flow without any satisfactory explanation.

SYMBOLS

A	gas-phase (Knudsen) flow coefficient
a	constant

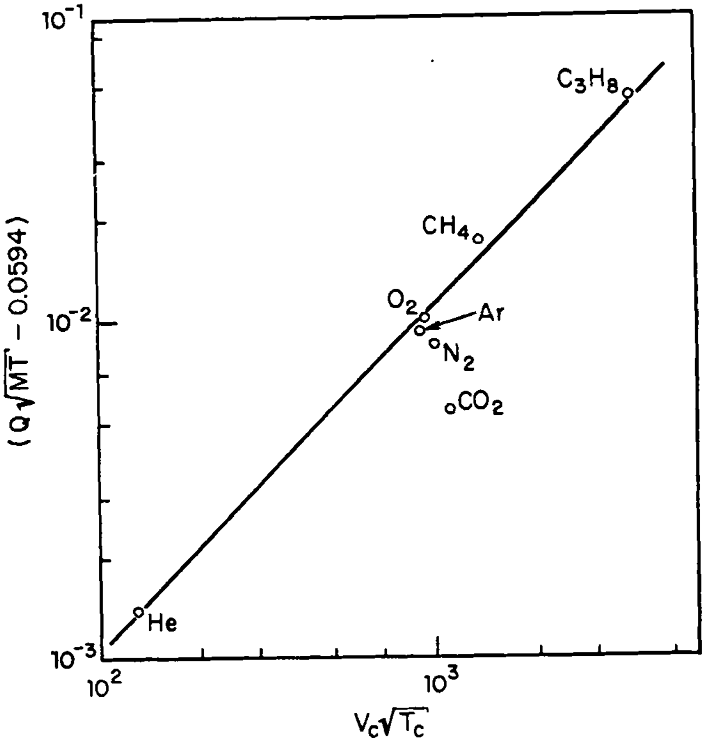

FIG. 5. Correlation of surface diffusion for VF-Millipore.

B	surface flow coefficient
b	constant
C	concentration of adsorbed gas
D	diffusivity
F	flow rate
f	adsorption isotherm
M	molecular weight
P	pressure
Q	permeability
R	gas constant
R_1, R_2, R_3	resistances
R_a	adsorption resistance
R_g	gas-phase resistance

R_s	surface-phase resistance
S	macroscopic cross-sectional area
T	absolute temperature
V	specific volume
x	distance
Δ	constant

Subscripts

c	critical
g	gas phase
s	surface phase

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