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Interpretation of Surface Flow Phenomenon of Adsorbed Gases by Hopping Model

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The mechanism of surface flow of adsorbing gas molecules through the porous adsorbent is interpreted, and a new hopping model is derived by separately taking into account the hopping behaviors of monolayer and multilayer molecules. The reported experimental results containing the data measured here are correlated well. Finally, some considerations are given to the two experimental constants appearing in the model.

SCOPE

Besides gaseous diffusion and flow in pores, surface flow of physically adsorbed gases is important in evaluating the apparent mass transfer rates through adsorptive porous materials.

The most commonly used models to interpret the surface flow mechanism are essentially divided into the following.

1. Hydrodynamic model, which regards the phase of the adsorbed gas on the solid surface as a laminar-flowing film of viscous liquid (Babbit, 1950; Gilliland et al., 1958).

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2. Random hopping model, which pictures the adsorbed gas molecules as being randomly hopping and migrating from site to site on the surface (Hill, 1956; Higashi et al., 1963).

3. Mechanistic hopping model, which is based on calculations of the trajectories of hopping molecules along the solid surface (Smith and Metzner, 1964; Weaver and Metzner, 1966; Ponzi et al., 1977).

Despite many studies using these models, there are still some ambiguities in interpreting the dependence of the surface flow coefficient on the surface concentration of the adsorbate (Horiguchi et al., 1971).

The purpose of this paper is to improve the random hopping model by introducing the average holding times of the molecules adsorbed in the monolayer and multilayer to hop to a neighboring site. It also tries to obtain new experimental data on surface flow coefficients and to compare the published data as well as the present ones with the theoretical model.

CONCLUSIONS AND SIGNIFICANCE

By taking into account the hopping behaviors of molecules adsorbing in the monolayer and multilayer separately, a hopping model was proposed. Based on the model, a new formula for surface flow coefficient, having two experimental constants being proper to the system of the adsorbent and the adsorbate gas, was derived to prescribe the dependence of the coefficient on the surface concentration of adsorbate.

The surface flow rates of C_2H_4, C_3H_6, iC_4H_{10} and SO_2 through porous Vycor glass in the wide range of surface concentration were observed. By choosing the optimum values for the experimental constants in the formula, previously published data as well as the present data were well correlated. One of these constants was considered by introducing the mean holding time of adsorption. It was suggested that, if data on a particular gas on an adsorbent are available, the surface flow coefficient of another gas on the same adsorbent might be roughly estimated.

In the range of low partial pressure of the adsorbate, monolayer adsorption predominates, and as the pressure increases the multilayer adsorbed phase gradually increases, principally according to the B.E.T. theory. Further, when the pressure is approaching the saturated pressure of the adsorbate, capillary condensation begins in the pores of the adsorbent. This means that the molecules adsorbed in both the monolayer and multilayer gradually accumulate to become the capillary condensed phase. Therefore, the apparent phase of adsorption should be divided into two phases. That is, the adsorbed phase and the capillary condensed phase for interpretation of mechanism of surface flow.

From the viewpoint of the random hopping model, the transport of the adsorbed molecules in the adsorbed phase is attributed to the gradient of its surface concentration of the adsorbate; that is, the gradient of the number density of the hopping molecules makes a contribution to surface migration.

On the other hand, the transport of the capillary condensed phase can be regarded as Poiseuille flow of viscous liquid filling the pores of adsorbent by the gradient of the capillary force (Krisher, 1963).

Consequently, to interpret the apparent mechanism of surface flow, we should separately consider these two kinds of transport mechanisms and should regard it as a simultaneous process of surface migration in adsorbed phase and capillary flow in the capillary condensed phase. The objective of this paper is to interpret the mechanism of surface flow, whereas the mechanism of transport in a capillary condensed phase will be reported in another paper.

THEORETICAL CONSIDERATION

New Hopping Model for Surface Flow

Hill (1956) and Higashi et al. (1963) regarded the surface flow phenomenon as a random walk process of the so-called "hopping molecules" on the surface. The authors chose the case that $E_{a0} > E_{s0} > RT$ as the basis for the present work, and propose the model for surface flow, where E_{s0}, E_{a0} and RT are the potential barrier among adsorption sites, the differential heat of adsorption and the thermal motion energy of molecules respectively. In the case that $E_{a0} < E_{s0}$, the surface flow does not take place. If $E_{s0} < RT$, an adsorbed molecule would be expected to behave as a molecule in a two-dimensional gas.

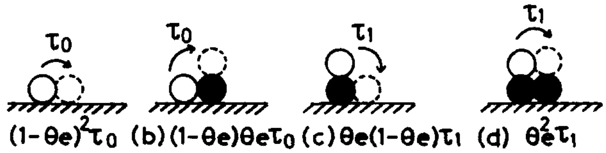
When an adsorbed molecule gains energy E between E_{s0} and E_{a0}, this molecule hops from site to site in the adsorption state. Before the molecule is desorbed, several "hoppings" occur and therefore surface flow ensues. On the other hand, an adsorbed molecule remains on the adsorption site when $E < E_{s0}$, and is desorbed in the case that $E > E_{a0}$.

Consider the migration of "hopping molecules" on the surface. Figure 1 shows the hopping of adsorbed molecules. These molecules randomly hop to one of the neighboring sites after various holding times as shown in Figure 1. Here, it is assumed that only the adsorbed molecules exposed to the gas phase contribute to the surface flow and the adsorbed molecules in the lower layer do not make any contribution to the surface flow. Further, we divide the molecules exposed to the gas phase into two groups. One group is the molecules adsorbed on the vacant sites, and the other is the molecules forming a multilayer. All molecules of latter group make same contribution to the surface flow.

From the basis of the molecular kinetic theory, it can be considered that the adsorbed molecules vibrate in the perpendicular direction with frequency $1/\tau_{s0}$. For molecules in the first layer, the mean holding time τ_0 is given by Eq. 1. The upper limit of integration is chosen so that the molecules are desorbed; i.e., E_{a0}.

$$\tau_0 = \tau_{s0}\int_0^{E_{a0}} f_{s0}(E)dE \Big/ \int_{E_{s0}}^{E_{a0}} f_{s0}(E)dE \tag{1}$$

where the distribution function of energy $f_{s0}(E)$ is defined by:



(a) $(1-\theta e)^2\tau_0$ (b) $(1-\theta e)\theta e\tau_0$ (c) $\theta e(1-\theta e)\tau_1$ (d) $\theta e^2\tau_1$

Figure 1. Hopping modes of adsorbed molecules.

$$f_{s0} = \frac{1}{RT}\, e^{-E/RT} \qquad (2)$$

Substitution of Eq. 2 into Eq. 1 yields

$$\tau_0 = \tau_{s0}(1 - e^{-E_{a0}/RT})/(e^{-E_{s0}/RT} - e^{-E_{a0}/RT}) \qquad (3)$$

Similarly, for molecules in all layers above the first layer,

$$\tau_1 = \tau_{s1}(1 - e^{-E_{a1}/RT})/(e^{-E_{s1}/RT} - e^{-E_{a1}/RT}) \qquad (4)$$

where E_{a1} is equal to the heat of vaporization of the adsorbate by making the same assumption as in the B.E.T. theory. E_{s1} is the activation energy for migration in the all layers above the first layer. As a simple approximation, it may be assumed that:

$$\tau_{s0} \cong \tau_{s1} \qquad (5)$$

The differential heat of adsorption E_{a0} is independent of the amount adsorbed on the energetically homogeneous surface. E_{a0} on the heterogeneous surface, on the other hand, drops monotonously with the amount adsorbed.

Case 1: Homogeneous Surface. Figure 1 shows the four kinds of hopping modes of adsorbed molecules. For example, in case (a) of Figure 1, the probability of hopping is $(1 - \theta_e)^2$ at the surface coverage θ_e, because the probabilities that an adsorbed molecule is placed on a vacant site and it hops to another vacant site are both $1 - \theta_e$. Also the holding time is τ_0. Accordingly, the expected value τ of the holding time is given by:

$$\begin{aligned}\tau = {} & (1 - \theta_e)^2\tau_0 + \theta_e(1 - \theta_e)\tau_0 \\ & + (1 - \theta_e)\theta_e\tau_1 + \theta_e^2\tau_1 \\ = {} & (1 - \theta_e)\tau_0 + \theta_e\tau_1 \end{aligned} \qquad (6)$$

Surface flow is regarded as a random walk process, so the surface flow coefficient D_s can be expressed by the Einstein's equation:

$$D_s(\theta_e) = C'\delta^2/\tau = C'\delta^2/\{\tau_0[1 - \theta_e(1 - \tau_1/\tau_0)]\} \qquad (7)$$

where C' is a constant determined from the tortuosity factor of porous media and the geometrical configuration of adsorption site. δ is a distance between neighboring adsorption sites and θ_e denotes the effective surface coverage of adsorbed molecules for surface flow.

As a simple approximation, it is assumed that the ratio of the activation energy E_{s0} and the differential heat of adsorption E_{a0} is constant as well as in previous papers (de Boer, 1952; Gilliland et al., 1974).

$$E_{s0} = a \cdot E_{a0} \qquad (8)$$

where a depends on both adsorbent and adsorbate.

The flux of surface flow is expressed by Eq. 9, because the surface flow is caused by the gradient of the number density of the hopping molecules (amount adsorbed) making a contribution to surface flow.

$$N_s = -\rho_{app}D_s(\theta_e)A\,dq_e/d\ell \qquad (9)$$

while the surface flow coefficient D_s has been defined by Eq. 10 in previous papers (Carman and Raal, 1951; Gilliland et al., 1958 and 1974; Higashi et al., 1963; Horiguchi et al., 1971; Ross and Good, 1956):

$$N_s = -\rho_{app}AD_s\,dq/d\ell \qquad (10)$$

The driving force $(dq_e/d\ell)$ in Eq. 9 is different from $(dq/d\ell)$ in Eq. 10. Therefore, the surface flow coefficient D_s is obtained from Eqs. 3 to 5 and 7 to 10.

$$\begin{aligned}D_s = D_{s0}F = D_{s0}(\theta_e/\theta)(e^{-aE_{a0}/RT} - e^{-E_{a0}/RT})/\{(1 \\ - e^{-E_{a0}/RT})[1 - \theta_e(1 - \tau_1/\tau_0)]\}\end{aligned} \qquad (11)$$

where

$$\begin{aligned}\tau_1/\tau_0 = (e^{-aE_{a0}/RT} - e^{-E_{a0}/RT})(1 \\ - e^{-E_{a1}/RT})/\{(e^{-E_{s1}/RT} - e^{-E_{a1}/RT})(1 - e^{-E_{a0}/RT})\}\end{aligned} \qquad (12)$$

Case 2: Heterogeneous Surface. It has been experimentally shown that the differential heat of adsorption decreases with the amount adsorbed on the energetically heterogeneous surface, because adsorption successively proceeds from the site of large heat of adsorption to that of small heat of adsorption. Therefore, the molecules adsorbed have various heats of adsorption E.

$$D_s = D_{s0}F = \frac{D_{s0}(\theta_e/\theta)\int_{E^\circ_{a0}}^{E_{a0}} ((e^{-aE/RT} - e^{-E/RT})/\{(1 - e^{-E/RT})[1 - \theta_e(1 - \tau_1/\tau_0)]\})g(E)dE}{\int_{E^\circ_{a0}}^{E_{a0}} g(E)dE} \qquad (13)$$

where

$$\begin{aligned}\tau_1/\tau_0 = (e^{-aE/RT} - e^{-E/RT})(1 - e^{-E_{a1}/RT})/\{(1 \\ -e^{-E/RT})(e^{-E_{s1}/RT} - e^{-E_{a1}/RT})\}\end{aligned} \qquad (14)$$

Here $g(E)$ is the number of molecules adsorbed which have heats of adsorption between E and $(E + dE)$, and E_{a0} and E°_{a0} are the heats of adsorption at θ_e and $\theta_e = 0$, respectively.

In summary, the surface flow rate is expressed as Eq. 10. The surface flow coefficient D_s in Eq. 10 is given by Eq. 11 or 13 using the hopping model proposed in the present work. These correlating equations contain two parameters (a and D_{s0}) and are just quantitative statements of the dependence of the surface flow coefficient on the amount adsorbed and the temperature. We need to estimate θ_e, E_{s1}, E_{a1}, E_{a0} and $g(E)$ to calculate F in Eq. 11 or 13.

Estimation of θ_e. In the case where multilayer adsorption takes place, the molecule under a certain molecule does not contribute to the surface flow. Therefore, the effective surface coverage θ_e reduces to the coverage of the first layer. This coverage can be estimated from an adsorption model. If an adsorption isotherm can be expressed by the Langmuir equation,

$$\theta = \theta_e = bp/(1 + bp) \qquad (15)$$

If an adsorption isotherm obeys the B.E.T. equation,

$$\theta_e = \theta(1 - x) \qquad (16)$$

where x is the relative pressure $(=p/p_s)$, and θ is given by:

$$\theta = Cx/\{(1 - x)(1 - x + Cx)\} \qquad (17)$$

The above isotherm equations have been derived from the dynamical equilibrium between the gas phase and adsorbed phase without considering the surface migration of adsorbed molecules. Accordingly, we must estimate θ_e using the adsorption equation in which the effect of surface migration is taken into account. However, assuming that the surface migration makes a small influence on the adsorption equilibrium, the published equations are applied to estimate θ_e as a first approximation.

Estimation of E_{s1} and E_{a1}. If the surface migration in all layers above the first layer is analogous to the momentum transport of liquid under shear stress, the activation energy for migration E_{s1} may be approximately estimated from the temperature dependence of viscosity in the liquid state.

$$\mu_L = KTe^{E_{s1}/RT} \qquad (18)$$

This equation was derived by Frenkel (1955). The temperature dependence of viscosity is presented in the literature (Gallent, 1968; Plank, 1959). For example, plots of $ln(\mu_L/T)$ vs. $1/T$ are shown in Figure 2 and from these slopes E_{s1} can be estimated. The heat of vaporization E_{a1} is given in the literature (Gallent, 1968; Plank, 1959).

Estimation of E_{a0} and $g(E)$. The isosteric heat of adsorption E_{st} is determined from adsorption isotherms at various tempera-

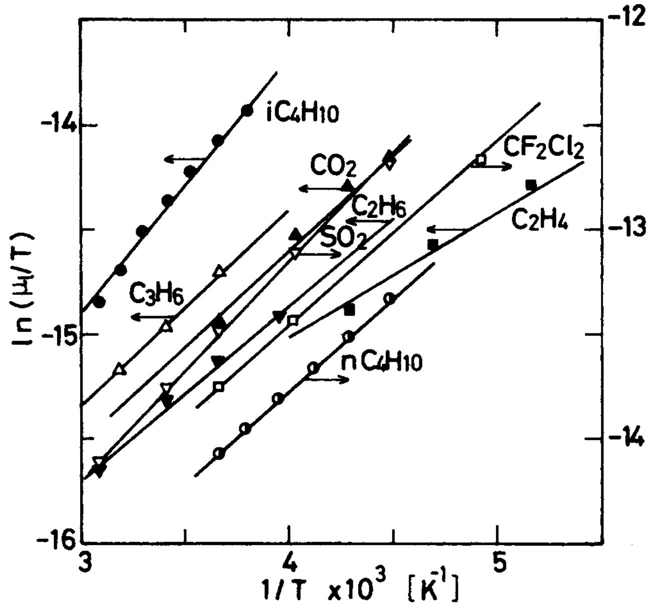


Figure 2. Correlating results using Eq. 18.

tures using the Clausius-Clapeyron equation.

$$E_{st} = -R\left[\frac{\partial \ln p}{\partial(1/T)}\right]_q \qquad (19)$$

The differential heat of adsorption can be estimated by Eq. 19. However, we should notice that this heat of adsorption contains both the effects of E_{a0} in the first layer and E_{a1} in all layers above the first layer, when multilayer adsorption occurs. If the adsorption equilibrium obeys the B.E.T. equation,

$$E_{a0} = (E_{st} - RT - xE_{a1})/(1 - x) \qquad (20)$$

On the other hand, when multilayer adsorption does not take place,

$$E_{a0} = E_{st} - RT \qquad (21)$$

As $g(E)$ is the number of molecules adsorbed which have a differential heat of adsorption between E and $(E + dE)$, $g(E)$ can be easily evaluated from the relation between E_{a0} and the amount adsorbed.

EXPERIMENTAL

Experimental Method

The surface flow of adsorbed gases is measured by determining the contribution of this flow to the total flow of gases through porous media.

If the mean free path of gas molecules is much larger than the mean pore diameter, the flow rate of nonadsorbable gas obeys the Knudsen equation.

$$N_g = -P_gAdp/d\ell = -(\epsilon AD_k)/(k_g^2RT)dp/d\ell \qquad (22)$$

where P_g is a permeability of nonadsorbable gas, D_k is a Knudsen diffusivity and k_g is a tortuosity factor.

$$D_k = (2/3)\sqrt{(8RT)/(\pi M)}\,\bar{r} \qquad (23)$$

In the region of Knudsen flow, $P_g\sqrt{MT}$ should be independent of pressure, temperature and the kind of gases.

The total transport rate of adsorbable gas is expressed as follows:

$$N_T = -P_TAdp/d\ell \qquad (24)$$

where P_T is a total permeability and p is the partial pressure of adsorbable component. The surface transport of adsorbed gas is determined by subtracting a gas-phase permeability P'_g from a total permeability P_T as follows:

$$P_s = P_T - P'_g \qquad (25)$$

where P_s is a surface permeability and P'_g is given by Eq. 26 which takes into account the blockage effect of pores by adsorbate. (See Appendix.)

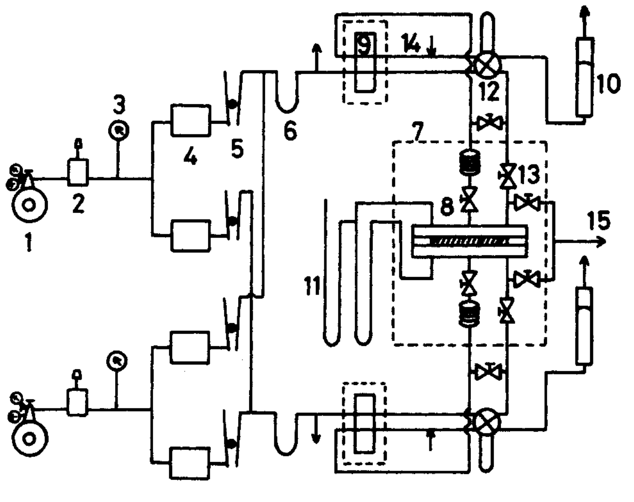


Figure 3. Experimental apparatus. 1. Gas cylinder 2. Pressure valve 3. Pressure gauge 4. Flow control valve 5. Rotameter 6. Dryer (CaCl₂) 7. Temperature-controlled bath 8. Diffusion cell 9. Thermal conductivity cell 10. Gas sampler 11. Manometer 12. Soap film meter 13. Cock 14. Sampling hole 15. Diffusion pump

$$P'_g\sqrt{M'T} = P_g\sqrt{MT}\,\{1 - (1.14q\rho_{app}M')/(\epsilon\rho_L)\}^{3/2} \qquad (26)$$

The surface transport rate is expressed as:

$$N_s = -P_sAdp/d\ell = -\rho_{app}D_sA(dq/dp)(dp/d\ell) \qquad (27)$$

where D_s is an apparent surface flow coefficient. It should be noted that its value is the product of the surface flow coefficient and the reciprocal of the tortuosity factor. To calculate a surface flow coefficient, a local gas-solid adsorption equilibrium is assumed. Providing that an adsorption isotherm is known, the term of dq/dp can be evaluated and the coefficient can be determined from Eq. 27.

Apparatus and Procedure

Figure 3 shows a schematic drawing of the experimental apparatus, which is a constant-pressure, countercurrent diffusion apparatus (Wicke-Kallenbach type). Before starting a run with new gases, the sample of porous Vycor glass was evacuated to less than 7×10^{-2} Pa for a day. To perform an experiment, two kinds of gases (one is a nonadsorbed gas; N_2, He, and the other is an adsorbed gas; C_2H_4, C_3H_6, iC_4H_{10}, SO_2) were regulated at a constant flow rate by a flow control valve and mixed with each other and then passed through a calcium chloride tube to remove water.

The two streams, whose compositions were a little different to each other, were introduced into the diffusion cell 8. During the experiment of diffusion, the difference of pressure at both sides of the cell was kept zero. The diffusion cell was immersed in a temperature-controlled water bath at 30°C.

The composition of the gas at the inlet to the diffusion cell was analyzed with a thermal conductivity detector of a gas chromatograph (Shimadzu GC-3AH).

In the case of a diffusion experiment of mixed gases, the composition difference between the inlet and outlet streams is small so that the difference of the peak area of the chromatograms between both streams is not obvious in the composition analysis using a gas chromatograph. That difference is within the analysis error of gas chromatograph under extreme experimental conditions.

Accordingly, the inlet mixed gases were used as the carrier gas for the thermal conductivity cell to attain a remarkable improvement of the sensitivity of thermal conductivity cell. The outlet gas was sampled and

TABLE 1. PROPERTIES OF DIFFUSION DISK

Disk Sectional Area, cm²	19.96
Thickness, cm	0.12
Disk Density, kg/m³	1354
Porosity, −	0.311
True Density, kg/m³	1966
Surface area, (m²/kg) × 10³	117.0
Mean pore radius, cm × 10⁸	35.0

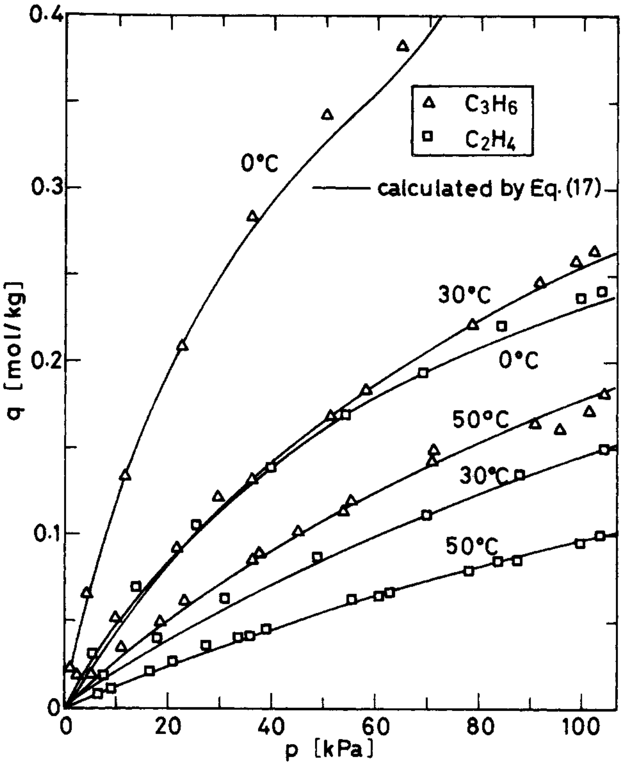


Figure 4. Adsorption isotherms of C_2H_4 and C_3H_6 on porous Vycor glass.

analyzed with that cell. The instrument was calibrated by the introduction of known quantities of pure gas (diffusive component) from a gas-tight syringe. Injection of a known amount of pure gas resulted in a pulse being produced on a recorder, and its area is proportional to the amount of pure gas injected, even if a carrier gas is a mixed one. The calibration was made before each run, because the composition of carrier gas changed during each experiment.

After steady state was reached, the inlet and outlet compositions were measured and the outlet flow rates were also determined by soap film meters. The total flux N_T was calculated from a material balance of these measured quantities.

A standard volumetric apparatus was used to obtain adsorption isotherms.

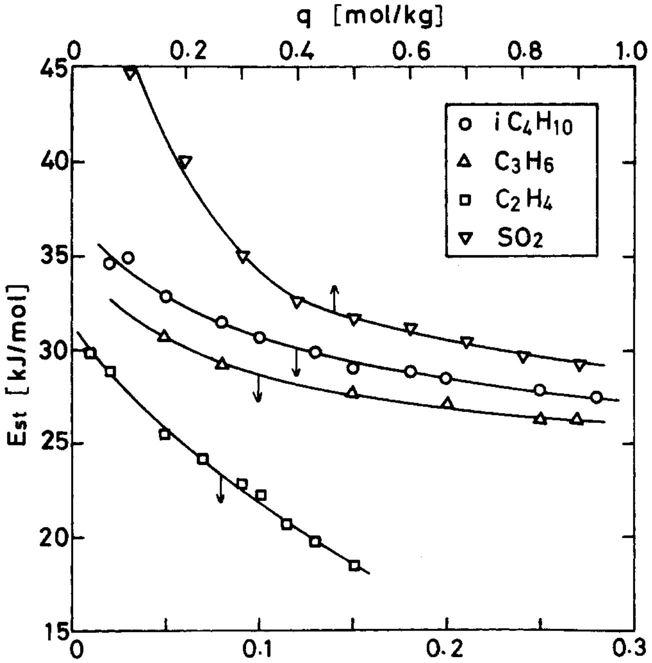


Figure 6. Isosteric heats of adsorption on porous Vycor glass.

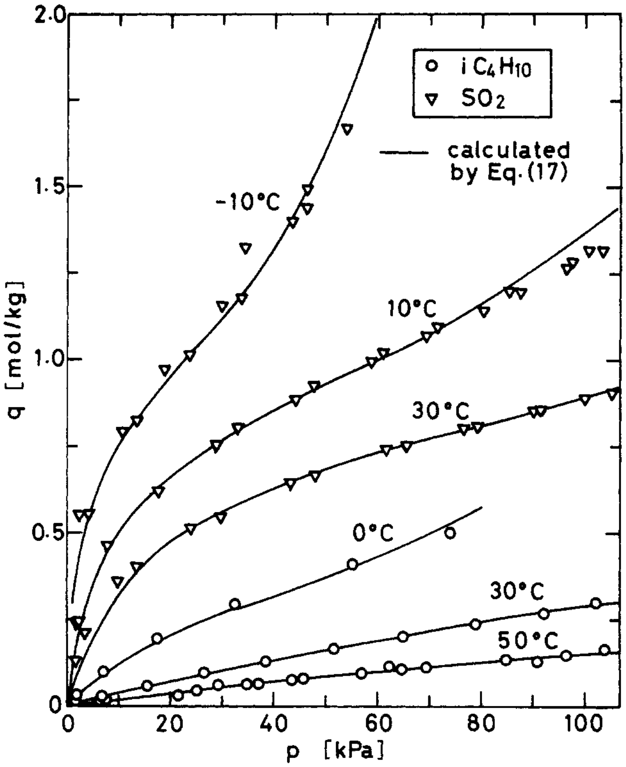


Figure 5. Adsorption isotherms of iC_4H_{10} and SO_2 on porous Vycor glass.

Properties of Porous Solid

A disk of porous Vycor glass obtained from Corning Glass Co. Ltd. was used. The physical properties are listed in Table 1.

RESULTS

Adsorption Equilibria

Adsorption equilibria are necessary to calculate surface flow coefficient according to Eq. 27 and isosteric heat of adsorption according to the Clausius-Clapeyron equation (Eq. 19). Adsorption isotherms for C_2H_4, C_3H_6, iC_4H_{10} and SO_2 are shown in Figures 4 and 5. These isotherms obey the B.E.T. equation, and monolayer surface coverage values were calculated from the B.E.T. equation.

The plots of *ln(p)* vs. *1/T* were found to yield straight lines. The isosteric heats of adsorption are shown in Figure 6. It is certain that the isosteric heats of adsorption are much larger than that of vaporization of adsorbates as saturated liquids and drop monotonously with amount adsorbed. Therefore, porous Vycor glass has the energetically heterogeneous surface.

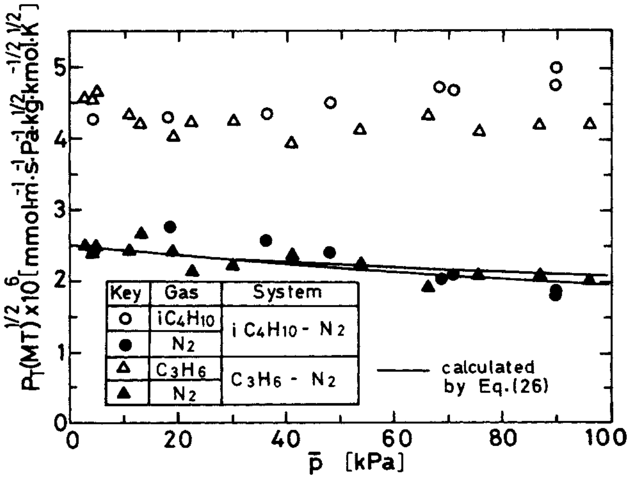


Figure 7. Total permeabilities on porous Vycor glass (30°C).

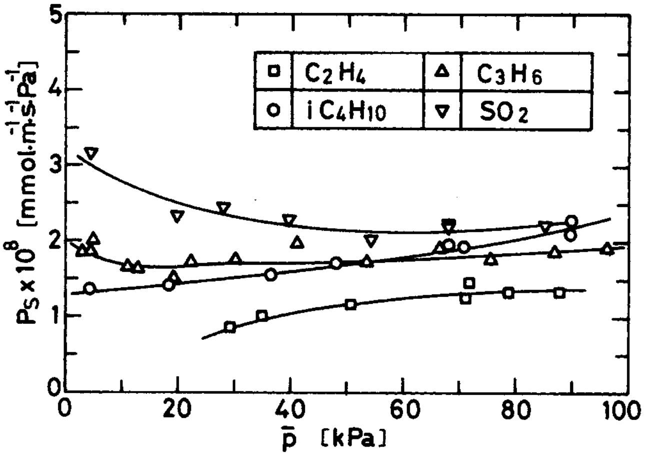


Figure 8. Surface permeabilities on porous Vycor glass (30°C).

Surface Flow

Permeability. Permeabilities for He-N_2, N_2-Ar and Ar – He systems were measured. $P_g\sqrt{MT}$ for these systems were 2.5×10^{-6} mmol · m^{-1} · s^{-1} · Pa^{-1} · kg$^{1/2}$ · kmol$^{-1/2}$ · K$^{1/2}$ and independent of pressure and the kind of gases. Hence, the gas-phase flow through porous Vycor glass obeys the Knudsen equation. On the other hand, permeabilities of adsorbed gases such as C_2H_4, C_3H_6, iC_4H_{10} and SO_2 are much greater than expected from the Knudsen mechanism.

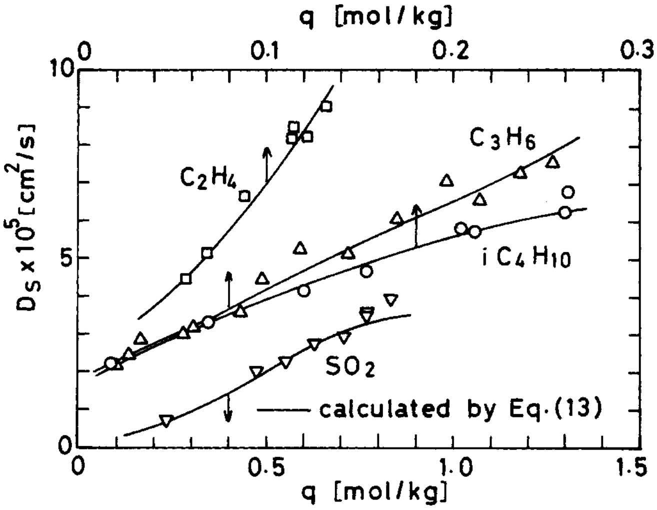


Figure 9. Surface flow coefficients on porous Vycor glass (30°C).

For example, total permeabilities for C_3H_6 and iC_4H_{10} in N_2-C_3H_6 and N_2-iC_4H_{10} systems are shown in Figure 7. Therefore, it is evident that the flow of adsorbed gases through porous Vycor glass cannot be explained without considering the surface flow mechanism. Permeabilities for N_2 in N_2-C_3H_6 and N_2-iC_4H_{10} systems are also shown in Figure 7.

TABLE 2. CORRELATING RESULTS FOR EXPERIMENTAL DATA USING EQ. 11 OR 13

Gas	Porous Solid	Temp. °C	θ	$D_s \times 10^5$	a	D_{s0}	E_{s1}	Accuracy*	Ref.	Data No.**
C_2H_4	Vycor	30.0	0.13 ~ 0.31	4.4 ~ 9.1	0.39	2.13×10^{-3}	4.98	0.040	This Work	1
C_3H_6	Vycor	30.0	0.04 ~ 0.60	2.2 ~ 7.5	0.45	5.41×10^{-3}	7.79	0.065	This Work	2
iC_4H_{10}	Vycor	30.0	0.04 ~ 0.73	2.2 ~ 6.7	0.48	11.9×10^{-3}	10.4	0.037	This Work	3
SO_2	Vycor	30.0	0.29 ~ 1.07	0.8 ~ 4.0	0.38	2.16×10^{-3}	8.75	0.058	This Work	4
CF_2Cl_2	Linde Silica	−33.1	0.47 ~ 1.61	2.1 ~ 5.3	0.49	9.20×10^{-3}	7.49	0.075	Carman and Raal (1951)	5
		−21.5	0.21 ~ 2.66	1.9 ~ 7.0						
SO_2	Linde Silica	−10.0	0.46 ~ 2.13	2.8 ~ 7.6	0.41	8.14×10^{-3}	8.75	0.043	Carman and Raal (1951)	6
		0.0	0.36 ~ 1.71	2.6 ~ 9.2						
CF_2Cl_2	Carbolac	−33.1	0.85 ~ 2.30	3.2 ~ 10	0.41	7.67×10^{-3}	7.49	0.130	Carman and Raal (1951)	7
		−21.5	0.61 ~ 1.71	2.7 ~ 11						
		0.0	0.48 ~ 1.16	3.0 ~ 15						
		20.0	0.32 ~ 1.10	2.8 ~ 16						
CO_2	Carbolac	−33.1	0.13 ~ 0.53	3.6 ~ 13	0.54	3.41×10^{-3}	7.83	0.058	Carman and Raal	8 (1951)
		−21.5	0.14 ~ 0.41	5.8 ~ 14						
		0.0	0.04 ~ 0.26	5.1 ~ 16						
		20.0	0.03 ~ 0.17	7.5 ~ 17						
SO_2	Vycor	15.0	0.37 ~ 0.84	0.8 ~ 3.3	0.46	5.02×10^{-3}	8.75	0.138	Gilliland et al. (1974)	9
		30.0	0.27 ~ 0.67	0.8 ~ 2.6						
CO_2	Vycor	−78.0	0.63 ~ 0.89	0.7 ~ 1.3	0.51	9.95×10^{-3}	7.83	0.168	Gilliland et al. (1974)	10
		−50.0	0.38 ~ 0.78	0.6 ~ 2.5						
C_3H_6	Vycor	0.0	0.14 ~ 0.99	0.5 ~ 7.7	0.45	4.29×10^{-3}	7.79	0.094	Gilliland et al. (1958)	11
		25.0	0.07 ~ 0.71	0.9 ~ 6.2						
		40.0	0.07 ~ 0.61	0.5 ~ 6.8						
iC_4H_{10}	Vycor	0.0	0.16 ~ 0.48	0.7 ~ 2.0	0.56	1.06×10^{-2}	10.4	0.096	Gilliland et al. (1958)	12
C_2H_6	Vycor	0.0	0.02 ~ 0.25	2.7 ~ 11	0.54	1.47×10^{-2}	6.95	0.179	Horiguchi et al. (1971)	13
		25.0	< 0.15	3.3 ~ 15						
		50.0	< 0.12	5.7 ~ 8.8						
C_3H_6	Vycor	0.0	0.12 ~ 0.81	1.1 ~ 15	0.52	1.47×10^{-2}	7.79	0.230	Horiguchi et al. (1971)	14
		25.0	0.06 ~ 0.69	1.0 ~ 11						
		50.0	0.03 ~ 0.50	0.9 ~ 10						
CF_2Cl_2	Carbon Regal	−5.0	0.26 ~ 1.20	4.0 ~ 34	0.66	5.75×10^{-2}	7.49	0.151	Ponzi et al. (1977)	15
		10.0	0.12 ~ 1.02	3.5 ~ 39						
		20.0	0.07 ~ 0.86	5.9 ~ 39						
C_3H_6	Graphon	0.0	0.11 ~ 1.14	80 ~ 730	0.63	5.57×10^{-1}	7.79	0.163	Horiguchi et al. (1971)	16
		25.0	0.05 ~ 0.97	120 ~ 500						
		50.0	0.02 ~ 0.73	170 ~ 300						
nC_4H_{10}	Graphon	30.0	0.15 ~ 1.12	100 ~ 1300	0.48	6.39×10^{-1}	7.39	0.122	Ross and Good (1956)	17
		41.7	0.25 ~ 1.14	90 ~ 880						

Adsorption isotherms can be expressed by the B.E.T. equation.
*Mean square deviation = $\{(1/N) \sum_N (D_{sexp} - D_{scal})^2/D_{sexp}^2\}^{\frac{1}{2}}$
**Data No. is used in Figure 10 and Table 3.

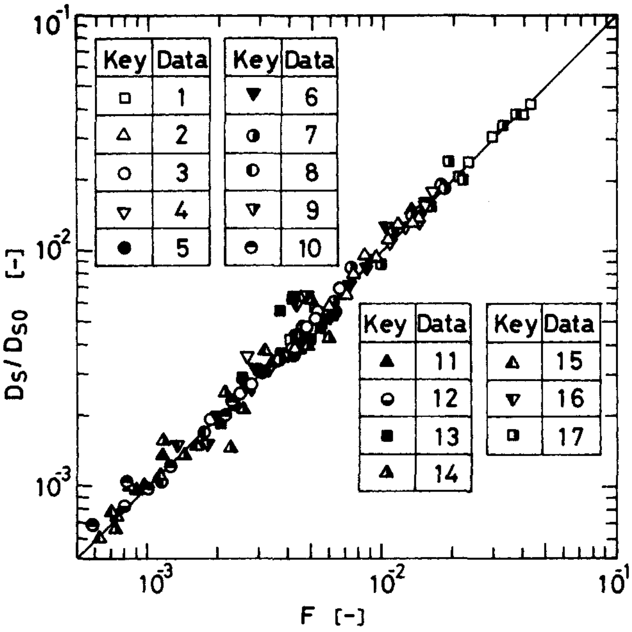


Figure 10. Correlation of surface flow coefficients by Eq. 11 or 13.

It can be seen that these permeabilities are reasonably expressed by Eq. 26 as shown in Figure 7. Accordingly, the effect of pore blockage by adsorbate on a gas-phase permeability of adsorbed gas can be estimated by Eq. 26. This equation is similarly valid for C_2H_4 and SO_2.

The surface permeabilities P_s of adsorbed gases calculated by Eqs. 22, 24, 25 and 26 are shown in Figure 8. The contributions of surface flow are about 0.4, 1.0, 1.3 and 2.5 times as that of the gas phase for C_2H_4, C_3H_6, iC_4H_{10} and SO_2, respectively.

Surface Flow Coefficient. The surface flow coefficient D_s is determined by Eq. 27. Figure 9 shows the coefficients for C_2H_4, C_3H_6, iC_4H_{10} and SO_2 on porous Vycor glass at 30°C. It can be seen that the coefficients increase appreciably with the amount adsorbed.

Correlation of Surface Flow

The surface flow coefficient D_s is expressed by Eq. 13 using the proposed model. Accordingly, a plot of D_s vs. F should give a straight line for each gas, if a optimum value of a is chosen. D_{s0} can be evaluated from a slope of this line. The accuracy of the correlation is presented in Table 2 and Figure 10. The surface flow coefficients calculated using the parameters a and D_{s0} listed in Table 2 are also shown in Figure 9.

Moreover, the results of the correlation using Eq. 11 or 13 are also presented in Table 2 and Figure 10 for other published experimental data. These data contain the surface flow coefficients on the both homogeneous surface (Horiguchi et al., 1971; Ross and Good, 1956) and heterogeneous surface (Carman and Raal, 1951; Gilliland et al., 1958 and 1974; Horiguchi et al., 1971; Ponzi et al., 1977). Horiguchi et al. (1971) and Gilliland et al. (1958 and 1974) used the following equation:

$$N_s = -(\rho_{app} A D'_s / k_s^2)(dq/d\ell) \tag{28}$$

where k_s is the tortuosity factor for surface flow and they adopted $k_s^2 = 4.30$ and 6.60, respectively. The surface flow coefficient D_s used is given from Eqs. 10 and 28.

$$D_s = D'_s / k_s^2 \tag{29}$$

Consequently, the correlating equation (Eq. 11 or 13) satisfactorily explains the dependence of surface flow coefficient on the amount adsorbed and temperature in the wide range from less than monolayer to multilayer adsorption.

DISCUSSION

Comparison of Present Model and Other Models

Providing that the following equations are accepted,

$$\tau_1 << \tau_0 \tag{30}$$

$$1 >> e^{-Es0/RT} >> e^{-Ea0/RT} \tag{31}$$

$$\theta_e = \theta \tag{32}$$

Eq. 11 is reduced to Eq. 33 derived by Higashi et al. (1963):

$$D_s = \{D_{s0}/(1 - \theta)\} e^{-Es0/RT} \tag{33}$$

For the several sets of observed data, Eq. 33 expresses the surface coverage dependence of D_s for the range $0 < \theta < 0.6$. Eqs. 30, 31 and 32 respectively show that the hopping resistance of adsorbed molecules in the multilayer is much smaller than that on the vacant sites, that E_{s0} is less than half of E_{a0}, and that the local formation of multilayer adsorption is neglected. Accordingly, we consider that the hopping model proposed by Higashi et al. (1963) is the special case of the present model.

Gilliland et al. (1974) attempted a correlation of surface flow for physisorbed and chemisorbed gases using Eqs. 8 and 34.

$$D_s = D_{s0} e^{-Es0/RT} \tag{34}$$

For a group of energetically heterogeneous surface, Eqs. 8 and 34 can be applied. On homogeneous surface, however, these equations cannot explain the dependence of D_s on the amount adsorbed q, because the differential heat of adsorption E_{a0} in Eq. 34 does not change with q.

Consideration of Parameter a

In the present model, the ratio of activation energy E_{s0} and differential heat of adsorption E_{a0} is assumed to be constant. The value of parameter a ranges from 0.4 to 0.6 for many experimental systems as shown in Table 2. de Boer (1952) supposed an atom to be adsorbed at the center of a square of four surface atoms and showed that the parameter a is of the order of magnitude of half. Gilliland et al. (1974) also correlated surface flow coefficient using Eqs. 8 and 34 and proposed that a is equal to 0.5. The parameter a determined in the present work is almost same with this value.

Consideration of Parameter D_{s0}

The parameter D_{s0} in Eq. 11 or 13 is listed in Table 2. This parameter is of the order of $10^{-3} \sim 10^{-2}$ cm²/s for energetically heterogeneous solids (porous Vycor glass, Linde-silica, Carbolac and Carbon Regal) and of 10^{-1} cm²/s for homogeneous solids (Graphon).

TABLE 3. CORRELATING RESULTS BY EQ. 13 (PARAMETER a IS CONSTANT ON SAME SOLID.)

Gas	Porous Solid	a	$D_{s0} \times 10^{-3}$	Accuracy*	Data No.
C_2H_4	Vycor	0.44	3.26	0.059	1
C_3H_6	Vycor	0.44	4.87	0.067	2
iC_4H_{10}	Vycor	0.44	7.91	0.081	3
SO_2	Vycor	0.44	3.57	0.103	4
CF_2Cl_2	Linde silica	0.46	6.81	0.113	5
SO_2	Linde silica	0.46	13.0	0.131	6
CF_2Cl_2	Carbolac	0.42	8.53	0.135	7
CO_2	Carbolac	0.42	9.23	0.129	8
SO_2	Vycor	0.48	6.23	0.140	9
CO_2	Vycor	0.48	6.75	0.173	10
C_2H_6	Vycor	0.53	13.2	0.180	13
C_3H_6	Vycor	0.53	18.0	0.231	14

*Mean square deviation = $\{(1/N) \sum_N (D_{sexp} - D_{scal})^2 / D_{sexp}^2\}^{1/2}$

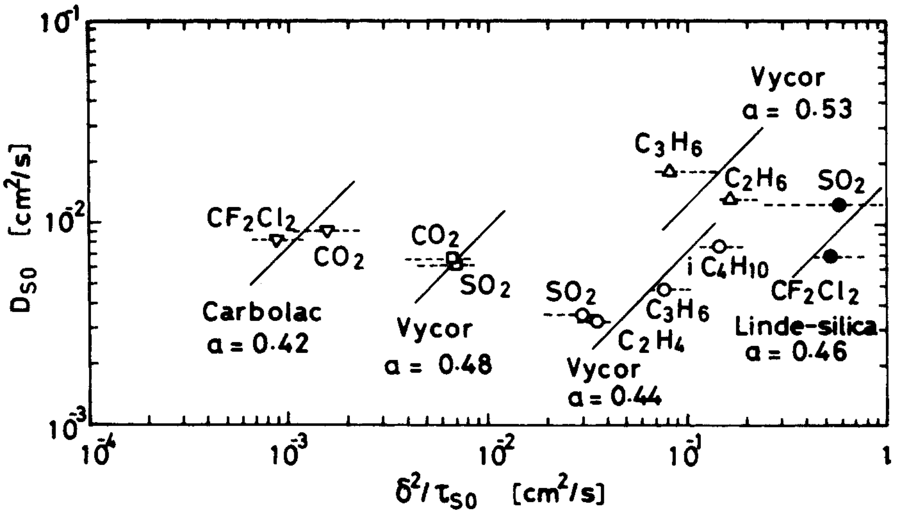


Figure 11. Correlation of D_{s0} by δ^2/τ_{s0}.

The parameter D_{s0} can be expressed from Eqs. 3, 7 and 11 or 13 as follows.

$$D_{s0} = C'\delta^2/\tau_{s0} \tag{35}$$

where C' can be assumed to be independent from the kind of adsorbate and depends on the adsorbent.

If it can be assumed that the distance of the adsorption sites δ is approximately equal to the diameter of adsorbed molecule, δ can be evaluated from the area occupied by an adsorbed molecule, for hexagonal close packing (Young and Crowell, 1962).

$$\delta = 2\{M/(4\sqrt{2}\,N_A\rho_L)\}^{1/3} \tag{36}$$

On the other hand, τ_{s0} depends on both the adsorbate and the adsorbent. Then, we try to estimate the value of τ_{s0} as follows. The mean holding time of adsorption τ_a is given by Eq. 37.

$$\tau_a = \tau_{s0}e^{Ea0/RT} \tag{37}$$

From the kinetic theory of gases, the number of molecules N which collide with surface is as:

$$N = p/\sqrt{2\pi mkT} \tag{38}$$

where m is the mass of the molecule and k is the Boltzman constant. If S is defined as the sticking probability (condensation coefficient), NS is the number of molecules which collide with the surface and are caught there.

In the Case of Langmuir Equation. The sticking probability S is directly proportional to $(1 - \theta)$.

$$S = S_0(1 - \theta) \tag{39}$$

where S_0 is the probability in which molecules colliding with vacant sites are adsorbed. τ_a can be evaluated by Eq. 40 due to the Langmuir adsorption model and Eqs. 38 and 39.

$$\tau_a = \sqrt{2\pi kmT}\sigma_m b/S_0 \tag{40}$$

where σ_m is the number of adsorbed molecules in the monolayer.

In the Case of B.E.T. Equation. When the B.E.T. theory is applied to adsorption equilibria, the relation of θ_0 and θ_1 is given as (θ_0 is the portion of vacant sites and θ_1 is the coverage with the first layer).

$$\theta_1 = Cx\theta_0 \tag{41}$$

As the sticking probability S, in which a molecule on the vacant surface forms the first layer, is proportional to θ_0,

$$S = S_0\theta_0 \tag{42}$$

From the B.E.T. adsorption model and Eqs. 38, 41 and 42,

$$\tau_a = \sqrt{2\pi mkT}\sigma_m C/(p_s S_0) \tag{43}$$

As we can estimate τ_a by Eq. 40 or 43, τ_{s0} can be calculated from the intercept of the straight line which is obtained by plotting $ln(\tau_a)$ vs. $1/T$ according to Eq. 37.

τ_{s0} was determined for the published data and the experimental data of this paper, where S_0 was assumed to be unity in the calculation of τ_a. There is still great room for discussion of this assumption. This assumption, however, has been used, because it is a conventional procedure in the calculation of mean adsorption time. The results correlated by Eq. 13 are presented in Table 3, with the parameter a as a constant on the same adsorbent. Though the correlating results in Table 3 are inferior to those in Table 2 in accuracy, this correlating method can well explain the dependence of surface flow coefficient on the amount adsorbed and temperature.

Figure 11 shows the plots of D_{s0} in Table 3 vs. δ^2/τ_{s0}. It is seen that D_{s0} for various gases can be roughly correlated by δ^2/τ_{s0} on the same adsorbent. The solid lines shown in Figure 11 were drawn through the determined values of D_{s0} according to Eq. 35. Therefore, it seems that D_{s0} for other gases on the same adsorbent can be roughly estimated from these lines. However, it should be noted that considerable errors occur in the calculation of τ_{s0} as shown in Figure 11, because the adsorption equilibria must be measured over a wide temperature range and the equilibria must be accurately expressed by the Langmuir or the B.E.T. equation.

Providing that the surface flow is measured and the parameters a and D_{s0} are determined for a set of gas and adsorbent, the surface flow rate for other gases on the same adsorbent might be roughly estimated. The surface flow, however, cannot be predicted from adsorption isotherms and the nature of the adsorbate and adsorbent without using experimental results for surface flow. More investigations about a and D_{s0} will be needed in the future.

APPENDIX

Assuming that the porous solid is a bundle of parallel capillaries and adsorption takes place uniformly on the surface of pores, the effective pore volume for the gas-phase flow in the presence of adsorption layers is given as the following equation.

$$n\pi r_e^2\ell_c = AL\epsilon - N_A\sigma^{3/2}qW \tag{A-1}$$

where n is the number of capillaries, ℓ_c is the length of capillaries, r_e is the effective pore radius for gas-phase flow, σ is the area occupied by an adsorbed molecule, and W is the weight of porous media.

From Eq. A-1,

$$r_e/r = \{1 - (N_A\sigma^{3/2}qW)/(AL\epsilon)\}^{1/2} = \{1 - (N_A\sigma^{3/2}q\rho_{app})/\epsilon\}^{1/2} \tag{A-2}$$

If the gas-phase flow obeys the Knudsen equation, the permeability of gas-phase flow in the presence of adsorption layers P'_g is expressed as follows from Eqs. 22, 23 and A-2,

$$P'_g/P_g = (r_e/r)^3 = \{1 - (N_A\sigma^{3/2}q\rho_{app})/\epsilon\}^{3/2} \tag{A-3}$$

where P_g is the Knudsen permeability. The area occupied by an adsorbed molecule σ is estimated by Eq. A-4 (Young and Crowell, 1962).

$$\sigma = 2\sqrt{3}\,\{M/(4\sqrt{2}\,N_A\rho_L)\}^{2/3} \tag{A-4}$$

where ρ_L is the density of adsorbate in the liquid state. From Eqs. A-3 and A-4, the following equation is obtained.

$$\begin{aligned} P'_g/P_g &= \{1 - [(2\sqrt{3})^{3/2}qM\rho_{app}]/(4\sqrt{2}\,\rho_L\epsilon)\}^{3/2} \\ &= \{1 - (1.14qM\rho_{app})/(\rho_L\epsilon)\}^{3/2} \end{aligned} \tag{A-5}$$

When the kinds of gases are different for P'_g and P_g, the correction of molecular weight must be made, and Eq. A-5 is rewritten to Eq. 26.

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NOTATION

A = cross-sectional area of plug, cm^2
a = parameter defined in Eq. 8
b = constant defined in Eq. 15, kPa^{-1}
C = constant defined in Eq. 17
C' = constant defined in Eq. 35
D_k = Knudsen diffusivity, cm^2/s
D_s = surface flow coefficient, cm^2/s
D'_s = surface flow coefficient ($=D_s k_s^2$), cm^2/s
D_{s0} = parameter defined in Eq. 11 or 13, cm^2/s
E = adsorption energy, kJ/mol
E_{a0} = differential heat of adsorption, kJ/mol
E_{a1} = heat of vaporization, kJ/mol
E_{s0} = activation energy for surface flow, kJ/mol
E_{st} = isotropic heat of adsorption, kJ/mol
E_{s1} = activation energy for migration in all layers above first layer, kJ/mol
F = function defined in Eq. 11 or 13
$g(E)$ = number of molecules adsorbed which have the heat of adsorption between E and $(E + dE)$
K = constant defined in Eq. 18, Pa · s · K^{-1}
k = Boltzman constant, J/K
k_g = tortuosity factor for gas-phase flow
k_s = tortuosity factor for surface flow
L = length of plug, cm
ℓ = dimension along axis, cm
ℓ_c = length of capillary, cm
M = molecular weight, kg/kmol
m = mass of molecule, kg
N = number of molecules colliding with surface, s^{-1}
N_A = Avogadro's number, mol^{-1}
N_g = flow rate of nonadsorbable gas, mol/s
N_s = rate of surface flow, mol/s
N_T = total flow rate of adsorbable gas, mol/s
n = number of capillaries
P_g = permeability of nonadsorbable gas, mmol · m^{-1} · s^{-1} · Pa^{-1}
P'_g = gas-phase permeability in presence of adsorption layers, mmol · m^{-1} · s^{-1} · Pa^{-1}
P_s = surface permeability, mmol · m^{-1} · s^{-1} · Pa^{-1}
P_T = total permeability of adsorbable gas, mmol · m^{-1} · s^{-1} · Pa^{-1}
p = partial pressure, kPa
$\bar{p}$ = average partial pressure, kPa
p_s = saturated vapor pressure, kPa
q = amount adsorbed, mol/kg
q_e = effective amount adsorbed for surface flow, mol/kg
R = gas constant, J · K^{-1} · mol^{-1}
r = pore radius, cm
$\bar{r}$ = average pore radius, cm
r_e = effective pore radius defined in Eq. A-1, cm
S = sticking probability (condensation coefficient)
S_0 = probability defined in Eq. 39 or 42
T = temperature, K
W = weight of sample, kg
x = relative pressure ($=p/p_s$)

Greek Letters

δ = distance between adsorption sites, cm
ϵ = porosity
θ = surface coverage (=amount adsorbed/monolayer amount adsorbed)
θ_e = effective surface coverage for surface flow
μ_L = viscosity in liquid state, Pa · s
ρ_{app} = apparent density of porous material plug, kg/m^3
ρ_L = density of saturated liquid, kg/m^3
τ = expectation value of holding time, s
τ_a = mean holding time of adsorption, s
τ_{s0} = constant defined in Eq. 3, s
τ_{s1} = constant defined in Eq. 4, s
τ_0 = mean holding time for migration in first layer, s
τ_1 = mean holding time for migration in all layers above first layer, s
σ = area occupied by adsorbed molecule, cm^2
σ_m = number of adsorbed molecules in monolayer

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