Flow of Gases Through Porous Solids Under the Influence of Temperature Gradients

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The isothermal and isobaric flow of pure gases and vapors through microporous Vycor glass was investigated under such conditions that the gas-phase flow occurred by Knudsen diffusion. The isothermal flows and the isobaric flow of nonadsorbed gases are correlated by existing relationships.

On the assumption that surface flow is a diffusive process and that equilibrium exists between the vapor and solid throughout the porous media, a correlation for the nonisothermal surface flow is developed. The factors determining the rate of surface flow are the physical properties of the solid, the temperature level and gradient, the enthalpy of adsorption, the surface concentration and spreading pressure of the adsorbed phase, and the activation energy and coefficient of resistance for surface diffusion. The latter two factors can be evaluated from isothermal surface flow measurements; hence no new arbitrary constants are required in the correlation. Agreement between predicted and measured surface flows is good for ethylene and propylene at a mean temperature of 25°C. Both the gas-phase and surface flows are from the cold to hot end of the porous solid.

It is suggested that the use of temperature gradients in porous solids and plastic films for separating mixtures of vapors be investigated.

The transport of gases and vapors through porous solids finds many industrial applications at the present time. A large number of such applications are influenced to a greater or lesser, but usually unknown, degree by the flow of adsorbed gases along the surface of the pores of the solid. Heterogeneous reactions catalyzed on solid surfaces, separation of mixtures of gases by porous barriers, and gas chromatography are only some of the more obvious processes in which surface flow may be a large, or even the controlling, factor which determines the rate of mass transport.

A large amount of effort has been expended on the investigation of the isothermal flow of nonadsorbed gases, such as hydrogen, helium, and nitrogen, through porous solids (*5, 8, 17, 32*). Several different regimes of flow have been encountered with these nonadsorbed gases (*6*); however the only regime of interest in the present investigation is that of free-molecular, or Knudsen, flow. For straight capillaries free-molecular flow occurs under conditions such that the ratio of the mean free path of the gas molecules to the mean pore diameter is 10 or greater (*12*). The equation for isothermal, free-molecular flow, as derived by Knudsen (*27*) and applied to porous media, can be written in the form

$$\frac{(N_g)(L_P)}{(\Delta p)(A_P)}\sqrt{MT} \equiv P_g\sqrt{MT} = \frac{4r\epsilon}{3k^2}\sqrt{\frac{2}{\pi R}} \qquad (1)$$

Equation (1) is based on the assumption that the reflection coefficient is unity; that is that all molecules are reflected diffusely. Direct measurement of the mode of reflection from solid surfaces (*10*) shows that reflection of gas molecules is almost completely diffuse except from the smooth surfaces of cleavage planes of crystals.

For the nonisothermal case and under conditions such that the pressure of the nonadsorbed gas is the same at both ends of the porous solid, an equation derived by Kennard (*26*) may be very closely approximated by

$$\frac{(N_g)(L_P)}{(\Delta T_P)(A_P)}\frac{\sqrt{MT_m^3}}{p} \equiv B_g\frac{\sqrt{MT_m^3}}{p} = \frac{2r\epsilon}{3k^2}\sqrt{\frac{2}{\pi R}} \qquad (2)$$

for small temperature differences across the porous solid; under the above-stated condition the flow of gas is from low to high temperature. It is seen that the isothermal and isobaric permeabilities are related by

$$B_g\frac{\sqrt{MT_m^3}}{p} = \frac{1}{2}P_g\sqrt{MT} \qquad (3)$$

and hence the isothermal measurements may be used to predict the flow which occurs in the nonisothermal, equal-end-pressure case.

The isothermal rate of flow of gases that are appreciably adsorbed on the surface of the porous solid are generally greater than those predicted by Equation (1). The discrepancy has been attributed to a net migration of the adsorbed gas along the surface in addition to the gas-phase flow. Several methods of correlating the isothermal surface flow have been attempted (*7, 20, 21*). The method of Gilliland, Baddour, and Russell (*17*) has been successful in correlating the surface flow of several systems for surface concentrations ranging from one tenth of a monolayer up to and including the capillary condensation region by means of a one-constant equation:

$$N_s = -\frac{(A_P)(\rho_{app})(s_s)RT}{k^2\ c_R}\ \frac{\sigma^2}{p}\ \frac{dp}{dl_p} \qquad (4)$$

The coefficient of resistance is independent of surface concentration and is an exponential function of the temperature. The form of the temperature dependence is taken to be

$$c_R = c'_{R_0}\sqrt{T}\,e^{E'/RT} \qquad (5)$$

Equations of a similar form have been derived by Flood and co-workers (*15, 16, 20*).

The fact that temperature gradients due to the heat of reaction, as well as partial pressure gradients, usually exist within a catalyst, or that greater efficiencies of separation might be obtained by the use of temperature gradients, seems to have been completely overlooked. The primary purpose of this investigation was to study the flow of pure, adsorbed gases through porous solids under the influence of temperature gradients and under such conditions that the pressure of the adsorbed gas was the same at both ends of the porous solid.

DERIVATION

The mechanism by which surface flow of gases adsorbed on solids occurs has not been definitely established. Thus in the isothermal case the driving force causing surface flow has been taken by various investigators as the concentration gradient (*9, 33, 34*), the gradient of some function of the surface concentration (*21*), or the gradient of the spreading pressure (*1, 17, 20*). In the more general case of nonisothermal conditions Hill (*19*) also assumes that the gradient of the surface concentration is the driving force causing flow of adsorbed gases. However in nonisothermal cases, the direction of mass flow for diffusive processes does not necessarily occur from high to low concentration (*11*), and in the case of thermal transpiration it is a combination of the gradients of the concentration and the molecular velocity that determines the driving

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force. If it can be assumed that surface flow, at concentrations below a monolayer, is similar to the mechanism of thermal transpiration in that the rate of collision between adsorbed molecules undergoing migration is small compared with the rate of collision between the adsorbed gas and the atoms which constitute the solid surface, then the driving force for surface flow may be obtained as the gradient of the function (*14*) $\dfrac{\phi}{\sqrt{T}\, e^{E'/RT}}$. The spreading pressure is defined as (*18*)

$$\phi \equiv \gamma_o - \gamma_s \qquad (6)$$

and may be evaluated by

$$\phi = RT \int_0^p \frac{\sigma}{p}\, dp \qquad (7)$$

Assuming that the rate of surface flow is proportional to the product of the surface concentration and the driving force, one obtains

$$N_s = - \frac{(A_P)(\rho_{\text{app}})(s_s)}{k^2\, c'_{R_o}}\, \sigma\, \frac{d(\phi/\sqrt{T}\, e^{E'/RT})}{dl_p} \qquad (8)$$

For the isothermal case general Equation (8) reduces to a form equivalent to Equation (4); that is

$$N_s = - \frac{(A_P)(\rho_{\text{app}})(s_s)}{k^2\, c_R}\, \sigma\, \frac{d\phi}{dl_p} \qquad (9)$$

With the aid of the thermodynamic relationship of two-dimensional phases developed by Hill (*18*)

$$dF_s = -S_s dT + a_s d\phi \qquad (10)$$

and the analogous expression for a three-dimensional phase

$$dF_g = -S_g dT + V_g dp \qquad (11)$$

and the assumption that equilibrium exists between the gas and adsorbed phases at each point in the porous solid, Equation (8) may be used to develop a relationship expressing the rate of surface flow under a temperature gradient and at constant pressure in the form (*14*)

$$N_s = - \frac{(A_P)(\rho_{\text{app}})(s_s)}{k^2\, c_R}\, \frac{\sigma^2}{T} \left[\Delta H + \frac{\phi}{2\sigma}\left(\frac{2E'}{RT} - 1\right)\right] \frac{dT}{dl_p} \qquad (12)$$

It may be remarked that the direction of flow is dependent upon the relative magnitudes of ΔH and $\phi/2\sigma \left(\dfrac{2E'}{RT} - 1\right)$, the former being negative for physical adsorption and the latter positive for large values of E', the energy of activation for surface flow. It should be noted that each term appearing in Equation (12) can be determined from measurements other than temperature-gradient runs. The terms outside the brackets may be evaluated from isothermal flow data. ΔH can be determined from a Clausius-Clapeyron type of relationship which can be obtained from Equations (10) and (11):

$$\Delta H = R \left[\frac{d(\ln p)}{d(1/T)}\right]_\phi \qquad (13)$$

The spreading pressure can be obtained from Equation (7) and E' from isothermal, pressure-gradient runs. Because no new arbitrary constants appear in Equation (12) a comparison between theory and experiment should be a critical test of the assumptions made in the derivation.

APPARATUS AND PROCEDURE

The solid chosen for the study of surface flow was a porous, intermediate product in the manufacture of Vycor glass. It was well suited for a study of surface flow because of its large specific surface area, about 1.4 × 10^6 sq. cm./g. (*3*); its small mean pore diameter, about 6 × 10^{-7} cm. (*17*); and its small range of pore size distribution (*13*). The nonadsorbed gases employed were hydrogen, helium, nitrogen, and argon; ethylene and propylene were the adsorbed gases used.

To avoid the introduction of any complicating factors, the nonisothermal studies were restricted to the flow of one-component gases under conditions which kept the pressure of the gas equal on both ends of the porous solid. The equipment used to accomplish this is shown in Figure 1. Essentially the apparatus consisted of a plug assembly, shown in Figure 2, a manometer, and various glass stopcocks and tubing, including two 18 in.-long precision-bore tubes mounted in a horizontal position. Each precision-bore tube contained a little slug of mercury which completely filled the cross-sectional area; to insure the smooth movement of the mercury slugs a small amount of two-ethyl hexyl sebecate was added with the mercury to wet the glass and prevent sticking of the mercury. Furthermore the tubes were gently vibrated by a piece of rubber tubing attached to the striker of an ordinary bell. The pressure difference required to make the mercury slugs move under these conditions was less than 0.25 mm. Hg.

The plug assembly consisted of two pieces of copper, two thin plates of porous stainless steel, the porous Vycor, and a piece of neoprene tubing. The large portion of the copper end pieces was about 1½ in. in diameter and 1 in. long; the small portion was 0.480 in. in diameter and about ½ in. long. A 1/16-in. in diameter hole was drilled the entire length of each copper block. To each small end of the copper was soldered a piece of porous, stainless steel plate about 1/16 in. thick and 0.500 in. in diameter. A groove about 1/32 in. deep, 1/32 in. wide, and ¼ in. in diameter, shown in the end view in Figure 2, was cut into each face of the copper touching the porous steel; the purpose of the groove was to distribute gas more uniformly over the porous steel. In turn the porous steel was to allow the flow of both heat and mass to be uniformly distributed over the entire face of the Vycor glass. Between the two pieces of porous steel was the porous Vycor in the form of a cylindrical plug, 0.554 in. long and 0.517 in. in diameter. Around the Vycor plug was a piece of standard ⅜-in. piece of neoprene tubing held tightly against the Vycor by strands of picture wire.

The glass apparatus and the plug assembly were situated in a water tank fitted with partitions that separated the tank into three distinct, constant-temperature baths. The two precision-bore tubes were in one bath, and each copper end piece of the plug assembly was in contact with one of the other two baths. By maintaining the latter two baths at different temperatures a temperature gradient could be established in the Vycor plug. Originally thermocouples were to be imbedded in the Vycor; however the required holes could not be drilled without cracking the plug. A cold trap between S_4 and the vacuum pump and a tube filled with calcium sulfate between S_1 and the gas cylinder are not shown in the figures.

Before a run was initiated the plug assembly was evacuated to about 20 μ Hg and simultaneously heated to about 100°C. for about 18 hr. Then a pure gas was introduced into the system and the temperature of the baths adjusted to produce a desired gradient in the Vycor plug. During the portion of the run in which the temperature gradient and steady state concentration of the gas within the plug were being established, any gas transported through the plug could flow around loop Y_1-S_2-Y_2. When steady state was reached, stopcocks Y_1 and Y_2 were turned in order to require gas moving through the plug to travel around path Y_1-S_6-S_7-Y_2, forcing the mercury slugs to move; the vibrator was turned on, the pressure in the system recorded, and S_5 was closed. The mass rate of flow was determined from the rate of movement of the mercury slugs and the known temperature and pressure.

To calibrate the Vycor plug isothermal, pressure-gradient runs with adsorbed and nonadsorbed gases were also conducted. The equipment described above was adapted to the isothermal runs by placing an additional manometer between S_4 and the cold trap.

Adsorption isotherms of ethylene and propylene on Vycor were measured over the temperature and pressure range covered by the flow measurements. A standard volumetric technique was employed in these determinations. The isotherms measured in this investigation were similar in shape to the ones reported by Gilliland, Baddour, and Russell (*17*).

RESULTS AND DISCUSSION

Isothermal Runs

The results of the isothermal runs with the nonadsorbed gases, hydrogen, helium, nitrogen, and argon, in two different plug assemblies yielded average values of $P_g'\sqrt{MT}$ equal to 1.10 × 10^{-2} and 1.21 × 10^{-2} (mg. mole/hr.-mm. Hg-cm.) ($\sqrt{\text{g.}}$-°K./g. mole)

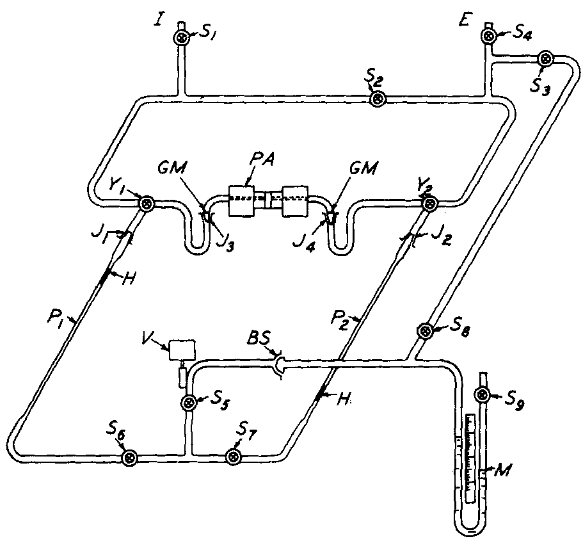

Fig. 1. Diagram of isobaric flow rate apparatus. *BS*—ball-and-socket joint, *E*—to cold trap and vacuum pump, *GM*—glass-to-metal seals (2), *H*—mercury slugs (2), *I*—inlet from gas cylinder, *J*—ground-glass joints (4), *M*—manometer, *P*—precision-bore tubes (2), *PA*—plug assembly, *S*—stopcocks (9), *V*—vibrator, *Y*—three-way stopcocks (2).

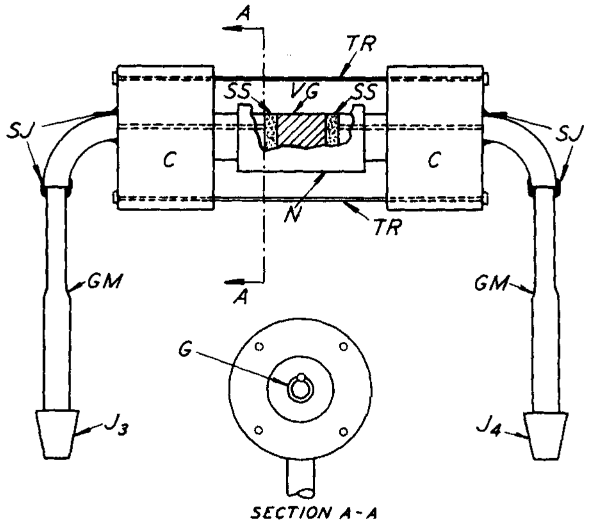

Fig. 2. Diagram of plug assembly. *C*—copper end pieces (2), *G*—groove 1/32 in. wide by 1/32 in. deep, *GM*—glass-to-metal seals (2), *J*—ground-glass joints (2), *N*—neoprene tubing, *SJ*—solder joints (4), *SS*—porous stainless steel plates (2), *TR*—tie rods (4), *VG*—porous Vycor glass.

for plugs *A* and *B*, respectively, independent of pressure level, pressure gradient, and type of nonadsorbed gas. These values are about 10 to 20% higher than those reported in reference *17*.

With an assumed value of k of 2.56 as found by Barrer and Barrie (*3*) for Vycor glass, and the experimentally determined value of 0.28 for ϵ, the mean radius of the pores is calculated to be 5×10^{-7} cm. By means of the simple pore model suggested by Barrer (*2*) the specific surface area is calculated to be 7.4×10^{5} sq.cm./g. from the permeability results. This compares favorably with the value of 8.2×10^{5} sq.cm./g. for the specific surface area as determined from low-temperature, nitrogen adsorption. Calculation of the mean free path of the gas by an equation derived by Kennard (*24*) shows that the ratio of λ/d is greater than 10 for all runs made with the nonadsorbed gases. This is an additional indication that the mechanism of flow was by free-molecular diffusion.

Recently Kammermeyer and coworkers (*22, 23*) have suggested that appreciable surface flow occurs for such gases as hydrogen, nitrogen, argon, and perhaps even for helium in porous glass with an average pore diameter of about 4×10^{-7} cm. and at room temperature. Undoubtedly, as the pore size is reduced, the migrating molecules travel within the force field of the surface to a greater extent, and deviations from the free-molecular-flow equation may be expected even in the case of the so-called *permanent gases.* However Barrer and Barrie (*3*) were unable to detect steady state surface flow of helium, nitrogen, oxygen, argon, and krypton through porous Vycor glass with an average pore size of about 3×10^{-7} cm., although Barrer and Strachan (*4*) measured appreciable steady state surface flow of nitrogen, argon, and krypton through Carbolac with pores down to 1.3×10^{-7} cm. in diameter. Gilliland, Baddour, and Russell (*17*) concluded that the steady state flow of the helium, hydrogen, argon, and nitrogen through porous Vycor glass with pores 6×10^{-7} cm. in diameter agreed with the Knudsen equation.

To obtain the amount of isothermal surface flow the corrected gas-phase flow was subtracted from the total vapor flow measured; the correction applied to the gas-phase flow accounts for the partial blocking of the pores by the presence of the adsorbed phase (*17*).

Correlation of the isothermal, surface flow is made by a modified form of Equation (4). It should be noted that if the value of σ^2/p in Equation (4) is linear with p over the range of pressure existing within the plug in any given run, then, independent of the magnitude of Δp

$$\int_{p_1}^{p_2} \frac{\sigma^2}{p} dp = \frac{\sigma_m{}^2}{p_m} \Delta p \qquad (14)$$

TABLE 1. RATIO OF CALCULATED TEMPERATURE DIFFERENCES ACROSS PLUGS TO MEASURE TEMPERATURE DIFFERENCES OF BATHS

	Average $\Delta T_p/\Delta T_c$	
	Plug A	Plug B
H_2	0.63	0.71
He	0.74	0.78
N_2	0.42	0.52
A	0.42	0.53

This linearity is very closely approximated by the adsorbed gases used in this investigation over the range of Δp for each run, and hence the modified form of Equation (4) used to correlate the data was

$$P_s = \frac{(\rho_{\text{app}})(s_s)\, RT}{k^2\, c_R} \frac{\sigma^2{}_m}{p_m} \qquad (15)$$

With Equation (15) the coefficient of resistance calculated from the isothermal runs in the present investigation in plug assembly *B* is, for ethylene

$$c_R = 1.11 \times 10^4 \text{ at } 25°\text{C.}$$

$$c_R = 0.846 \times 10^4 \text{ at } 40°\text{C.}$$

and, for propylene

$$c_R = 3.18 \times 10^4 \text{ at } 25°\text{C.}$$

$$c_R = 2.46 \times 10^4 \text{ at } 40°\text{C.}$$

From these quantities the value of E' in Equation (5) is calculated to be 1.48×10^{11} and 1.38×10^{11} for ethylene and propylene, respectively. Although the values of the coefficient of resistance obtained in this study are not the same as those reported in (*17*) for the same systems, the energy of activation for ethylene and propylene are the same. It should also be pointed out that the numerical values of c_R quoted above probably do not have any physical significance in themselves; the reason is that an assumed value of 6.55 for k^2, as determined by Barrer and Barrie (*3*), and the specific surface area of 8.2×10^{5} sq.cm./g., as determined by low-temperature, nitrogen adsorption were used in Equation (15). Not enough information on surface flow is available to determine the true values of these factors that should be used in the surface-flow equation. However if it is correct to assume that the specific surface area is not a function of temperature, the values of E' given above are valid.

Nonisothermal Runs

Nonadsorbed gases. The temperature gradients existing within the porous Vycor could not be measured directly owing to the impracticality of imbedding thermocouples in the glass. It was hoped therefore that a relationship between ΔT_P and ΔT_C which imposed the temperature gradient in the plug could be established; ΔT_P was calculated from the measured flow rates under nonisothermal conditions, Equation (3), and the results of the isothermal experiments. However even though the ratio of the calculated ΔT_P to the measured temperature difference was found to be a constant for a given gas in a particular plug assembly independent of the temperature and pressure levels and the temperature gradient, this ratio was not the same for all the gases employed. Also for a given gas the ratio is not the same in the two different plug assemblies employed. The results of these calculations for the various, nonadsorbed gases are shown in Table 1 for the two different plugs.

One factor that might conceivably affect the thermal transpiration through the porous solid is the degree of energy interchange between the solid surface and the diffusing gas molecules striking the surface. The quantitative measure of this interchange is the accommodation coefficient defined by

$$a = \frac{T_i - T_r}{T_i - T_w} \tag{16}$$

Equation (2) has been derived on the assumption that the gas molecules are in thermal equilibrium with the solid at each point within the porous media. Nevertheless it can be shown (*14*) that even for the case in which the accommodation coefficient is zero, the net flow of a pure gas through a porous solid is given by Equation (2) provided that the reflection coefficient is equal to unity. Thus even though the interchange of energy between individual gas and solid molecules may be incomplete, the random motion of the gas within the pores produces an average temperature of the gas molecules which is the same as the solid temperature at each point within the porous solid. The different ratios of ΔT_P to ΔT_C calculated do not appear then to be caused by a misapplication of Equation (2). Accordingly any explanation given must be able to account for the ratios shown in Table 1.

One possibility is that the temperature drops across the various gas gaps from one copper end piece to the other may be an appreciable fraction of the temperature difference of the constant temperature baths establishing the gradient. For the runs with nitrogen and argon, heat transfer calculations based on the total estimated length of the gaps and the thermal conductivity of the gases yield an effective thermal conductivity for the porous Vycor of about 25% of the thermal conductivity of nonporous glass; these results appear to be reasonable. However for the hydrogen and helium runs the thermal conductivity calculated for the Vycor is only 8 to 10% of the value of glass. It thus appears that some factors other than the thermal conductivity of the gases involved determine the temperature drop across the gas gaps. One such factor may be the thermal accommodation coefficient. The accommodation coefficients of nitrogen and argon on most surfaces are close to unity, whereas these coefficients for hydrogen and helium are usually much less; hydrogen almost always has a lower accommodation coefficient than helium on the same surfaces (*25, 30*). In the transfer of heat from a solid surface to a gas phase an accommodation coefficient of less than unity creates a finite difference in temperature between the solid surface and the gas molecules very close to the surface; the smaller the accommodation coefficient the larger is this temperature jump. The temperature jump is equivalent to a resistance to heat transfer across the solid-gas boundary.

The regions in which the accommodation coefficient contributes an appreciable resistance to heat transfer is a function of the ratio of the mean free path of the gas to the distance through which the heat must be transferred in the gas phase. Studies in a region comparable to the ones encountered in the present work (*28*) show that the heat transfer coefficients for helium and air are in the ratio of about 3 to 1, whereas the thermal conductivities are in the ratio of 7 to 1. In the present work the ratio of heat conductance through the gas gaps in the apparatus for the case of helium to that for nitrogen is approximately 4 to 1; nitrogen and air have about the same thermal properties. It was also shown (*28*) that in the region of interest the heat transfer coefficients are only a very weak function of pressure. It thus appears that the calculated value of ΔT_P can be assumed to be a reasonably good representation of the temperature differences existing across the Vycor plugs in the isobaric runs.

The difference between plugs A and *B* may be explained by some slight difference in the mounting of the two Vycor plugs between the end pieces. In mounting plug *B* in the assembly a slightly greater pressure was applied through the tie rods than in mounting plug A. This may have caused the contact between the porous steel and the

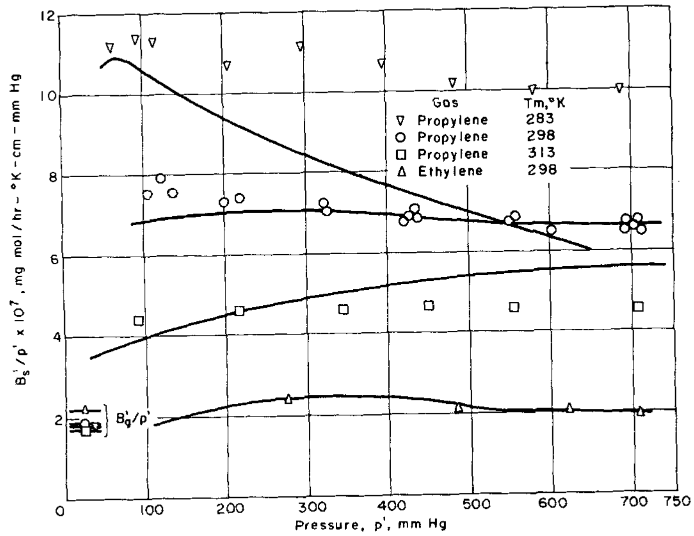

Fig. 3. Isobaric surface permeabilities.

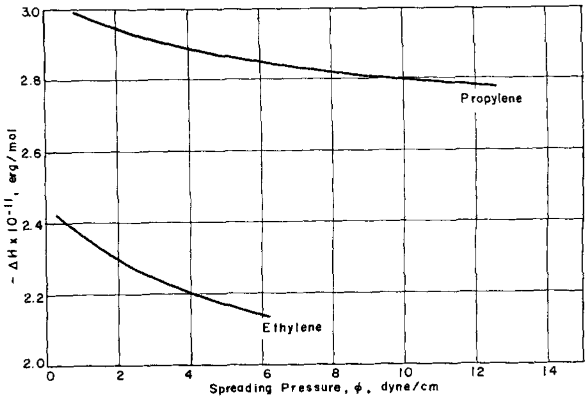

Fig. 4. ΔH of adsorption.

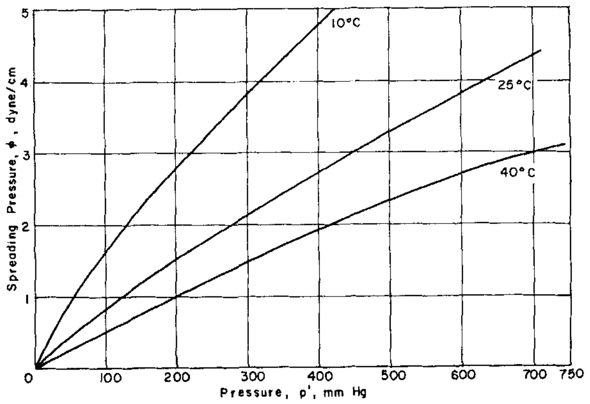

Fig. 5. Spreading pressure of ethylene.

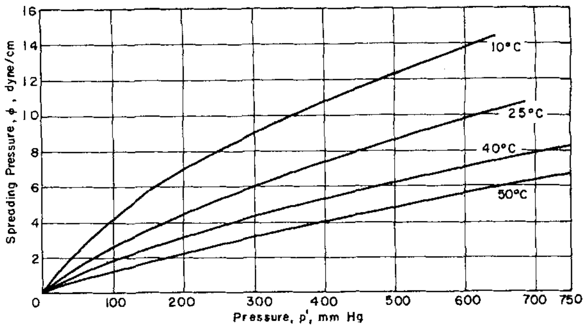

Fig. 6. Spreading pressure of propylene.

Vycor to be better in assembly B than in assembly A, and hence the fraction of the heat required to be transferred through the gas gaps would have been less in the former than in the latter. The relative resistances across the gas gaps for nitrogen, for example, in plugs A and B should therefore be in approximately the same ratio as the resistances for hydrogen. In fact the ratio of resistances for nitrogen in plug A to that of nitrogen in plug B is 1.49, and this same ratio for hydrogen is 1.43.

The ratio of ΔT_P to ΔT_C of 0.52, as determined from the nitrogen and argon runs in plug B, was chosen for the runs with ethylene and propylene in plug B because of the similarity of these four gases in the thermal conductivity and accommodation coefficient, the properties that are believed to influence the temperature differences across the plug for a given temperature difference of the baths imposing the gradient.

Absorbed gases. The flow of the adsorbed gases from low to high temperature is generally greater than predicted by Equation (2), and, with the value of 0.52 for $\Delta T_P/\Delta T_C$ the flow of propylene is as much as seven times the predicted value. As in the case of isothermal flow of adsorbed gases the additional flow is assumed to be due to a net migration of gas along the surface. The gas-phase flow predicted by Equation (3), corrected for partial blocking due to the presence of the adsorbed gas, was subtracted from the total flow measured. The results are shown in Figure 3 as symbols; the ordinate in each figure is the isobaric surface permeability defined by

$$B_s' \equiv \frac{(N_s')\,(L_P)}{(\Delta T_P)\,(A_P)} \qquad (17)$$

and divided by the absolute pressure of the gas at both ends of the plug. The data for ethylene are for an arithmetic mean temperature of the ends of the Vycor plug of 25°C.; for propylene, data are shown for mean temperatures of 10°, 25°, and 40°C. For the sake of comparison the value of the isobaric gas-phase permeability divided by the absolute pressure B_g'/p' as calculated from Equation (3) are indicated on Figure 3. Thus for the case of ethylene it is seen that the gas-phase and surface flows are approximately equal in magnitude, and for propylene the surface flow is as much as six times the rate of gas-phase flow predicted by Equation (3).

Even though the pressure is the same at both ends of the plug in the nonisothermal runs, the fact that at steady state the total flow is constant throughout the length of the plug requires that pressure gradients exist within the plug for a linear temperature gradient; in both the nonadsorbed and adsorbed gas runs a linear temperature gradient may be assumed to exist within the porous solid. For the nonadsorbed gases the equation derived by Kennard (*26*) predicts that the maximum pressure occurs very nearly at the center of the porous plug, and for the flow rates measured in this investigation the maximum pressure never exceeded the externally applied pressure by more than 0.5%. Numerical calculations with an equation that accounts for both gas-phase and surface flows under the simultaneous influence of temperature and pressure gradients (*14*) show that, for the adsorbed gases under the conditions of the experiment, the maximum pressure also occurs near the center of the plug and is never more than 1.5% greater than the externally imposed pressure. Thus for all practical purposes the nonisothermal runs might also be considered to be isobaric experiments.

With the introduction of a linear temperature gradient Equation (12) may be rewritten in the form

$$B_s = -\frac{(\rho_{\text{app}})\,(S_s)}{k^2\, c_R}\,\frac{\sigma^2}{T_m}\left[\Delta H + \frac{\phi}{2\sigma}\left(\frac{2E'}{RT_m} - 1\right)\right] \qquad (18)$$

It should be noted that both Equations (12) and (18) apply only in the case of zero pressure gradients. Since in the nonisothermal runs the pressure at a point within the porous Vycor where the pressure gradient is zero is not very different from the externally imposed pressure, the gas-phase flow calculated for the adsorbed gases by Equation (3) should be a very good approximation of the actual gas-phase flow at the midpoint of the plug, and the symbols shown in Figure 3 should be a good representation of the surface flow physically occurring at the center of the porous Vycor. In order to compare theory with experiment the variables appearing in Equation (18) should be evaluated at the arithmetic mean of the temperature of the ends of the plug and the pressure existing at the center of the plug; however as mentioned above the maximum pressure never exceeded the externally applied pressure by more than 1.5% in this investigation, and hence the pressure of the gas at the ends of the porous solid was used in evaluating the pressure dependent variables in Equation (18).

The relatively narrow range of temperature over which the isotherms were measured did not permit determination of any temperature dependence of ΔH; the mean temperature range over which isotherms for ethylene and propylene were determined is about 25°C. It was therefore assumed that the ΔH evaluated from the adsorption data by Equation (13) is valid not only at the mean temperature of the adsorption isotherms of 25°C. but also at 10° and 40°C. and that ΔH is only a function of the spreading pressure as shown in Figure 4. The spreading pressure of the two hydrocarbons on Vycor is given in Figures 5 and 6.

The solid lines in Figure 3 are the values of the surface permeability predicted by Equation (18) with a ΔH which is independent of temperature. The agreement between theory and experiment at a mean temperature of 25°C. for ethylene and propylene is very good. For propylene at 25°C. the maximum deviation from the theoretically predicted value is about 13%, based on the experimentally determined value, and the mean deviation is about ± 2%; for ethylene the limited experimental data agree with the predicted values within ± 2%. The mean deviation for both gases is well within the accuracy of the experimental determination of the flow rates.

At a mean temperature of 40°C. the predicted value is generally higher than the experimentally determined one, the maximum deviation being about + 20%. At 10°C. the predicted flow rate is consistently low, the maximum deviation being about − 40%.

Literature data (*31*) indicate that ΔH is not only a function of the spreading pressure but is also a function of the temperature; hence the values of ΔH shown in Figure 4 may represent the true value of ΔH only at 25°C., the approximate mean temperature of the isotherm determination. In light of this the agreement between theory and experiment at an arithmetic mean temperature of 25°C. and the discrepancy in the flow rates at the other mean temperatures is not surprising.

Equation (18) would correlate the permeability data for propylene at 40°C. quite well if the value of ΔH at 40°C. were consistently about 5% smaller in absolute magnitude than the values determined by assuming ΔH to be independent of the temperature. At 10°C. the agreement between theory and experiment would be satisfactory if the value of ΔH were about 8% higher than the one determined. Although this variation of ΔH with temperature is in qualitative agreement with data in the literature, insufficient data are available to make any quantitative comparison.

It should be noted that Equation (18) contains a factor which is the sum of two terms of opposite sign, namely ΔH and $\phi/2\sigma\left(\frac{2E'}{RT_m} - 1\right)$. In the case of ethylene near atmospheric pressure this sum is as low as 16% of ΔH, so an error of only 5% in both of these terms could conceivably result in an error of over 55% in the predicted value of the flow rate. Also in the case of propylene at 10°C. and atmospheric pressure the value of the sum of the same two terms is only 20% of ΔH, so a similar 5% error in both terms could explain the discrepancy noted in the correlation. Nevertheless it is believed that the primary cause of the difference between theory and experiment lies in the evaluation of the ΔH term, because it is known with the least accuracy.

Based on the above discussion it appears that experimental verification of Equation (12) beyond any reasonable doubt is difficult. Owing to the form of the equation reasonably accurate prediction of flow rates requires that very accurate values of ΔH, ϕ/σ, and E' be employed. Data compiled by Carman (*7*) and the results of reference *17* indicate that E' is usually about one half of the magnitude of ΔH; ϕ/σ is normally greater than RT on a surface which is made up of heterogeneous adsorption sites. The net result is that the factor $\Delta H + \phi/2\sigma \left(\frac{2E'}{RT} - 1\right)$ is in general less than 50% of ΔH. In the systems employed in this investigation it is found that this factor increases in absolute magnitude with decreasing pressure. Thus flow rate measurements at pressures below 100 mm. Hg may be required to establish the validity of Equation (12). The method of measuring the rates of flow employed in the present work afforded only a limited number of runs below 100 mm. Hg to be made. Perhaps other methods for measuring very small flow rates can be devised.

All the surface flow runs in this investigation were conducted well below the monolayer capacity of the hydrocarbon vapors on Vycor glass. At surface concentrations below a monolayer the thermodynamic concepts used in developing the surface flow Equation (12) should be applicable. However that these concepts are valid in the capillary condensation region is not immediately obvious. Nevertheless Carman (*7*), based on concepts quite different from those used by Gilliland, Baddour, and Russell (*17*), was able to derive for the capillary condensation region an equation quite similar in form to Equation (4). In fact surface flow for surface concentrations ranging from less than a monolayer up to and including the capillary condensation region was correlated by Equation (4) (*17*). The success of this equation over such a wide range suggests that Equation (12) may also be valid over the entire range of concentrations.

From the assumptions made in deriving Equation (12) it appears that the mechanism of surface flow is more akin to a diffusive process than to bulk flow, at least up to surface concentrations where collisions among adsorbed molecules undergoing actual surface migration are small compared with the rate of collisions between migrating molecules and the surface. It follows therefore that in a binary mixture of adsorbed gases each species should migrate under its own gradient.

Based on the considerations of the proposed mechanism of surface diffusion it appears that flow of adsorbed gases might be a potent tool in the separation of gases or vapors. The factors present in the surface flow Equations (4) and (12) make it clear that the rate of surface flow is specific in that both the equations for isothermal and isobaric surface flow contain the surface concentration to the second power. Furthermore the isobaric equation includes the factor $\Delta H + \phi/2\sigma \left(\frac{2E'}{RT} - 1\right)$ which may actually increase the specificity of surface flow over that which can be attributed to surface concentration. For example the ratio of propylene to ethylene surface flow of the pure gases under isothermal conditions is about 1.7 at the same externally imposed conditions, whereas under similar conditions in the presence of a temperature gradient the ratio of propylene to ethylene surface flow is 3.5. The effect of the factor $\Delta H + \phi/2\sigma \left(\frac{2E'}{RT} - 1\right)$ is to increase the relative flow rates of the pure gases by a factor of 2. However this does not imply that in the presence of each other the relative flow rate of propylene to ethylene would be in this same ratio; the presence of one vapor may greatly influence the spreading pressure of the other. The effect of this can only be determined from experimental measurement of the isotherms of the mixtures of the gases.

Another advantage that isobaric surface flow has over isothermal flow in potential applications to separation processes is that in the former the fraction of the total flow that occurs on the surface is much larger than the fraction in the latter case. For ethylene the fraction of flow occurring on the surface is 0.1 to 0.25 for the pressure-gradient runs and about 0.5 for the temperature-gradient runs; in the case of propylene the fraction of flow occurring on the surface is about 0.3 and 0.8 for the isothermal and isobaric experiments, respectively. This is important since the gas-phase flow may partially nullify the separation produced by the surface flow. The obvious step to take would be to reduce the area for gas-phase flow. It is therefore suggested that the possibility of using temperature gradients in plastic membranes as a means of separating mixtures of gases or vapors be investigated.

CONCLUSIONS

1. Isobaric permeabilities of the pure, adsorbed gases investigated are considerably higher than the values predicted from correlations based on

free-molecular-flow data. The higher rates of flow are attributed to a net migration of adsorbed gas along the surface of the pores.

2. An equation of surface flow under the influence of temperature gradients has been developed by considering the surface flow to be a diffusive process akin to free-molecular flow; all terms appearing in the equation may be evaluated from experiments other than temperature-gradient runs. The equation satisfactorily correlates the isobaric surface flow for ethylene and propylene at an arithmetic mean temperature of 25°C. At mean temperatures of 40° and 10°C. the discrepancy between theory and experiment can be reconciled by a maximum variation of 8% in the value of ΔH with temperature. In order to establish the validity of the proposed mechanism of surface flow it is recommended that the counterdiffusion of binary mixtures of adsorbed gases be investigated.

3. It is also recommended that the use of temperature gradients in porous barriers and plastic membranes as a means of separating mixtures of gases be investigated.

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NOTATION

a = thermal accommodation coefficient
A_P = cross-sectional area of porous solid, sq.cm.
a_s = specific surface area occupied by adsorbed gas, sq.cm./g. mole
B_g = isobaric gas-phase permeability, g. mole/sec.-°K.-cm.
B_s, B_s' = isobaric surface permeability, g. mole/sec.-°K.-cm. and mg. mole/hr.-°K.-cm., respectively
c_B = coefficient of resistance for surface flow, g./sec.-sq.cm.
c'_{R_0} = constant defined by Equation (5), g./sec.-sq.cm.-(°K.)$^{1/2}$
d = mean diameter of pores, cm.
E' = energy of activation for surface flow, erg./g. mole
f = reflection coefficient
F_g, F_s = Gibbs free energy of gas and surface phases, respectively, erg./g. mole
ΔH = change of enthalpy of adsorption, erg./g. mole
k = tortuosity of pores, assumed equal to 2.56
l_p = distance measured along length of porous solid, cm.
L_P = length of porous solid, cm.
M = molecular weight of gas, g./g. mole
N_g = rate of gas-phase flow, g. mole/sec.
N_s, N_s' = rate of surface flow, g. mole/sec. and mg. mole/hr., respectively
p, p' = absolute pressure, dyne/sq. cm. and mm., Hg, respectively
p_m = arithmetic mean pressure, dyne/sq.cm.
Δp = pressure difference across porous solid, dyne/sq.cm.
P_g, P_g' = isothermal gas-phase permeability, g. mole/sec.-(dyne/sq.cm.)-cm. and mg. mole/hr.-mm. Hg-cm., respectively
P_s = isothermal surface permeability, g. mole/sec.-(dyne/sq. cm.)-cm.
r = mean radius of pores, cm.
R = gas constant, 8.31 × 10^7 erg./g. mole-°K.
S_g, S_s = entropy of gas and surface phases, respectively, erg./g. mole °K.
s_s = specific surface area of porous solid, sq.cm./g.
T = absolute temperature, °K.
T_i = absolute temperature of molecules incident upon surface, °K.
T_m = arithmetic mean of absolute temperatures, °K.
T_r = absolute temperature of molecules leaving surface, °K.
T_w = absolute temperature of surface, °K.
ΔT_C = temperature difference of constant-temperature baths establishing the temperature gradient in porous solid, °K.
ΔT_P = temperature difference across porous solid, °K.
V_g = specific volume of gas phase, cc./g. mole

Greek Letters

γ_o = surface tension of clean, solid surface, dyne/cm.
γ_s = surface tension of solid surface with adsorbed gas on it, dyne/cm.
ϵ = porosity of solid, void volume per total volume of voids and solid
λ = mean free path of gas molecules, cm.
ρ_{app} = apparent density of porous solid, weight of solid per unit volume of voids and solid, g./cc.
σ = surface concentration of adsorbed gas, g. mole/sq.cm.
σ_m = surface concentration at pressure p_m, g. mole/sq.cm.
ϕ = spreading pressure of surface phase, dyne/cm.

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