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Interaction Energy in Surface Diffusion

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The gas-solid interaction is the most important quantity in the physical adsorption of gas molecules on solids. If the surface diffusion of the adsorbed molecule is to be studied fundamentally, then it seems logical to investigate and analyze the gas-solid interaction energy for the system. There are some publications (*2, 3, 6, 7, 12, 14*) which deal with the calculation of the dispersion energy for both homogeneous and heterogeneous systems. However, no one has attempted to apply those techniques to the study of surface diffusion.

In the present paper, various correlations are presented for the gas-solid interaction energies and fundamental physical properties of the gases. These correlations were found to be very useful in predicting the amount of surface diffusion, which will occur when a gas or vapor flows through a microporous medium.

SURFACE DIFFUSION

The surface diffusion of gases and vapors through microporous media represents a significant contribution to the total transport. If the surface coverage of the adsorbed molecules is low and the Knudsen regime prevails Equation (1) will prove to be adequate over a wide temperature range to explain the flow data of many gases and vapors through microporous Vycor glass (*9* to *11*):

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

Here A represents the Knudsen flow, which thus remains constant for a given microporous medium. The second term representing the surface flow, however, is a function of values of B and Δ which vary from gas to gas. The definition of Δ is

$$\Delta = \frac{\epsilon^* - \epsilon^\ddagger}{k} \tag{2}$$

where ϵ^* is the gas-solid interaction energy and $\epsilon^\ddagger$ is the activation energy of surface diffusion for an adsorbed molecule. Therefore, the value of Δ is a measure of the interaction energy between the gas molecule and the solid surface. This was demonstrated in an earlier crude correlation (*9*). Since there exists an interrelationship [(*9*) also, see Figure 4 of the present paper] between B and Δ, if the value of Δ can be estimated from other physical properties, then one can easily calculate the

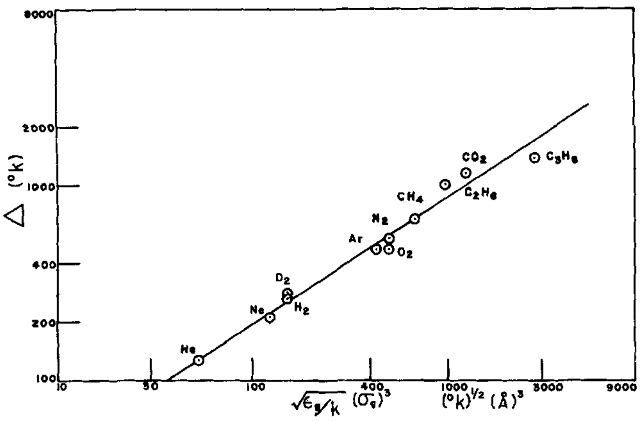

Fig. 1. Correlation of Δ with the Lennard-Jones parameters.

amount of the surface diffusion, which is the second term in Equation (1).

A recent study (*11*) reveals that helium flow also obeys Equation (*1*), and the fraction of surface diffusion varies from 0.133 at 100°K. to 0.367 at 20.4°K. Therefore the total permeability of helium should not be used in the estimation of the Knudsen flow for any gas. One correct way is to study the temperature effect on permeability, then fit the experimental data to Equation (1) to obtain the values of *A*, *B*, and Δ. The detailed procedure is given elsewhere (*9*).

VARIOUS CORRELATIONS

Because the gas-solid interaction energy, ϵ^*, can not be found in the literature, except for the work by Steele and Halsey (*15*) it is impossible to make a direct examination of the various combining rules for a gas-solid system. Furthermore, as previously mentioned, the accurate information on the molecular properties is not available. Consequently, the present status allows at the most a qualitative study of the gas-solid interaction energy.

The activation energy of the surface diffusion, $\epsilon^\ddagger$, is actually created by the variation of the gas-solid interaction energy (or adsorption potential) due to the energetic heterogeneity of the solid surface. Therefore, it can be assumed that the degree of change in $\epsilon^\ddagger$ from one gas to another be the same as the degree of change in ϵ^*. Then the difference, Δ, should bear some kind of relationship to the fundamental molecular properties. This is the basis of the present empirical correlations of Δ with the potential parameters (Figure 1), and with the critical properties (Figure 2).

The presently known combining rules (*3, 6, 7, 14, 15*) involve the Lennard-Jones parameters and some other molecular properties, such as the diamagnetic susceptibility or the ionization potential, for both gas and solid. For some gases, these are available (*6*), but for solids they are frequently unknown. Furthermore, none of the combining rules was found to give a good correlation, even for those systems where physical properties are available.

The failure of the presently known theories calls for an empirical correlation. The first attempt involved correlating Δ and a quantity $\sqrt{\epsilon_g}\,\sigma_g^3$, in Figure 1, which is not bad, but not entirely satisfactory.

The next correlation was made with critical constants in Figure 2 on the basis of the fact that ϵ_g is roughly proportional to the critical temperature, and σ_g^3 to the critical volume (*16*). Surprisingly, all the points except that of carbon dioxide fell on a straight line. This plot is especially useful because the critical data are rather easy to obtain.

The values of ϵ^* from Steele and Halsey (*15*) are plotted in Figure 3, which further supports the validity of Figure 2.

APPLICATION

The extremely good correlation of Δ with the critical properties in Figure 2 permits us to predict the amount of surface diffusion and in turn the total permeability of a new gas through a microporous media. In order to do this we have to know the value of *A* and the interrelationship between *B* and Δ as shown in Figure 4. For the case of porous Vycor glass, these are available from the previous study (9, *10*). By using Equation (1) the total permeabilities are estimated for krypton, ethylene, propene and *n*-butane. They are compared with the experimental values in Table 2.

To illustrate the steps required in the calculations, propene is chosen at 298.2°K. When we know the value of *A* to be equal to 4.02 × 10^{-4} (*9*), the gas phase permeability is readily computed by dividing $\sqrt{MT}$ into *A*, which yields 3.6 × 10^{-6}. In order to calculate the permeability for surface diffusion from the second term of Equation (1), two coefficients, *B* and Δ, must be estimated first. From Figure 2, the value of Δ is obtained as 1,290, which gives the value of *B* as 0.24 × 10^{-7} from the curve in Figure 4. Having estimated these constants, the surface permeability is calculated finally as 4.87 × 10^{-6}. The sum of gas phase permeability and surface permeability becomes the total permeability, 8.47 × 10^{-6}, which is shown in Table 2. All of the units used in the above calculations are such that the final permeability comes out in the unit specified in this paper.

The sources of experimental data are all different but agreements are excellent. It should be noted here that no investigators reported the permeability in the same unit, thus, the conversion of units was necessary for comparison. The more important fact is that each investigator has a slightly different scale factor in the permeability data. This could be easily resolved by making a cross plot of data for the same systems.

The example is again for the case of propene. Gilliland, et al. (*4*) reported the permeability of propene through Vycor porous glass at 298.2°K. The value ranged from 5 × 10^{-6} to 6 × 10^{-6} for the product of permeability and $\sqrt{MT}$. However, for the sake of comparison, 'the lower limiting number, 5 × 10^{-6} was taken. Then, their data for hydrogen, argon, nitrogen, and helium are plotted against the corresponding permeabilities given elsewhere (9). This gives a straight line going through the origin,

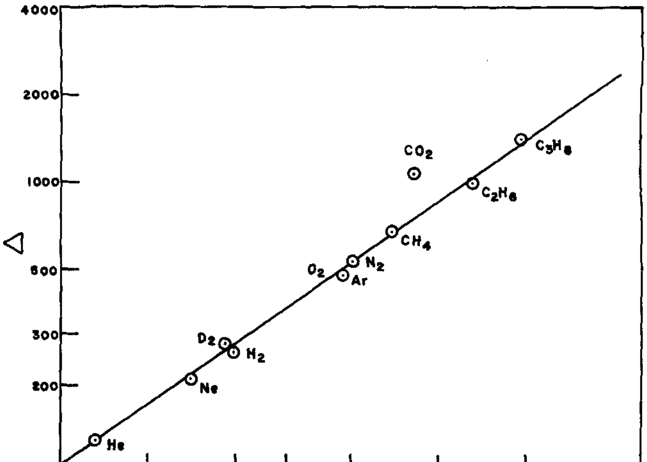

Fig. 2. Correlation of Δ with the critical properties.

which means that both sets of data are consistent. From this plot, the value of Q equal to 8.00×10^{-6} is obtained which is shown in Table 2.

TABLE 1. PHYSICAL PROPERTIES OF GASES AND VAPORS

Gas	ϵ_g/k(°K.) *(6)*	σ_g(Å.) *(6)*	T_c(°K) *(15)*	v_c(cc./g.-mole) *(15)*	Δ(°K) *(9, 10)*
He	10.2	2.556	5.20	57.76	127
Ne	35.6	2.749	44.5	41.7	211
H_2	37.0	2.928	33.18	66.95	266
D_2	37.0	2.928	38.3	60.3	272
Ar	119.8	3.405	151.2	75.22	483
O_2	117.5	3.58	154.8	74.4	487
N_2	95.05	3.698	126.2	90.1	532
CH_4	148.2	3.817	191.1	99.01	676
C_2H_6	243	3.954	305.5	148.1	1,003
CO_2	189	4.486	304.2	94.24	1,079
C_3H_8	242	5.637	370.0	200.4	1,397
Kr	171	3.60	209.4	92.29	655*
C_2H_4	199.2	4.523	283.1	123.6	895*
C_3H_6	303	4.67	365.0	180.6	1,290*
n-C_4H_{10}	297	4.971	425.2	254.9	1,740*

* These values are estimated from the Figure 2.

TABLE 2. COMPARISON OF THE EXPERIMENTAL AND ESTIMATED PERMEABILITIES THROUGH VYCOR POROUS GLASS

Gas	T(°K.)	$Q \times 10^6$ (estimated)	$Q \times 10^6$ (experimental)	Investigator
Kr	294	3.55	3.4	Barrer *(1)*
C_2H_4	304.2	8.0	8.2	Huckins *(8)*
C_3H_6	298.2	8.47	8.00	Gilliland *(4)*
n-C_4H_{10}	308.2	12.9	13.0	Higashi *(5)*

DISCUSSION AND CONCLUSION

It is found that the gas-solid interaction energy can be correlated better with the critical properties than with the Lennard-Jones parameters.

Even though straight lines are obtained in Figures 1, 2 and 3, the slopes are different from unity which means that the quantities involved are not related by a simple proportionality.

Nevertheless, the estimated permeabilities from the present study agree exceptionally well with the experimental data.

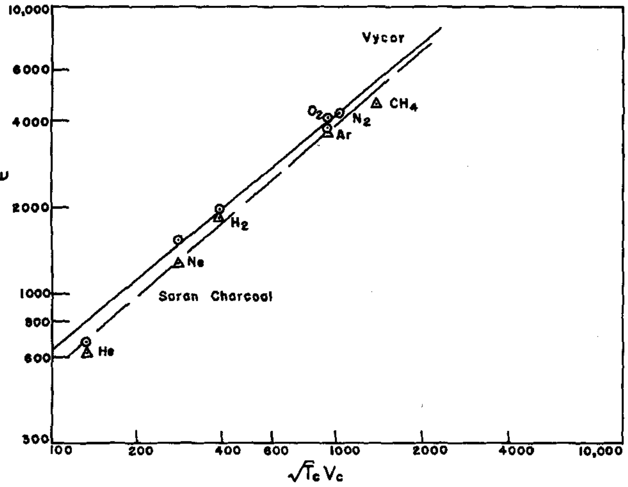

Fig. 3. Correlation of gas-solid interaction energies with the critical properties.

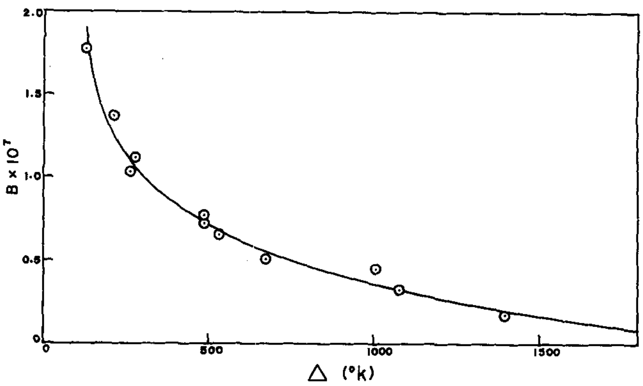

Fig. 4. Interrelationship between B and Δ.

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NOTATION

A = gas phase flow coefficient in Equation (1)
B = surface flow coefficient in Equation (1)
k = Boltzmann constant
M = molecular weight
Q = gas permeability, std.cc.-cm./sec.-sq.cm.-cm.Hg.
T = absolute temperature, °K.
v = specific volume, cc./g.-mole

Greek Letters

Δ = energy quantity defined by Equation (2), °K.
ϵ = potential minimum between the same kind of molecules
ϵ^* = gas-solid interaction energy, cal./g.-mole
$\epsilon^\dagger$ = activation energy of surface diffusion for an adsorbed molecule
σ = intermolecular separation, Å.

Subscripts

c = critical condition
g = gas

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