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Letter to the Editor

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Activated Diffusion of Gases in Solids

THE letter by R. B. ANDERSON and L. J. E. HOFER first submitted to the editor in March 1965¹ has just been brought to our attention. The letter suggests that activation energies reported by P. L. WALKER JR and co-workers^{2, 3} for diffusion of gases in zeolites and coals are too high because we should be concerned with the diffusion parameter $D^{1/2}/ar_0$ instead of $D^{1/2}/r_0$, where a is the constant in the adsorption isotherm equation $Q_\infty = aC$. Q_∞ and C are the concentration of adsorbed material at time infinity and the concentration in the gas phase. Since a decreases with increasing temperature, they say that by ignoring a in the diffusion parameter, activation energies calculated for D will thus be too large. We wish to comment briefly on our views of this situation.

As discussed in our recent chapter¹, there are two models of importance for diffusion in porous solids: the 'occluded gas' model and the 'adsorption-free gas' model. In the occluded gas model, the rate of diffusion is proportional to $\partial C/\partial x$, C being the concentration of occluded gas and x being distance in the diffusing direction. In the adsorption-free gas model, gas diffuses via 'free' molecules, with gas adsorbed on the walls of the pores acting as a reservoir which replenishes the free gas space. The rate of diffusion is proportional to $\partial C_1/\partial x$, where C_1 is the concentration of free gas.

The relation between C_1 and the total gas concentration C is

$$C = C_1\varepsilon + f(C_1) \quad \dots [1]$$

where ε is the open porosity within the particles of the solid which is filled with gas of concentration C_1 and $f(C_1)$ is the adsorption isotherm. If C_s is the amount of adsorbed gas at saturation and if the Langmuir isotherm for non-dissociative adsorption applies, then

$$C = C_1\varepsilon + [KC_1/(1 + KC_1)] C_s \quad \dots [2]$$

where K is the equilibrium constant of adsorption. At relatively low pressures and high temperatures, KC_1 will be small; the Langmuir isotherm reduces to a Henry's law form (amount adsorbed proportional to pressure) and

$$C_1 = C/(\varepsilon + KC_s) \quad \dots [3]$$

It is then readily shown that the effective diffusion coefficient \bar{D} is given by

$$\bar{D} = D/(\varepsilon + KC_s) \quad \dots [4]$$

where D is the true diffusion coefficient (independent of pressure). For

activated diffusion $D = D_0 \exp(-\Delta H^*/RT)$, where ΔH^* is the enthalpy of activation and D_0 the pre-exponential rate factor. The equilibrium constant K can be put as $K = K_0 \exp(-\Delta H_0/RT)$, where ΔH_0 is the enthalpy of adsorption.

The overall temperature dependence of the apparent diffusion coefficient for the 'adsorption-free gas' model is

$$\bar{D} = \frac{D_0 \exp(-\Delta H^*/RT)}{\varepsilon + C_s K_0 \exp(-\Delta H_0/RT)} \quad \dots [5]$$

At low temperatures and high pressures where the quantity of adsorbed gas is high relative to the amount of free gas, ε can be neglected giving

$$\bar{D} = (D_0/C_s K_0) \exp[-(\Delta H^* - \Delta H_0)/RT] \quad \dots [6]$$

This is the form used by Anderson and Hofer, with the symbols E' and E replacing ΔH^* and $(\Delta H^* - \Delta H_0)$, respectively. At higher temperatures where the quantity of adsorbed gas is small,

$$\bar{D} = (D_0/\varepsilon) \exp(-\Delta H^*/RT) \quad \dots [7]$$

For the 'occluded gas' model, the true diffusion constant is obtained and

$$D = D_0 \exp(-\Delta H^*/RT) \quad \dots [8]$$

applies under all conditions.

It is clear that in any investigation of activated diffusion it is necessary to determine which model applies before a precise meaning can be assigned to the overall energy of diffusion. There are several guides which can be used, including the following:

(1) Experimental results will only agree with analytical solutions of Fick's law when (a) the 'occluded gas' model applies or (b) the surface is not near saturation with adsorbed gas over the range of experimental conditions used. Since the surface must not be near saturation at the lowest experimental temperature used, then a considerable increase in temperature may produce a transition from equation 6 to equation 7. An Arrhenius plot of $\log \bar{D}$ versus $1/T$ will not be a straight line over a wide temperature range.

(2) For equation 6 to apply, it is necessary for a van't Hoff plot of $\log(Q_\infty - Q_0)$ versus $1/T$ to be a straight line, where $(Q_\infty - Q_0)$ is the quantity of gas adsorbed or desorbed at equilibrium for a given pressure differential.

(3) For equation 6 to apply, it is necessary for the amount of adsorbed gas to be greater than the amount of free gas in the pores. At the same time, the rate of diffusion is assumed to be controlled by the passage of free gas molecules over an activation energy barrier. If molecules can pass directly over the activation energy barrier from their adsorbed position, then the 'occluded gas' model applies. (This is activated surface diffusion with the rate-controlling energy barrier occurring at certain positions in the surface geometry and not between every adsorption position. For example, adsorbed

molecules may be able to move freely over the surface of the cavities of zeolite molecular sieves but not freely through the holes connecting the cavities.)

These three guides have been applied to experiments on the diffusion of inert gases through zeolites²⁻⁶. On the first count, linear Arrhenius plots were obtained over such temperature ranges as 230° to 400°C. Secondly, van't Hoff plots of the amount desorbed versus temperature were not linear. Thirdly, calculations of potential energy barriers indicated that the most favoured path was directly from potential energy troughs near the walls of the cavities (adsorption positions) through holes connecting cavities. It was concluded, therefore, that the 'occluded gas' model was applicable and that the different activation energies of diffusion were true energies.

In summary, our principal objection to the communication of Anderson and Hofer is that they *assume* equation 6 to be always applicable (not only to their own results but to those of the other workers they quote), whereas there is an alternative model leading to equation 8, the validity of which is supported by some experimental evidence. Anderson and Hofer consider activation energies of 10 kcal/mole as 'surprisingly large', but there seems no reason to us why the energy barrier of a large molecule passing through a small hole should not be large. In fact activation energies of this magnitude and larger have been theoretically predicted by us from potential energy calculations for rare gases diffusing through Type 3A zeolites¹.

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