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The role of adsorption on the observed temperature dependencies of diffusion coefficients

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Abstract

In measurements of diffusion coefficients of gases in porous solids by unsteady-state (transient) methods, adsorption on the walls of the pores affects the analysis. Failure to account for the net adsorption or desorption occurring during the perturbation associated with such measurements yields apparent diffusion coefficients that are lower than the true values. Moreover, the temperature dependence is not the relatively weak dependence expected from the kinetic theory of gases for true gas diffusion coefficients, even when the pores are orders of magnitude larger than molecular dimensions. Instead it is exponential in nature, being determined largely by the temperature dependence of the adsorption process occurring in the pores. Thus, the diffusion process seems to be an activated one, although in fact there may not be a true activation barrier.

The analysis presented in this paper appears to be very general, extending even to zeolites where the pore dimensions are of the order of molecular dimensions. It appears to account for the commonly reported observations in the literature that diffusion coefficients for gases in microporous solids obtained by transient methods can sometimes be as much as two to four orders of magnitude lower and can simultaneously exhibit temperature dependencies much stronger than those obtained under equilibrium conditions utilizing nuclear magnetic resonance. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Diffusion of molecules within porous materials is a necessary step in adsorption, separations, and heterogeneous catalytic processes. A fundamental understanding of the process of diffusion is important because the rate at which molecules access the interior space of a porous solid can sometimes control the performance of adsorbents, membranes and catalysts. Some of the most commonly used techniques for measuring diffusion coefficients in porous solids rely on a change in external pressure associated with a perturbation of the system from its equilibrium state. This pressure change is generally kept small to ensure that the measured diffusivity corresponds to conditions that remain essentially constant during the measurement. However, as a result of the pressure change, albeit small, these techniques operate under transient conditions where there may be a net adsorption or desorption of molecules occurring during the measurement. If the change in the number of molecules adsorbed on the surface, as a result of the pressure change, is not small compared to the change in the number of gas phase molecules in the pores, adsorption has a significant effect on the analysis. The key factors controlling the net adsorption or desorption of molecules are the adsorption relaxation frequency and the slope of the adsorption isotherm in the pressure region where

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the pressure change is applied [1]. The largest change in the number of molecules adsorbed or desorbed for a given pressure change is expected to occur in the low-pressure, Henry's law, region where the slope of the adsorption isotherm is highest.

In a recent theoretical and experimental study of diffusion via frequency response methods [1], we have demonstrated that concurrent equilibrated adsorption (i.e., when the adsorption relaxation frequency is much higher than the diffusion relaxation frequency) leads to an apparent diffusion coefficient of the form:

$$D(\mathrm{app}) = \frac{D}{1+\beta\cdot T\cdot \mathrm{d}\theta/\mathrm{d}P} \qquad (1)$$

In this equation, D(app) and D are the apparent and true values of the diffusion coefficient, respectively. θ is the surface coverage at the temperature T and pressure P of the experiments and β is a quantity that is proportional to the adsorptive capacity of the solid at saturation. This equation clearly shows that adsorption leads to apparent diffusion coefficients that are smaller than the true values. The value of D(app) depends on the slope of the adsorption isotherm. For non-adsorbing gases, the values of D(app) and D are identical. When $\beta{\cdot}T{\cdot}\mathrm{d}\theta/\mathrm{d}P$ is small compared to unity, they are not very different. As $\beta{\cdot}T{\cdot}\mathrm{d}\theta/\mathrm{d}P$ increases, however, the difference between D(app) and D becomes more evident and can be very large. For example, in measurements of diffusion of gases in mesoporous silica particles, we have found that for N_2 at high temperatures (573 K) the value of D(app) is nearly the same as D. For isobutane around ambient temperature (308 K), on the other hand, D(app) is about one order of magnitude smaller than D. In general, the ratio of D(app) to D decreases as the temperature and pressure decreases and is strongly dependent on the nature of the porous solid and of the diffusing molecule.

The relationship between D(app) and D given in Eq. (1) is not a result that is unique to frequency response techniques. The same equation applies to other transient diffusion measurement methods that rely on an external pressure change. Eq. (1) is simply the result of a material balance that accounts for the total number of molecules (gas + surface) that are transported into or out of the porous solid when the external pressure is changed. In fact, also in the context of transient diffusion measurements, a similar expression was derived by Barrer and Grove [2] many decades ago and later by Ruthven and Derrah [3].

Note that in addition to accounting for the observed diffusion coefficient being lower than the true value, Eq. (1) can also account for the effect of adsorption in masking the true temperature dependence of the diffusion coefficient. An analysis of this effect is the subject of the present paper.

2. Mathematical derivation and analysis

A simple inspection of Eq. (1) indicates that the apparent diffusion coefficient potentially combines the temperature dependencies of the diffusion and the adsorption process and this effect should become more apparent as the quantity $\beta{\cdot}T{\cdot}\mathrm{d}\theta/\mathrm{d}P$ becomes larger than unity. In fact, a closely related example of this coupling in temperature dependencies is that of unimolecular reactions on catalytic surfaces where the adsorption process can lead to apparent activation energies that are much lower than their intrinsic values. By analyzing the low coverage region of a Langmuir surface, Hinshelwood [4] demonstrated that the true activation energy of the reaction is reduced by the heat of adsorption of the molecules on the catalytic surface. The underlying arguments in the analysis of the present (diffusion + adsorption) case are so closely related to the (reaction + adsorption) case treated by Hinshelwood [4] that a parallel development offers some pedagogical benefits.

The analysis presented here is limited to a unimolecular surface reaction and the adsorption process is assumed to be equilibrated and to be described by a Langmuir adsorption isotherm. The following expressions can be written for the rate of the catalytic reaction and the diffusion flux within the porous solid:

$$\text{Catalytic rate} = k\cdot\theta \qquad (2)$$

$$\text{Diffusion flux} = \left(\frac{D}{1+\beta\cdot T\cdot \mathrm{d}\theta/\mathrm{d}P}\right)\nabla c \qquad (3)$$

In these equations, k is the intrinsic kinetic rate constant and ∇c is the concentration gradient. Assuming that θ is given by the Langmuir adsorption isotherm in Eqs. (2) and (3), we obtain:

$$\text{Catalytic rate} = k\cdot\left(\frac{KP}{1+KP}\right) \qquad (4)$$

$$\text{Diffusion flux} = \left(\frac{D}{1+\beta \cdot T \cdot K/(1+KP)^2}\right)\nabla c \tag{5}$$

In the limit of high pressure, these equations reduce to:

$$\text{Catalytic rate} = \text{k} \tag{6}$$

$$\text{Diffusion flux} = D \cdot \nabla c \tag{7}$$

Therefore, when the surface is saturated, the temperature dependencies of the reaction and diffusion processes become their respective intrinsic values. The catalytic rate becomes independent of pressure and the experimental activation energy for the reaction is the true activation energy for the surface reaction step. Similarly, in the diffusion case, the net adsorption vanishes and therefore the temperature dependence is solely that of diffusion through the pore space.

In the low pressure region, on the other hand, the kinetic rate constant and the diffusion coefficient become apparent values that incorporate the adsorption equilibrium constant K:

$$k(\text{app}) = k \cdot K \tag{8}$$

$$D(\text{app}) = \frac{D}{1+\beta \cdot T \cdot K} \tag{9}$$

In situations where $\beta \cdot T \cdot K \gg 1$, Eq. (9) can be rewritten as:

$$D(\text{app}) = \frac{1}{\beta} \cdot \left(\frac{D}{TK}\right) \tag{10}$$

In order to extract the ultimate temperature dependencies of k(app) and D(app), we need expressions for k, K, and D. Diffusion processes generally exhibit a weak temperature dependence that can be derived from the kinetic theory of gases. Thus, for example, depending on whether the mean free path of the molecules is larger or smaller than the characteristic pore sizes, these temperature dependencies become $T^{1/2}$ and $T^{3/2}$ in the Knudsen and molecular diffusion regimes, respectively. The equations that follow, therefore, consider a temperature dependence of the form T^n. As discussed later, the conclusions obtained from this T^n dependence remain unchanged if the process of diffusion involves instead an activation energy barrier.

The temperature dependencies of k, K, and D can therefore be expressed as:

$$k = k_{\text{o}} \cdot \mathrm{e}^{-E_{\text{r}}/RT} \tag{11}$$

$$K = \mathrm{e}^{\Delta S/R} \cdot \mathrm{e}^{Q/RT} \tag{12}$$

$$D = D_{\text{o}} \cdot T^n \tag{13}$$

Here, E_{r} is the true activation energy of the catalytic reaction and ΔS and Q are the entropy and heat of adsorption, respectively. By incorporating the above equations into the expressions for k(app) and D(app) we obtain:

$$k(\text{app}) = k_{\text{oo}} \cdot \mathrm{e}^{-(E_{\text{r}}-Q)/RT} \tag{14}$$

$$D(\text{app}) = D_{\text{oo}} \cdot T^{n-1} \cdot \mathrm{e}^{-Q/RT} \tag{15}$$

Here, k_{oo} and D_{oo} are new coefficients that depend on the values of k_{o}, D_{o}, R, β and ΔS.

Eqs. (14) and (15) clearly show that adsorption modifies the true temperature dependencies of the reaction and diffusion processes. As previously demonstrated by Hinshelwood [4], the true activation energy of the reaction is reduced by the heat of adsorption. In the case of diffusion, on the other hand, the temperature dependence is augmented by an exponential involving the heat of adsorption. Eq. (15) suggests that transient diffusion techniques that do not explicitly separate the adsorption from the diffusion process in the analysis measure an overall temperature dependence that is dominated by the heat of adsorption and not by the diffusion process. In fact, using frequency response experiments, we have simultaneously measured the true temperature dependence of the diffusion process and the heats and entropies of adsorption for N_2, Xe, and isobutane on mesoporous silica particles [1]. Our results show that the diffusion coefficients correctly exhibit the $T^{1/2}$ dependence expected in the Knudsen regime that is applicable at the conditions of our experiments. Moreover, the heats of adsorption are consistent with values normally expected. Finally, the entropies of adsorption indicate a loss of one degree of translational freedom, as would be expected for adsorption processes that are physical rather than chemical in nature.

3. Conclusions

The analysis presented in this paper shows how the determination of diffusion coefficients of gases in porous solids by unsteady state (transient) methods is influenced by adsorption on the walls of the pores. Failure to account for the net adsorption or desorption occurring during the perturbations of a variable such as pressure introduced in such measurements yields apparent diffusion coefficients that are lower than the true values. Moreover, the temperature dependence of these apparent diffusivities is not the relatively mild one expected from the kinetic theory of gases for true gas diffusion coefficients, even when the pores are one or two orders of magnitude larger than molecular dimensions. Instead, the temperature dependence is exponential in nature and is determined largely by the temperature dependence of the adsorption process occurring in the pores. Thus, the diffusion process may seem to be an activated one, although in fact there is no activation barrier at all.

Our analysis provides a simple explanation for the commonly reported observations in the literature that diffusion coefficients for gases in porous solids obtained by transient methods can sometimes be much lower than those obtained under equilibrium conditions utilizing nuclear magnetic resonance [5]. It also accounts for the observations that transient methods sometimes exhibit much stronger temperature dependencies of the diffusivities than the latter type of measurement [5].

The important features of the present analysis have been anticipated in large part by Barrer and Grove [2] a long time ago and somewhat later by Ruthven and Derrah [3] for porous solids having pore sizes much larger than molecular dimensions. However, we have observed that the analysis extends even to zeolites in which the pore dimensions are of the order of molecular dimensions. An account of this work is currently in preparation for publication elsewhere. In extending the analysis to zeolites, we have simply applied the same phenomenological description of diffusion used for mesoporous solids to the case where the pores are of molecular dimensions. In doing so, we find that the magnitudes of the diffusion coefficients obtained in such an analysis, as well as the temperature dependencies of these coefficients, are consistent with results on these quantities obtained from measurements under equilibrium conditions employing nuclear magnetic resonance [5]. This supports the validity of extending the phenomenological analysis to the much smaller pores characteristic of zeolites. As far as we know, this does not seem to have been done previously. For microporous solids, it has been common practice to formulate the analysis of the diffusion process differently, considering only adsorbed species [6]. That is, an entity corresponding to the gas phase in the pores of a mesoporous solid is no longer included in the analysis of microporous solids. When this is done, the correspondence of results obtained by transient methods with those obtained under equilibrium conditions by nuclear magnetic resonance is very poor. Thus, despite any conceptual difficulties involving a gas phase in pores of molecular dimensions, it appears that the phenomenological description of diffusion in porous solids remains unchanged down to this level of pore sizes.

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