

ACTIVATED DIFFUSION OF METHANE IN COAL

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Unsteady state diffusion of methane in powdered coal has been measured by two experimental approaches. In the first, methane diffused out of a sample previously equilibrated with methane at about 1.5 atmospheres to a space maintained at a constant pressure of one atmosphere. Unsteady state diffusion is relatively insensitive to particle shape and so coal particles could be treated as spheres of equivalent volume as that of the actual particles. The well known (1) solution of Fick's Law for a concentration independent D , under the boundary conditions imposed by the experimental technique, has been used to determine the micropore diffusion parameter ($D^{1/2}/r_0$). In the second method, the rate of sorption of methane into degassed samples was measured. The pressure change during the measurements was in the range of eight to two atmospheres. It has been shown by Barrer (2) that if the diffusion coefficient is concentration independent and if the isotherm obeys Henry's Law, then for a constant volume but variable pressure system, the solution of Fick's Law for very small times reduces to the following equation:

$$\frac{Q_t}{Q_\infty} = \frac{Q_0}{(Q_0 - Q_\infty)} \frac{6}{r_0} \sqrt{Dt/\pi}$$

where Q_0 = quantity of gas initially in the gas phase
 Q_t and Q_∞ = adsorption at $t = t$ and $t = \infty$
 D = diffusion coefficient.

The above expression differs from the solution of Fick's Law in the constant pressure case only by the factor $Q_0/(Q_0 - Q_\infty)$. The micropore diffusion parameter was obtained in this case from the initial slope of Q_t/Q_∞ vs \sqrt{t} plots. Satisfactory agreement was obtained between the values of the micropore diffusion parameter obtained by the two methods.

Twelve samples of (100x150) mesh coals of volatile matter ranging from 4 to 40% (d.a.f.) and three sizes, (42x65), (65x100) and (100x150), of two anthracites were used in this study. Adsorption isotherms of methane up to a pressure of 15 atmospheres in the temperature range 25 to 75°C were measured on an anthracite and two bituminous coals. The isotherms for the two bituminous coals are linear with pressure, but for the anthracite there is a slight bending towards the pressure axis. However, over a smaller pressure range the isotherms approximate Henry's Law behavior. In agreement with earlier findings, (3) anthracite adsorbs more methane compared to the bituminous coals under the same experimental conditions. For the (100x150) mesh samples, diffusion was measured over the temperature range 50 to 150°C; and for the (42x65) and (65x100) mesh sizes, the temperature range was 120 to 300°C. It was found that methane diffusion was activated for all samples. The activation energy of diffusion was obtained from the slope of $\ln(D^{1/2}/r_0)$ vs $1/T$ plots. It was found that in cases where the temperature range of measurement was more than 100°C the slope becomes greater at higher temperatures.

Two distinct physical models (4) might be applicable in the methane-coal system. In the first, the gas held by the solid can be considered to be in an occluded state (one phase). In the second, the gas might be in two phases:

1) as relatively free molecules in the open porosity, 2) as relatively non-mobile molecules present on the internal surface of the solid. In both cases the same differential equation results, but the diffusion coefficient \bar{D} of the second model is related to D for the first model by the relation

$$\bar{D} = D/(\epsilon + KC_g)$$

where ϵ = open porosity

K = equilibrium constant of adsorption

C_g = adsorption at saturation

It can be shown that for the first model the slope of the Arrhenius plot should be constant and for the second model at low temperatures, where the quantity of adsorbed gas is high, the porosity term would be negligible and the heat of adsorption would be added to the true activation energy. At higher temperatures, the contribution of heat of adsorption would diminish. Therefore, as the temperature is increased, the slope of the Arrhenius plot should become smaller in magnitude for the second model. The results obtained tend to show that the first model is still generally applicable, but at higher temperatures pores of smaller diameter start contributing significantly. It might be added, however, that in the case of (100x150) mesh samples relatively good straight line plots were obtained in the temperature range 50 to 150°C.

For the twelve samples, the values of activation energy vary from 3.5 kcal/mole for an anthracite of 4.2% V.M. to 5.2 kcal/mole for an anthracite of 9.0% V.M. The activation energy does not change significantly in the bituminous range, with a value of about 7.0 kcal/mole being obtained for the six samples studied. These results are in disagreement with those of the argon-coal system, (5) where a maximum in activation energy appears in the range of good coking coals. A probable explanation could be found by considering the following. The activation energy is related to the interaction energy of the gas-solid system. The interaction energy is a strong function of the geometry (pore diameter) of the solid as well as its chemical nature. Making a gross simplification, one can imagine that on the pore surface of a high rank coal, like anthracite, the predominant atomic species would be carbon. As the rank becomes lower the carbon atoms are being substituted by oxygen groups on the surface. Therefore, the change in chemical nature of the surface atoms may mask the effect of pore geometry to some extent. This change is likely to alter methane diffusion more than that of argon as the methane molecule is more polarizable. (6) Other complicating factors are the size distribution in the micropores and the presence of different petrographic constituents in bituminous coals.

Diffusion parameters obtained from three sieve sizes of the two anthracites tend to give higher activation energies for the larger particles. Evaluation of the diffusion coefficient (D) from the experimental diffusion parameter ($D^{1/2}/r_0$) poses problems because of the difficulty in estimating the diffusion path length (r_0). As the diffusion path length should be temperature independent, the value of activation energy should not be affected. Different approaches for the estimation of r_0 are indicated.

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