ON RITCHIE’S EQUATION FOR ADSORPTION KINETICS OF GASES ON SOLIDS

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Ritchie’s equation for the kinetic adsorption isotherm has been derived on the basis of the theory describing the kinetics of adsorption of gases on energetically heterogeneous solid surfaces. This equation has also been generalized to the kinetics of adsorption of multicomponent gas mixtures.

Recently Ritchie /1/ derived an equation for the adsorption kinetics of single gases on solids by assuming the homogeneity of the adsorbent surface. This equation gives very good agreement with the experimental data of Austin et al. /2/, Bansal et al. /3/, Samuel and Yeddanapalli /4/, and Deitz and Turner /5/. It will be shown here that Ritchie’s equation, which is an alternative to the Elovich equation, may be derived on the basis of the theory describing the adsorption kinetics of gases on heterogeneous solid surfaces /6–9/. In this paper we shall also generalize this equation to the adsorption kinetics of multicomponent gas mixtures.

The approach presented by Crickmore and Wojciechowski /6/, concerning the adsorption kinetics of single gases on energetically heterogeneous solid surfaces, leads to the following formulation of the sorption rate law:

\[
\frac{d\theta}{dt} = R^a - R^d = \frac{k^a}{p(1 - \theta)^{w+1}} - \frac{k^d}{\theta^{m+1}}
\]  

(1)
where $\theta$ is the monolayer surface coverage of a single gas at time $t$, $p$ is the adsorbate pressure, $R^a$ and $R^d$ are rates of adsorption and desorption, respectively, $w$ and $m$ are exponents of the functions approximating the adsorption and desorption rates of single gases on energetically heterogeneous solid surfaces, respectively. The last two constants may be treated as parameters of adsorbent heterogeneity measured with respect to the activation energies of adsorption and desorption.

In the case of $R^a \gg R^d$, eq. (1) reduces to the following expression:

$$\frac{d\theta}{dt} = \frac{R^a}{k^a p} (1 - \theta)^{w+1}$$  \hspace{1cm} (2)

After integration of eq. (2), we obtain the equations proposed by Ritchie /1/:

$$(1 - \theta)^{-w} = \frac{w}{k^a p t} + 1 \quad \text{for } w > 0 \hspace{1cm} (3)$$

or

$$\theta = 1 - \exp(-\frac{k^a p t}{w}) \quad \text{for } w = 0 \hspace{1cm} (4)$$

An interesting equation is obtained for $w = 1$, when we have

$$(1 - \theta)^{-1} = \frac{k^a p t}{w} + 1 \quad \text{for } w = 1 \hspace{1cm} (5)$$

Thus, Ritchie's equations are valid if all assumptions leading to eq. (1) and the condition $R^a \gg R^d$ are satisfied. The last condition is also assumed in the derivation of Elovich's equation.

Generalization of eq. (1) to the adsorption kinetics of multicomponent gas mixtures on heterogeneous solid surfaces gives the following sorption rate law /7-9/:

$$\frac{d\theta_i(n)}{dt} = \frac{R^a}{I_i(n)} - \frac{R^d}{I_i(n)} = \frac{k^a}{k_i} p_i (1 - \theta_i(n))^{w+1} - \frac{m_{ij}}{k_i} \theta_i^{m_i + 1}$$  \hspace{1cm} (6)