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Jovanović Adsorption Isotherm for Gaseous Mixtures

Short Communication

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A derivation of the *Javanović* isotherm for mono and multilayer adsorption of gaseous mixtures was obtained.

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Jovanović-Adsorptions-Isotherme für Gasmischungen (Kurze Mitteilung)

Es wird die Ableitung der *Jovanović*-Adsorptionsisotherme für mono- und multimolekulare Adsorption angegeben.

In 1969 *Jovanović*[1] proposed an interesting adsorption theory. This adsorption model takes into account two additional types of collisions of molecules as distinct from the *Langmuir* theory. In the first case an impinging molecule strikes another one witch is already adsorbed. The molecule is reflected after an elastic collision. In the second case a molecule encounters another one that leaves the surface at the moment of collision. After elastic collision the incoming molecule will be reflected exchanging its kinetic energy with the desorbing molecule, which is sent back to the surface and readsorbed.

According to *Jovanović* the number of adsorbed molecules varies in the adsorption process, due to rapid fluctuations of molecules. Consequently in the equilibrium state the number of settled molecules on the surface fluctuates in the vicinity of the equilibrium amount.

Jovanović obtained the following equations on the basis of this model:

$$\Theta = 1 - \exp(-a p) \tag{1}$$

for monolayer adsorption, and for multilayer adsorption:

$$\Theta = [1 - \exp(-ap)] \exp(bp) \tag{2}$$

where a and b are constants and other symbols have usual designations.

We shall consider now the adsorption of one component from a mixture of gases on the basis of the *Jovanović* model.

To find the number of desorbed molecules we divide the settling time into k intervals $\Delta\tau$. In the $\Delta\tau_k$ interval the number of desorbed molecules will be:

$$N_{i,k}^{*} = \left[N_i \left(1 - \Delta\tau \sum_{i=1}^{n} \varphi_i p_i \sigma_i \right)^k \right] \Big/ k \tag{3}$$

The total number of desorbed molecules within τ, when k increases to infinity is given by:

$$N_i^{*} = N_i \exp\left(- \sum_{i=1}^{n} a_i p_i \right) \tag{4}$$

where $a_i = \tau \varphi_i \sigma_i$; $\varphi = 1/(2\pi M kT)^{1/2}$

The number of adsorbed molecules within $\Delta\tau_k$ will be:

$$N_{i,k}^{**} = \varphi_i p_i \Delta\tau \left(1 - \sum_{i=1}^{n} \Theta_i \right) \left(1 - \Delta\tau \sum_{i=1}^{n} \varphi_i p_i \sigma_i \right)^{k-1} \tag{5}$$

The total number of adsorbed molecules within τ is given by:

$$N_i^{**} = \sum_{j=1}^{k} N_{i,j}^{**} = \varphi_i p_i \Delta\tau \left(1 - \sum_{i=1}^{n} \Theta_i \right) \sum_{j=0}^{k-1} \left(1 - \Delta\tau \sum_{i=1}^{n} \varphi_i p_i \sigma_i \right)^j \tag{6}$$

When k increases to infinity:

$$N_i^{**} = \frac{a_i p_i \left(1 - \sum_{i=1}^{n} \Theta_i \right)}{\sigma_i \sum_{i=1}^{n} a_i p_i} \left[1 - \exp\left(- \sum_{i=1}^{n} a_i p_i \right) \right] \tag{7}$$

The equality $N_i^{**} = N_i^{*}$ gives

$$\frac{a_i p_i \left(1 - \sum_{i=1}^{n} \Theta_i \right)}{\sigma_i \sum_{i=1}^{n} a_i p_i} \left[1 - \exp\left(- \sum_{i=1}^{n} a_i p_i \right) \right] =$$

$$= N_i \exp\left(- \sum_{i=1}^{n} a_i p_i \right) \tag{8}$$

Substituing $N_i \sigma_i = \Theta_i$ and summing up this equation for all components we get:

$$\sum_{i=1}^{n} \Theta_i = 1 - \exp\left(-\sum_{i=1}^{n} a_i p_i\right) \tag{9}$$

From equations (8) and (9) we obtain

$$\Theta_i = \frac{a_i p_i}{\sum_{i=1}^{n} a_i p_i}\left[1 - \exp\left(-\sum_{i=1}^{n} a_i p_i\right)\right] \tag{10}$$

It is the isotherm for the monolayer adsorption from gaseous mixtures. To describe the multilayer adsorption we apply the *Hüttig* mechanism[2]. For m-th layer and i-th component in equilibrium state we can write:

$$a_{i,m} p_i \left(\sum_{i=1}^{n} \Theta_{i,m-1} - \sum_{i=1}^{n} \Theta_{i,m}\right)\left[1 - \exp\left(-\sum_{i=1}^{n} a_{i,m} p_i\right)\right] = \Theta_{i,m}\left(\sum_{i=1}^{n} a_{i,m} p_i\right)\exp\left(-\sum_{i=1}^{n} a_i p_i\right)$$

Assuming

$$a_{i,2} = a_{i,3} = \ldots = a_{i,m} = b_i \tag{12}$$

$$\frac{\Theta_{i,1}}{\sum_{i=1}^{n} \Theta_{i,1}} = \frac{\Theta_{i,m}}{\sum_{i=1}^{n} \Theta_{i,m}} \tag{13}$$

and calculating total adsorption for all layers when m increases to infinity we obtain the isotherm for the multilayer adsorption:

$$\Theta_i = \frac{a_i p_i}{\sum_{i=1}^{n} a_i p_i}\left[1 - \exp\left(-\sum_{i=1}^{n} a_i p_i\right)\right]\exp\left(\sum_{i=1}^{n} b_i p_i\right) \tag{14}$$

For the case of total adsorption, equations (10) and (14) take the same form as the ones obtained by *Jaroniec*[3,4].

References

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