

KINETICS OF ADSORPTION AND DESORPTION IN SOLID-GAS SYSTEMS AND THE LOGARITHMIC RATE LAW

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A model for explaining the logarithmic rate law used in adsorption and desorption phenomena of gases on or from solid surfaces is presented. This model is based on the sites number variation of the surface.

INTRODUCTION

The formal kinetics of adsorption in solid-gas systems is determined by the logarithmic rate law used either in its integral form:

$$q = \frac{1}{b} [\ln(t + t_0) - \ln t_0] \quad (1)$$

or in its differential one:

$$\frac{dq}{dt} = a \exp(-bq) \quad (2)$$

where q is the adsorbed gas quantity at the t moment, a and b are constants and $t_0 = \frac{1}{ab}$ if for $t=0$, $q=0$. The differential form of the logarithmic law can be also represented by an other form of equation, namely:

$$\frac{dq}{dt} = \frac{1}{b} \cdot \frac{1}{t + t_0} \quad (3)$$

All these forms (1) – (3) have been intensively studied¹⁻⁶ and three classes of models based on: sites number variation; variable activation energy or nonuniform surfaces have been proposed for the explanation of this law.

The aim of the present paper is to describe a new model describing the logarithmic temporal behavior of the adsorption and desorption in solid-gas systems.

THE MODEL

The adsorption process of gases onto solid surfaces is assimilated with a probabilistic discontinuous process q , which progresses in discrete steps in a background of fluctuations.

If each forward gas adsorption step is assumed to decrease the number of free sites p , a hypothesis which can be easily admitted, then the further step of adsorption occurs by an amount proportional with the inverse number of free sites. In these conditions, the model is represented by the following system of equations:

$$\begin{aligned} \frac{dq}{dt} &= Np \\ -\frac{dq}{dp} &= \frac{k}{p} \end{aligned} \quad (4)$$

where N represents the number of impacts of gas molecules with the surface expressed per unit area and unit time and k a constant >0 .

By integrating the second equation of system (4), with the conditions $q=0$, $p=p_0$, p_0 being the total number of free sites, one obtains:

$$-q/k = \ln p/p_0 \quad (5)$$

or

$$p = p_0 \exp(-q/k) \quad (6)$$

Using relationship (6) the first equation of system (4) becomes:

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$$dq/dt = N p_0 \exp(-q/k) \quad (7)$$

which is nothing else than the differential form (2) of the logarithmic rate law, which by integration leads to the equation (1).

The model represented by the system (4) can also describe, with some modification, the logarithmic law of gas desorption from solid surfaces.

Let the modified system (4) be:

$$\begin{aligned} -\frac{dQ}{dt} &= Np \\ \frac{dQ}{dp} &= k/p \end{aligned} \quad (8)$$

in which Q represents the desorbed gas quantity. In this case, each desorption step is assumed to increase the number of free sites p .

By integrating the second equation of system (8) with the conditions $Q=0$, $p=p_0$, p_0 being now the total number of free sites which are not covered by the adsorbed gas, it results:

$$p = p_0 \exp(Q/k) \quad (9)$$

and, by using relationship (9), the first equation of system (8) becomes:

$$-dQ/dt = Np_0 \exp(Q/k) \quad (10)$$

Equation (10) is nothing else than the logarithmic rate law of desorption, which, also by integration on obtains the integral law of desorption which has the form:

$$Q = \frac{1}{b} [\ln t_0 - \ln(t + t_0)] \quad (11)$$

So, following the rate of appearance or disappearance of free sites in time and the rate of decreasing or increasing respectively of the adsorbed gas with the inverse of free sites number one obtains both logarithmic rate laws of adsorption or desorption of gases on or from solid surfaces.

The impossibility to propose an adsorption or desorption mechanism only on the basis of fitting the experimental data with the logarithmic equation can be due to several reasons: the existence of two different differential equations, each based on an other model, leading to the same integral equation of the logarithmic law,⁷ the generalized Landsberg's model,⁸ the existence of a surface heterogeneity,^{9,10} the existence of conditions

in which a logarithmic law represents nothing else than a sum of other logarithmic equations,¹¹ the model based on the association of active sites,¹² the existence of an extra energy obtained during the formation of the solid surface^{13,14} or the surface charge transfer phenomena at the solid gas interface.¹⁵⁻²⁰

In order to built a realistic model for a logarithmic rate law of gas adsorption or desorption on/from solid surfaces one has to identify the relevant elementary steps composing its mechanism. Several models and mechanisms exist, but probably only few of them can be regarded as representing a realistic situation.

It must also be mentioned that the simple logarithmic rate law is not sufficiently flexible, the deviations in the initial stages of adsorption or desorption, discontinuities in the (q or $Q/\ln t$) plots or rates of readsorption on surfaces containing adsorbed gas cannot be explained without further assumption. The simple models describe only the normal behavior of adsorption or desorption phenomena in solid-gas system. The problem still remains open.

CONCLUSIONS

The logarithmic rate law experimentally observed in adsorption or desorption of gases on/ from solid surfaces can be explained by a simple model based on the sites number variation of the surfaces.

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