



CONCERNING THE FORMAL KINETICS OF GAS ADSORPTION ON SOLID SURFACES

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Two differential forms of the integrated logarithmic rate law could be obtained directly from one to the another. In the Landsberg's model of this law this fact is not possible without a further calculation. These Landsberg's equations have some particularities which are presented and discussed.

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

INTRODUCTION

The formal kinetics of gas adsorption on solid surfaces is usually determined by the logarithmic rate law:

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

This logarithmic rate law can be obtained from two different differential equations, namely:

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

and

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

where q is the adsorbed gas quantity at the t moment, a , b are constants and $t_0 = \frac{1}{ab}$ if $t=0$, $q=0$ in case of equations (1) and (2); in case of equation (3) when $t=0$, $q \neq 0$ and b is a constant. Equation (1)

was obtained first by Tamman¹ and was studied later by Zeldovich², Roginsky³ and Elovich³.

In this paper we intend to study some problems concerning the logarithmic law in the forms of equations (1)–(3).

THE MODEL

Let be the logarithmic law presented in relation (1). From this equation one can obtain by differentiation:

$$\frac{dq}{dt} = \frac{1}{b} \cdot \frac{1}{t + t_0} \quad (4)$$

From relation (1) one obtains also:

$$\ln(t + t_0) - \ln t_0 = qb \quad (5)$$

or

$$t + t_0 = t_0 \exp(bq) \quad (6)$$

Using equation (6) introduced in relation (4) leads to

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$$\frac{dq}{dt} = \frac{1}{bt_0} \exp(-bq) \quad (7)$$

And so, the two differential form of logarithmic equation (1), namely equations (2) and (3), are connected, both being obtained from the right or left term of equation (6). This means that these two differential equations (2) and (3) are not disconnected and, by a simple calculus, they can be obtained from one to another. Also, equation (1) is obtained directly by integration of equation (3) but in case of equation (2) the integration is not sufficient.

Another problem is represented by the fact that the constants a and b are not really constants but may vary with pressure or temperature and so some discontinuities will be reflected in equations (1)–(3).

The old model of the logarithmic law presented by Landsberg⁵, is:

$$\frac{dq}{dt} = Np \quad (8a)$$

$$-\frac{dp}{dt} = kp^2 \quad (8b)$$

where N is the number of events per unit time which are capable of carrying the process forward, but having only a probability, p , of occurring and k is a constant. This model can be connected with equation (2) because from equation (2) and (8a) one obtains p mathematically without to consider any physico-chemical process.

$$\frac{dp}{dt} = -b \frac{dq}{dt} \cdot \exp(-bq) = -bNp \cdot p = -bNp^2 \quad (9)$$

where the constant a being included in N and $b \equiv k$.

The two forms of differential equation (2) and (8a) are only formal different and they can describe one or other experiment. The mechanism of the reaction determines the use of one or another equation of these models.

Another problem connected with the Landsberg's model is what happens when instead of p a function $f(p)$, where $f(p)$ may be any function which can be differentiated, is used. Then the model becomes:

$$\frac{dq}{dt} = N \cdot f(p) \quad (10a)$$

$$\frac{df}{dp} \frac{dp}{dt} = f^2(p) \cdot (-k) \quad (10b)$$

The equation (10b) is now:

$$\frac{df}{dt} = -kf^2(p) \quad (11)$$

or

$$\frac{df}{f^2(p)} = -kdt \quad (12)$$

By integration of this last equation (12) one obtains:

$$-\frac{1}{f(p)} = -k(t + t_0) \quad (13)$$

with t_0 a constant.

Using equation (13) in equation (10a) it results:

$$\frac{dq}{dt} = \frac{kN}{t + t_0} \quad (14)$$

similar to equation (3) and finally the logarithmic law.

Till now there are not general models for the explanation for the logarithmic law used in adsorption of gases on solid surfaces.⁶ All the forms of this law presented in equations (1)–(3) have been studied and three classes of models have been proposed:⁷⁻¹² the site number variations, the existence of a variable activation energy and the presence of a non-uniform surfaces. These means the non-equivalence of the physico-chemicals models which lead to the (1)–(3) forms of the logarithmic equation. Also, these equations (1)–(3) are not sufficiently flexible because there are deviations in the initial stage of adsorption, discontinuities in the $(q, \log t)$ plots, rates of adsorption on surfaces containing residual adsorbate or the effects of pressure and temperature.

The existence of many models explaining the solid-gas adsorption phenomena is a reason for the impossibility to propose a model only on the basis of fitting the experimental data with a realistic model for a logarithmic law. In order to built a realistic model for a logarithmic rate law of gas adsorption on solid surfaces the relevant elementary steps comparing its mechanism must be identified. Till now only simple models describe the normal behavior of gas adsorption on solid surfaces.

In Physics and also in Chemistry is not unusual to explain a result by several different hypotheses. That is why for the logarithmic equations (1)–(3) there are so many mechanisms to explain the law, because from this equation one cannot conclude about the mechanism of the studied reaction.

CONCLUSIONS

The differential forms of the integrated logarithmic rate law could be obtained directly from one to another. Using the Landsberg's model this fact is not possible without further calculation. These last equations of this model present some particularities concerning their obtaining and form which have been discussed.

From the logarithmic rate law one cannot conclude about the mechanism of the reaction.

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