



## KINETICS OF GAS SORPTION ON SOLID SURFACES

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Received October 28, 2021

A kinetic model proposed for the adsorption or desorption of gases on/from solid surfaces was proposed. Depending on the sign “+” or “-” of the kinetic model equations the results obtained are either a desorption or an adsorption process with the surface.

$$\pm \frac{1}{q} = \frac{1}{k} \ln t$$

### INTRODUCTION

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

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

where  $q$  is the adsorbed gas quantity at the  $t$  moment,  $a$ ,  $b$  are constants and  $t_0 = \frac{1}{ab}$  if  $t=0$ ,  $q=0$ .

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

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

and

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

In case of equations (3), when the experiment begins on a surface not totally clean then if  $t=0$ ,  $q \neq 0$ . Normally, all these laws (1)-(3) were obtained with kinetic models where one active site

is involved for one gas molecule sorbed. All the forms of this law presented in equations (1)-(3) have been studied.<sup>1-8</sup>

In this paper we intend to study some problems of a new kinetic model proposed earlier<sup>9</sup> for this law.

### THE MODEL

The proposed model is:<sup>9</sup>

$$\frac{dq}{dt} = Npq^2 \quad (4a)$$

$$\frac{dp}{dt} = kNp^2 \quad (4b)$$

where  $q$  is the gas quantity,  $N$  is the number of events per unit time which are capable of carrying the process forward, but having a probability  $p$  of doing it and  $a$ ,  $b$  are constants. The evolution of the process is presented in equation (4a), the physical signification of  $p$  being connected with the free surface sites.

From equation (4b) one obtains also:

$$\frac{dp}{p^2} = kNdt \quad (5)$$

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or, by integration of equation (5):

$$-\frac{1}{p} = kNt \quad (6)$$

and finally:

$$\frac{dq}{q^2} = -\frac{Ndt}{kNt} = -\frac{1}{k} \cdot \frac{dt}{t} \quad (7)$$

By a new integration, one obtains:

$$-\frac{1}{q} = -\frac{1}{k} \ln t \quad (8)$$

or

$$\frac{1}{q} = \frac{1}{k} \ln t \quad (9)$$

an inverse adsorption *i.e.* a desorption process.

If the number of gas molecules on a surface is a constant monolayer in a Langmuir approximation, then:

$$q_t = q_a + q_d \quad (10)$$

where  $q_t$  is the total gas quantity which could be considered as a constant,  $q_a$  the adsorbed gas on the surface and  $q_d$  the gas which can be desorbed from the surface according to the reaction:



with  $q_a, q_d < q_t$ .

In the case of  $q_a$ , then:

$$\frac{1}{q_t - q_a} = \frac{1}{k} \ln t \quad (12)$$

when  $t$  increases,  $(q_t - q_a)$  diminishes, the result is a cleaner surface due to a desorption process

In the case of  $q_d$ , then:

$$\frac{1}{q_t - q_d} = \frac{1}{k} \ln t \quad (13)$$

Now, when  $t$  increases,  $(q_t - q_d)$  diminishes, the result being a cleaner surface due to a decrease of the gas quantity and a gas adsorption can occur.

Let be now the system:

$$\frac{dq}{dt} = Npq^2 \quad (14a)$$

$$-\frac{dp}{dt} = kNp^2 \quad (14b)$$

With the same calculus as before one obtains with equation (14b):

$$\frac{1}{p} = kNt \quad (15)$$

and from equation (14a):

$$\frac{dq}{q^2} = \frac{1}{k} \cdot \frac{dt}{t} \quad (16)$$

or by integrating:

$$-\frac{1}{q} = \frac{1}{k} \ln t \quad (17)$$

an inverse desorption, *i.e.* an adsorption process.

But, using now the Langmuir approximation for  $q_t$  and using the same form of equations (12) and (13) but with the sign “-“ the result are in opposite: when  $(q_t - q_a)$  diminishes the result is a cleaner surface and a gas adsorption can start. In case of  $(q_t - q_d)$  as before a gas adsorption can occur.

A new system is:

$$-\frac{dq}{dt} = Npq^2 \quad (18a)$$

$$\frac{dp}{dt} = kNp^2 \quad (18b)$$

The solution of the system is obtained easily as for the first two systems of equations:

$$-\frac{1}{p} = kNt \quad (19)$$

and

$$-\frac{dq}{q^2} = \frac{1}{k} \cdot \frac{dt}{t} \quad (20)$$

or by integrating equation (20):

$$-\frac{1}{q} = \frac{1}{k} \ln t \quad (21)$$

an inverse desorption, *i.e.* an adsorption process.

Equations (17) and (21) are identical and the discussion of the first are the same for the second one.

The last system which is presented is:

$$-\frac{dq}{dt} = Npq^2 \quad (22a)$$

$$-\frac{dp}{dt} = kNp^2 \quad (22b)$$

Table 1

Equations obtained from proposed model

Sign of the first equation of the model	Sign of the second equation of the model	The resulted logarithmic of equation
+	+	desorption
+	-	adsorption
-	+	desorption
-	-	adsorption

The solution of this system are:

$$\frac{1}{p} = kNt \quad (23)$$

and using this last value of  $p$  to integrate equation (22a) one obtains:

$$\frac{1}{q} = \frac{1}{k} \ln t \quad (24)$$

In this case also, equation (24) is identical with equation (9) an inverse adsorption i.e a desorption process and has the same interpretation.

The results obtained for the solutions of every studied system are depending on the sign “-“ or “+” of the two equations which form the model. If the sign are the same, the obtained results are the same. The results are summarized in Table 1.

The model proposed in equations (4a) and (4b) starts from an old model of Landsberg<sup>10,11</sup> with two major modifications: the term  $q^2$  introduced in equation (4a) and the sign “+” of the equation (4b).

The existence of many models explaining the adsorption or the desorption phenomena of gases on solid surfaces is a reason for the impossibility to purpose a model only on the basis of fitting experimental data with logarithmic law. Some of these models are: the generalized Landsberg’s model<sup>10,11</sup>, the existence of a surface heterogeneity,<sup>12,13</sup> the model based on the association of active sites<sup>14</sup> or the charge transfer phenomena at the solid interface.<sup>15-22</sup> The Landsberg’s model and the association of active sites are based on the site number variations, the heterogeneity is based on non-uniform surfaces and the transfer phenomena on variable activation energy. The model proposed is only an example. Many models and mechanisms in physics and chemistry exist for the explanation of this law but only few of them are realistic. The problem with the logarithmic law seems to be not finished.

## CONCLUSIONS

The logarithmic law of adsorption or desorption of a gas monolayer on/from the surface can be described by the same proposed equation. The adsorption or desorption of gases depend on the sign “+” or “-“ of one equation of the proposed model. The obtained results were discussed.

## REFERENCES

1. C. Aharoni and F. C. Tompkins, *Adv. Catalysis*, **1970**, *20*, 1.
2. K. Hauffe and S. R. Morrison, “Adsorption” de Gruyter Verlag, Berlin, 1974, p. 87.
3. P. Fejes, “Contact Catalysis”, Z. G. Szabo and D. Kallo (Eds.), Akademiai Kiado, vol.1, Budapest, 1976, p. 225.
4. S. R. Morrison, “The Chemical Physics of Surfaces”, Plenum Press, New York and London, 1978, p. 46, 241.
5. E. I. Segal, C. Iditoiu, N. Doca and D. Fatu, “Cataliza si catalizatori”, Ed. Facla, Timișoara, 1986, p. 40.
6. E. I. Segal, N. I. Ionescu, D. M. Razus and I. N. Salageanu, “Cinetica reactiilor catalitice eterogene”, vol. I, Ed. Academiei Române, 1992, p. 87.
7. E. Angelescu and A. Szabo, “Cataliza Eterogena”, Ed. Brilliant, București, 1998, p. 103.
8. M. I. Temkin, *Adv. Catalysis*, **1979**, *28*, 173.
9. N. I. Ionescu and V. Bratan, *Re. Roum. Chim.*, **2021**, *66*, 239.
10. P. T. Landsberg, *J. Chem. Phys.*, **1955**, *23*, 1079.
11. P. T. Landsberg, *J. Chem. Phys.*, **1962**, *33*, 2251.
12. N. I. Ionescu, *Rev. Roum. Chim.*, **2008**, *53*, 535.
13. C. F. Cerofolini, *Z. Phys. Chem. (Leipzig)*, **1978**, *259*, 1020
14. N. I. Ionescu, *Bulg. Chem. Commun.*, **1992**, *25*, 39.
15. N. I. Ionescu, *Z. Phys. Chem., Neue Folge*, **1978**, *109*, 95.
16. N. I. Ionescu, *Rev. Roum. Chim.*, **1992**, *37*, 509.
17. N. I. Ionescu, *Rev. Roum. Chim.*, **1995**, *40*, 629.
18. N. I. Ionescu and M. Caldararu, *Rev. Roum. Chim.*, **2002**, *47*, 1213.
19. N. I. Ionescu and M. Caldararu, *Rev. Roum. Chim.*, **2006**, *51*, 521.
20. N. I. Ionescu and M. Caldararu, *Rev. Roum. Chim.*, **2011**, *56*, 853.
21. N. I. Ionescu, *Surf. Sci.*, **1976**, *61*, 294.

