



*Dedicated to the memory of  
Dr. Henry V. Kehiaian (1929–2009)*

## KINETICS OF GAS DESORPTION FROM SOLID SURFACES

Niculae I. IONESCU\*

“Ilie Murgulescu” Institute of Physical Chemistry of the Roumanian Academy  
202 Splaiul Independentei, 060021 Bucharest, Roumania

*Received May 18, 2010*

---

A model explaining the logarithmic rate law used for describing desorption phenomena of gases from solid surfaces is presented. The model is based on the concept of surface heterogeneity.

---

### INTRODUCTION

The formal kinetics of desorption in solid-gas systems is very often described by the logarithmic rate law used either in its integral form or in its differential one.<sup>1-7</sup> The integral form used before is:<sup>1,8,9</sup>

$$\theta = \alpha \ln\left(\frac{t_0}{t + t_0}\right) \quad (1)$$

where  $\theta$  is the coverage of the surface which diminishes with the desorption of gas in time  $t$ .  $\alpha$  and  $t_0$  are constants.

In the model which describes equation (1) the surface was considered a homogeneous one.

In the present paper we aim at studying if the existence of a surface heterogeneity could justify equation (1).

### THE MODEL

Let's consider a surface with no interacting sites, which are not all identical.

The following assumptions are taken into consideration: (i) gas desorption is irreversible; (ii) all the sites desorb with the same kinetics.

In this case the sites can be characterized by a distribution function  $\varphi(E)$  of the activation energy of desorption;  $\varphi(E) dE$  represents the fraction of sites with an activation energy of desorption between  $E$  and  $E+dE$ . The kinetic law of desorption  $V_d$  for sites having the activation energy  $E$  has the form:

$$-V_d = \varphi(\theta_i, E) \quad (2)$$

where  $\varphi$  is a certain function to be determined and  $\theta_i$  the local coverage of the surface domain considered to be a homogeneous one. Because

$$-V_d = \frac{d\theta_i}{dt} \quad (3)$$

one obtains for equation (3) the form:

$$\frac{d\theta_i}{dt} = \varphi(\theta_i, E) \quad (4)$$

The evolution law of  $\theta$  becomes:

$$\theta_i = \theta_i(t, E) \quad (5)$$

---

\* Corresponding author: [ionescu@chimfiz.icf.ro](mailto:ionescu@chimfiz.icf.ro)

By means of relationship (5), equation (2) takes the form:

$$-V_d = \varphi[\theta_i(t, E), E] \quad (6)$$

i.e. a function of  $t$  and  $E$ .

Because the sites are independent, the overall desorption rate  $v_d$  is given by:

$$v_d = \int_0^{\infty} -V_d(t, E)\varphi(E)dE \quad (7)$$

or

$$-v_d = \int_0^{\infty} V_d(t, E)\varphi(E)dE \quad (8)$$

In order to use equation (8) it is necessary to know the functions  $V_d$  and  $\varphi(E)$ .

Concerning the function  $\varphi(E)$  it is known<sup>5</sup> that this function can be either an exponential, a power or a constant. We consider now a constant distribution:

$$-v_d = \int_0^{\infty} k_d \exp\left[-k_d t \exp\left(\frac{-E}{kT}\right)\right] \exp\left(\frac{-E}{kT}\right) \cdot \text{const} \cdot dE \quad (13)$$

or

$$-v_d = \frac{\text{const} \cdot kT}{t} \int_0^{\infty} \exp\left[-k_d t \exp\left(\frac{-E}{kT}\right)\right] k_d t \exp\left(\frac{-E}{kT}\right) \cdot \frac{dE}{kT} \quad (14)$$

By integration equation (14) the overall desorption rate has finally the form:

$$-v_d = \frac{\text{const}}{t} \exp\left[-k_d t \exp\left(\frac{-E}{kT}\right)\right]_0^{\infty} = \frac{\text{const}}{t} [1 - \exp(-k_d t)] \quad (15)$$

In case  $k_d t \gg 1$ , the exponential can be neglected against the unity so that:

$$-v_d = \frac{\text{const}}{t} \quad (16)$$

which is a form of the differential logarithmic rate law. But:

$$-v_d = \frac{d\theta}{dt} \text{ where } \theta = \sum \theta_i \quad (17)$$

and

$$-\frac{d\theta}{dt} = \frac{\text{const}}{t} \quad (18)$$

By integration of equation (18) one obtains the integral form of the logarithmic rate law (1).

Thus, the existence of a surface heterogeneity can be, in certain conditions, an explanation for the

$$\varphi(E) = \text{const} \quad (9)$$

and then, for a first order desorption kinetics, the usual relation:

$$-\frac{d\theta_i}{dt} = k_d \theta_i \exp\left(-\frac{E}{kT}\right) \quad (10)$$

where  $k_d$  is a constant. By integration, with the initial conditions  $t=0, \theta=1$  equation (10) has the form:

$$\theta_i = \exp\left[-k_d t \exp\left(\frac{-E}{kT}\right)\right] \quad (11)$$

Using equation (11) one obtains for  $V_d$ :

$$V_d = k_d \exp\left[-k_d t \exp\left(\frac{-E}{kT}\right)\right] \exp\left(\frac{-E}{kT}\right) \quad (12)$$

because for the activation energy  $E$ , we have assumed the usual Boltzmann distribution. Finally:

existence of a differential logarithmic rate law in desorption of gases from solid surfaces.

Usually, in order to claim the existence of a logarithmic kinetics for desorption processes from solid surfaces it is necessary to fit the data over a long range of experimental parameters.<sup>10-13</sup>

It must also be mentioned that in case of a simple logarithmic law, the deviations of the initial stages of desorption, discontinuities in the plots  $\theta / \ln t$  or the rates of readsorption of gases on the surfaces cannot be explained without further assumptions.<sup>14</sup> The simple model explained in this paper is valid only for a normal behavior of desorption phenomena in solid-gas systems.

## CONCLUSIONS

The formal kinetics of desorption in solid-gas systems described by the logarithmic rate law can

be explained in certain conditions using the concept of surface heterogeneity.

### REFERENCES

1. C. Aharoni and F.C. Tomkins, *Adv. Catalysis*, **1970**, *21*, 1.
2. G.C. Bond, "Catalysis by metals", Academic Press, London, 1962, p. 106.
3. P.G. Ashmore "Catalysis and Inhibition of Chemical Reactions", Butterworths, London, 1963, p. 127.
4. D.O. Hayward and B.M.W. Trapnell, "Chemisorption" 2<sup>nd</sup> Ed. Butterworths, London, 1964, p. 143.
5. S.Z. Roginsky, "Adsorption und Katalyse an Inhomogenen Oberflächen", Akademie Verlag, Berlin, 1958, p. 147.
6. P. Fejes, in "Contact Catalysis", ed. Z. G. Szabo and D. Kallo, Akademiai Kiado, Budapest, 1976, vol. 1, p. 225.
7. J.L. Robins, W.K. Warburton and T.N. Rhodin, *J. Chem. Phys.* **1967**, *46*, 665.
8. N.I. Ionescu, *Rev. Roum. Chim.*, **1979**, *24*, 399.
9. N.I. Ionescu, *Rev. Roum. Chim.*, **1980**, *25*, 663.
10. N.I. Ionescu and M. Căldăraru, *Rev. Roum. Chim.*, **2006**, *51*, 521.
11. N.I. Ionescu and M. Căldăraru, *Rev. Roum. Chim.*, **2008**, *53*, 603.
12. N.I. Ionescu, *Rev. Roum. Chim.*, **2008**, *53*, 535.
13. N.H. Turner, *J. Catalysis*, **1975**, *36*, 2622.
14. J. D. Low, *Chem. Rev.*, **1960**, *60*, 267.