



THE ADSORPTION OF O₂ ON ZnO AND THE LOGARITHMIC LAW

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The kinetics of oxygen adsorption on a n-type semiconductor like ZnO obeys normally a logarithmic rate law. But in cases when the ionosorbed form of oxygen, O⁻, is in excess on the semiconductor surface the logarithmic rate law cannot be applied.

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

INTRODUCTION

The formal kinetics of gas adsorption on solid surfaces is usually determined by the logarithmic rate law used either in its differential form:

$$\frac{dq}{dt} = a \cdot \exp(-bq) \quad (1)$$

or in its integral one:

$$q = \frac{1}{b} \cdot [\ln(t + t_0) - \ln t_0] \quad (2)$$

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

But the differential form of the logarithmic law can be represented also by another form, obtained from equation (1), namely:

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

In this case, the initial conditions $t=0$, $q=0$ cannot be applied because equation (3) becomes:

$$0 = \frac{1}{b} \cdot \frac{1}{t_0} \quad (4)$$

which is not true. The equation (3) is valid only if $t = 0$, $q \neq 0$ and b is a constant.

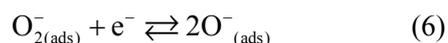
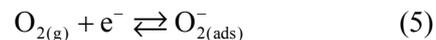
All the equations forms (1)-(3) have been intensively studied¹⁻⁶ and three classes of models for the explanation of this law, based on: active sites number variation, variable activation energy or non-uniform surface sites, have been developed.⁷

The adsorption of oxygen of an n-type oxide surfaces, like ZnO, was studied using also the logarithmic law and several kinetic models have been proposed.⁸⁻¹⁷

In this paper we intend to analyze if there are cases in which the adsorption of oxygen on ZnO cannot be described by these logarithmic rate law.

THE MODEL

Let the adsorption of O₂ on a ZnO solid surface be:



If

$$\Gamma_{O_2} \ll \Gamma_{O^-} \quad (7)$$

where Γ represents the surface concentrations of adsorbed oxygen species then:

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$$\frac{d\Gamma_{O^-}}{dt} = 2p_{O_2}[e^-]^2 \quad (8)$$

where $\frac{d\Gamma_{O^-}}{dt}$ represent the variation of concentration of oxygen ions, O^- , adsorbed on the surface in time, p_{O_2} – the oxygen partial pressure on the surface of the solid material and $[e^-]$ is the electron concentration. Neglecting an opposite reaction in formula (6), then after Boltzmann:

$$n_{e(x=0)} = n_{e(x=\infty)} \exp\left[-\frac{eV_D}{kT}\right] \quad (9)$$

with:

$$V_D = \varphi_{(x=\infty)} - \varphi_{(x=0)} \quad (10)$$

V_D – being the diffusion potential; $x = 0$ is on the surface and $x = \infty$, inside the solid; φ – the local electric potential, that can be estimated using a Poisson equation; $n_{e(x=0)}$ is the number of electrons at the surface; $n_{e(x=\infty)}$ – the number of electrons inside the solid; e – elementary charge; k – Boltzmann constant and T – the temperature expressed in K. For ZnO which is an n-type

semiconductor, neglecting the cations movement, one obtains:

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi\varphi}{\varepsilon} = -\frac{4\pi e}{\varepsilon}[n_{e(x=0)} - n_{e(x=\infty)}] \quad (11)$$

ε being the dielectric constant. But also, after Boltzmann:

$$n_e = n_{e(x=0)} \exp\left(\frac{e\varphi}{kT}\right) \quad (12)$$

where $\varphi_{(x=\infty)} = 0$. One obtains now:

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi en_{e(x=\infty)}}{\varepsilon}[1 - \exp\left(\frac{e\varphi}{kT}\right)] \quad (13)$$

or

$$\frac{1}{2}d\left(\frac{d\varphi}{dx}\right)^2 = -\frac{4\pi en_{e(x=\infty)}}{\varepsilon}[1 - \exp\left(\frac{e\varphi}{kT}\right)]d\varphi \quad (14)$$

The integration of equation (14) between:

$$\varphi(x=0) = -V_D, \varphi(x=\infty) = 0$$

and $\left(\frac{dq}{dx}\right)_{x=\infty} = 0$, leads finally:

$$0 - \frac{1}{2}d\left(\frac{d\varphi}{dx}\right)_{x=0} = 4\pi en_{e(x=\infty)}\{0 - (-V_D) - \frac{kT}{e}[\exp\left(-\frac{eV_D}{kT}\right) - 1]\} \quad (15)$$

Or

$$\left(\frac{d\varphi}{dx}\right)^2 = \frac{8\pi en_{e(x=\infty)}}{\varepsilon}\left[V_D + \frac{kT}{e}[1 - \exp\left(-\frac{eV_D}{kT}\right)]\right] \quad (16)$$

Concerning now only the adsorption of O^- ions it results:

$$\left(\frac{dq}{dx}\right)_{x=0} = \frac{4\pi e}{\varepsilon}\Gamma_{O^-} \quad (17)$$

By using equation (17) in equation (16) the result is:

$$\frac{16\pi^2 e^2 \Gamma_{O^-}^2}{\varepsilon^2} = 8\pi en_{e(x=\infty)}\left\{V_D + \frac{kT}{e}[1 - \exp\left(-\frac{eV_D}{kT}\right)]\right\} \quad (18)$$

In order to simplify the equation, it was assumed that

$$\frac{eV_D}{kT} \gg 1. \quad (19)$$

So, one obtains:

$$\frac{16\pi^2 e^2 \Gamma_{O^-}^2}{\varepsilon^2} \cong 8\pi en_{e(x=\infty)}\left(V_D + \frac{kT}{e}\right) \approx \frac{8\pi en_{e(x=\infty)}}{\varepsilon} V_D \quad (20)$$

and

$$V_D = \frac{2\pi e \Gamma_{O^-}^2}{\epsilon n_{e(x=\infty)}} \quad (21)$$

By introducing equations (9) and (21) in equation (8) it results:

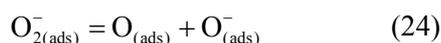
$$\frac{d\Gamma_{O^-}}{dt} = 2kp_{O_2} [n_{e(x=\infty)}]^2 \exp\left[-\frac{4\pi e^2 \Gamma_{O^-}^2}{\epsilon k T n_{e(x=\infty)}}\right] \quad (22)$$

or in a shorter form:

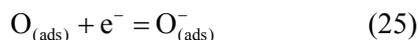
$$\frac{d\Gamma_{O^-}}{dt} = \alpha \exp(-\beta \Gamma_{O^-}^2) \quad (23)$$

which is not a logarithmic equation (α , β are constants).

In cases of the reactions:



or



one obtains, using the same form of calculus, the equation:

$$\frac{d\Gamma_{O^-}}{dt} = \alpha p_{O_2} n_{e(x=\infty)} \exp\left[-\frac{2\pi e^2 \Gamma_{O^-}^2}{\epsilon k T n_{e(x=\infty)}}\right] \quad (26)$$

Equation (26) is also not a logarithmic one.

Perhaps the cases presented in equations (5)–(7) and (24), (25) are not the only cases when the adsorption of oxygen on an n-type semiconductor like ZnO does not obey a logarithmic rate law.

It should be mentioned that in order to claim the existence or the non existence of a logarithmic kinetics for the oxygen adsorption or desorption processes it is necessary to fit the data over a wide range of experimental values.

Equations (23) and (26) demonstrate that the theory of ionosorption can be successfully used to describe cases in which different forms of adsorbed oxygen are in excess on a surface.

Several possible mechanisms containing relevant elementary steps for the ionosorption of oxygen on an n-type semiconductor can exist and the two cases presented in this paper could be some of them.

CONCLUSIONS

The kinetics of oxygen adsorption on an n-type semiconductor like ZnO obeys normally a logarithmic rate law. But in cases when different forms of ionosorbed oxygen are predominant on the surface, the logarithmic rate law kinetics cannot be used.

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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. 223.
4. S. R. Morrison, "The Chemical Physics of Surfaces", Plenum Press, New York and London, 1978, p. 46, 241.
5. 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.
6. E. I. Segal, C. Iditoiu, N. Doca and D. Fatu, "Cataliza si catalizatori", Ed. Facla, Timișoara, 1986, p. 40.
7. S. Morrison, *Sens. Actuators*, **1987**, *11*, 283.
8. N. I. Ionescu, *Surf. Sci.*, **1976**, *61*, 294.
9. N. I. Ionescu, *Z. Phys. Chemie- Neue Folge*, **1978**, *109*, 95.
10. N. I. Ionescu, *Bulg. Chem. Commun.*, **1992**, *25*, 39.
11. N. I. Ionescu and M. Caldararu, *Rev. Roum. Chim.*, **2002**, *47*, 1213.
12. N. I. Ionescu and M. Caldararu, *Rev. Roum. Chim.*, **2006**, *51*, 521.
13. N. I. Ionescu and M. Caldararu, *Rev. Roum. Chim.*, **2008**, *53*, 603.
14. J. F. Wager, *Thin Solid Films*, **2008**, *516*, 1755.
15. N. I. Ionescu, *Rev. Roum. Chim.*, **2008**, *53*, 603.
16. N. I. Ionescu and M. Caldararu, *Rev. Roum. Chim.*, **2010**, *55*, 365.
17. N. I. Ionescu, *Rev. Roum. Chim.*, **2011**, *56*, 483.

