

SIMULATION OF DIFFUSION EQUATION

Elena Maria PICĂ, Lorentz JÄNTSCHI

Technical University of Cluj-Napoca

Abstract. The paper presents a simulation model of diffusion equation which describes the variation rate of the particles concentration in time in a non-homogenous zone using an exact solution of the diffusion equation. It may be used to describe the electrode kinetics, too.

The diffusion equation being a differential order II equation, against distance and of first order against to time, for its solving the initial and limiting conditions have been taken into consideration.

1. Introduction

In the diffusion processes the heterogeneities are blurred in time. An example is the temperature of a metal rod/bar which *was* heated at an end; if the source of heat is removed the rod/bar will stabilize and get a steady temperature.

Another example, more relevant for chemistry is the distribution of the dissolved substance concentration in solution when the solvent is added.

The diffusion phenomenon in the case of the solution is analyzed. The method may be successfully applied also in the case of other physical properties, like temperature.

The aim of the paper is to obtain the equation of the rate of variation of the particle concentration as well as the equation of the electrode current in a KCl 0,1 M solution, initially saturated with oxygen.

Also, the discussion is continued on the graphical representation of the variations in time and their physico-chemical interpretation.

2. Theoretical Consideration. Equation Model

We start with the general equation of diffusion [1,2], which relates the rate of the concentration variation of a dissolved chemical species in time, $\partial c/\partial t$, at the coordinate-value x against the considered electrode, with the quadratic derivative of the concentration c with the coordinate x , $\partial^2 c/\partial x^2$ at the moment t :

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where: D is the diffusion coefficient of the species considered in the electrolyte film (m²/s). It is to be noticed that the equation (1) was established by Fick in 1855 and it is known under the name Fick's Second Diffusion Law.

Be it a thin layer of a cross section A which extends from x to $x + l$ as in Figure I, where the diffusion flux is graphical represented through a plane surface.

In figure I it is noticed that the net flux of diffusion is the difference between the input flux $J_D(x)$ and output flux $J_D(x+l)$.

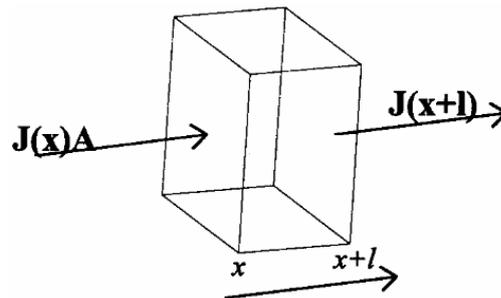


Fig.1.

Be it c the value of the concentration dissolved species, concentration which depends on the distance x and the temporal coordinate t . The quantity of particles entering the surface layer A in unit of time is $J_D(x) \cdot A$ and the variation rate of the molar concentration when entering the superficial layer of length l (with the volume $A \cdot l$) determined by the diffusion flux $J_D(x)$ is:

$$\frac{\partial c(x)}{\partial t} = \frac{J_D(x)A}{Al} = \frac{J_D(x)}{l} \quad (2)$$

The rate of the variation of molar concentration at the output from the layer of thickness l (and coordinate $x + l$), determined by the diffusion flux $J_D(x+l)$ is:

$$\frac{\partial c(x+l)}{\partial t} = \frac{J_D(x+l)A}{Al} = \frac{J_D(x+l)}{l} \quad (3)$$

Thus the plane variation of the concentration is:

$$\frac{\partial c(x)}{\partial t} - \frac{\partial c(x+l)}{\partial t} = \frac{J_D(x) - J_D(x+l)}{l} \quad (4)$$

Each flux is proportional with the concentration gradient in the layer considered. Using Fick's first law [1,2] we obtain:

$$\begin{aligned} J_D(x) - J_D(x+l) &= -D \frac{\partial}{\partial x} c(x) + D \frac{\partial}{\partial x} c(x+l) = \\ &= -D \frac{\partial c(x)}{\partial x} + D \frac{\partial}{\partial x} \left(c(x) + \frac{\partial c(x)}{\partial x} l \right) = D l \frac{\partial^2 c}{\partial x^2} \end{aligned} \quad (5)$$

Note that substituting the equation (5) in the equation (4) the expression of Fick's second law (1) is found again.

The diffusion equation (1) will be solved through a model of mathematical simulation, using an exact solution of the diffusion equation [3].

A similar treatment of the diffusion is presented in literature and it is even discussed but for the approximate solving of the equation [I] the numerical method is used, that is the divided differences method [4-6].

When the concentration varies suddenly as compared to the distance x , then the concentration varies quickly with the times t (see equation 1). Also, when the concentration decreases linearly with the distance x then, according to the equation (1) the time dependence of the concentration is a constant function (the concentration is unchanged in time). This represents the ideal case of the stationary diffusion.

The phenomenon of diffusion may be accompanied by the convection phenomenon. Convection is the transport of particles of the dissolved substance, caused by the motion of the solution layer.

Calculating *the flux of convection* $J_C(x)$ for the particles with the concentration $c(x)$, which cross the area A in the time interval $Ll t$ at the speed v , the following is obtained:

$$J_C(x) = \frac{c(x) A v \Delta t}{A \Delta t} = c(x) v \quad (6)$$

The variation of the concentration in time within a layer with a thickness l and area A is obtained on the way shown by the equation (2)-(4):

$$\frac{\partial c(x)}{\partial t} - \frac{\partial c(x+l)}{\partial t} = \frac{J_c(x) - J_c(x+l)}{l} \quad (7)$$

and $J_c(x) - J_c(x+l)$ are obtained through:

$$\begin{aligned} J_c(x) - J_c(x+l) &= c(x)v - c(x+l)v = \\ &= c(x)v - \left(c(x) + \frac{\partial c(x)}{\partial x} l \right) v = -vl \frac{\partial c(x)}{\partial x} \end{aligned} \quad (8)$$

Hence, the variation of the concentration, induced by the convection phenomenon, results:

$$\frac{\partial c(x)}{\partial t} - \frac{\partial c(x+l)}{\partial t} = -v \frac{\partial c(x)}{\partial x} \quad (9)$$

Taking into consideration both phenomena discussed, diffusion and convection, the total variation of the concentrations is given by the sum of the variations of the concentrations induced by the two phenomena and, after making the calculations the following is obtained:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (10)$$

The law is also known under the name of *general law of convective - diffusion* [1,2].

In the case of a chemical reaction, the variation of concentration may be induced by the development of the respective reaction, too. In this case, in the general expression of the diffusion equation besides the terms corresponding to the diffusion and convection some other terms also occur, terms characteristics to the respective chemical reaction. Such a situation is thoroughly discussed in [7].

3. Results and discussions

Equation (1) is a quadric differential equation against to the distance and of first order against time. Thus one must specify two limit conditions for the spatial dependence and an initial condition for the time dependence.

We consider the case of an electrode immersed in a solvent with the active surface considered plane in which the dissolved substance is, initially, on the surface of the electrode of an area A . As an initial condition, for $t = 0$ we have all the n_0 particles concentrated on the surface of the electrode ($x = 0$). Also, the concentration should be finite in any point and the total number of particles in the solution is at any moment n_0 . Hence, it results that the flux of diffusion $J_D(x)$ is zero on the surface of the electrode ($x = 0$) and at the limit of the system ($x = \infty$). In these conditions, the equation (1) is integrable and has the exact solution given by:

$$c = \frac{n_0}{A\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \quad (11)$$

Equation (11) may be checked by a direct substitution in the equation (1).

Equation (11) has been graphically represented in figure 2, for the following numerical values for the diffusion parameters.

$$\begin{aligned} \div n_0 &= 10^{-8} \text{ mol (the number of the moles initially present on the surface of the electrode)} \\ \div A &= 4 \cdot 10^{-2} \text{ m}^2 \text{ (the surface of the electrode)} \\ \div D &= 10^{-14} \text{ m}^2/\text{s (the diffusion coefficient of the dissolved species)} \\ \div x &= 2 \cdot 10^{-7} \text{ m (the limit of the diffusion layer)} \end{aligned} \quad (12)$$

For the time interval $t \in (0, 1s, 5s)$ the curve of the variation of the dissolved species concentration, imposed by relation (12), in figure 2 is presented.

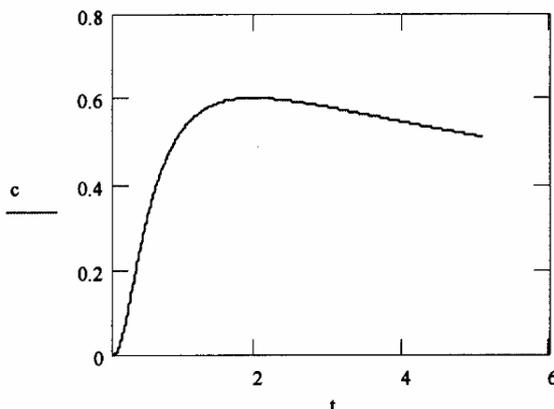


Fig.2.

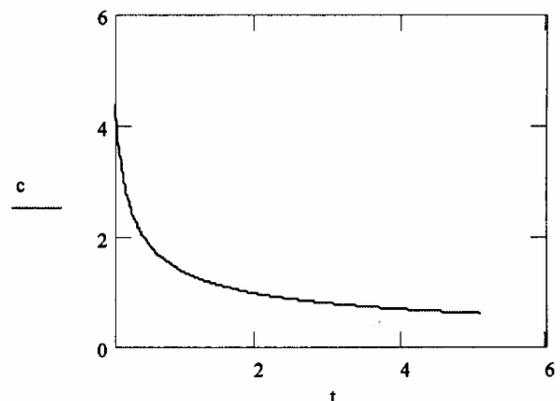


Fig.3.

As it is seen in figure 2, the curve describes a diffusion equation analogue with some sequences of chemical reactions when an intermediate is formed and when the rate constant of the rust reaction is higher than rate constant of the second reaction. Suppose the species dissolved was oxygen and it was reduced on the surface of an electrode, whose surface is equal with the plane surface of diffusion considered, indeed, if the reaction develops within two stages, with the formation of the peroxidic intermediate oxygenated water H_2O_2 , the diffusion process would be analogue to a reaction sequence. In this case, we leave the contribution of the terms of reaction, aside:

$$\begin{aligned}
 \div n_0 &= 10^{-8} \text{ mol (the number of the moles initially present on the surface of the electrode)} \\
 \div A &= 4 \cdot 10^{-2} \text{ m}^2 \text{ (the surface of the electrode)} \\
 \div D &= 10^{-14} \text{ m}^2/\text{s (the diffusion coefficient of the dissolved species)} \\
 \div x &= 8 \cdot 10^{-9} \text{ m (the limit of the diffusion layer)}
 \end{aligned} \tag{13}$$

For the same interval of time $t \in (0, 1s, 5s)$ the curve of the variation of the dissolved species concentration, imposed by relation (13), in figure 3 is presented.

As it is seen in figure 3, the diffusion equation is analogue with a chemical reaction of the first order. On the basis of the same hypotheses, but considering the present example, as a reaction of a general reduction of the oxygen the curve represented in figure 3, corresponds to a reduction equation of the first order. In fact, for the reaction of reducing the oxygen in the case of an oxygen sensor with membrane, the contribution of the reaction term, has been left aside [8,9].

Through the integration of the variation of the dissolved species concentration on the surface of the electrode ($x = 0$) (after the transfer function inferred from Faraday's and Fick's laws) [10] the following is obtained:

$$i(t) = n_0 F A D \frac{n_0}{A \cdot (\pi D t)^{0.5}} \tag{14}$$

and referring to the initial value $i(0)$ of the current, the relative current $w(t)$ is obtained:

$$w(t) = \frac{i(t)}{i(0)} \tag{15}$$

If we represent the relative current $w(t)$ produced on the electrode by shifting the chemical species, here in the case of reducing the oxygen, against the time for the equation (11) and the values of the diffusion parameters given by the equation (12), the curve in figure 4 is obtained.

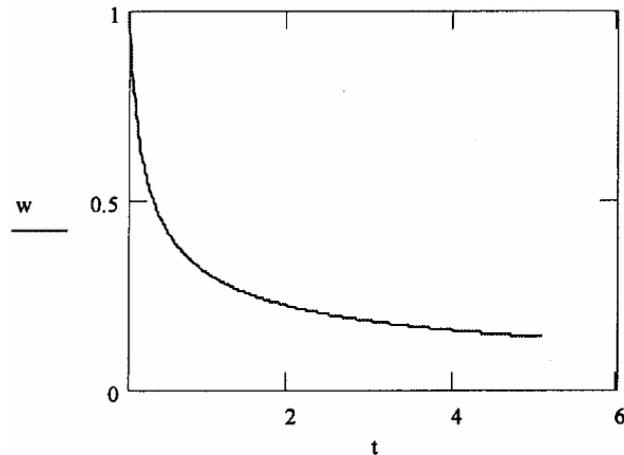


Fig.4.

As it is seen from figure 4, the curve of variation of the current is decreasing, as it must be obtained when the particles which diffuse, are reduced on the electrode surface, so it is consumed when the solution is no more saturated with the dissolved substance; in the present case the dissolved oxygen.

4. Conclusions

We tried to represent the diffusion equation by means of a mathematical model which uses an exact solution for diffusion, not the numerical methods of an approximate solving.

We found a variation of concentration against to time, for the conditions given by the relations discovered. This variation is analogue either with the successive reactions with an intermediate and when the rate constant of the first reaction is higher than the that of the second reaction, or with a reaction of the first order.

The function of the current variation is decreasing and depends on the conditions imposed by the discovered relation.

The performed study is, in fact, a first attempt of solving the physical aspects in solutions, within which chemical reactions are also developed, either in the solution or on the surface of some electrodes.

We have in view to go deeply into these studies, taking, into consideration the additional terms that occur, owing to the chemical reactions or to the types of chemical bonds which are established among different particles.

References

1. Antropov L. I., Teoreticheskaya Electrokhimiya 1-ed. Moskva, 1965.
2. Bockris J. O'M., Reddy A. K. N., Modern Electrochemistry, Plenum Press, New York, 1970, vol.1, cap.4.
3. ***, Matcad 7. Professional 1986, 1997, Math Soft, Inc. U.S. Pat. Nos. 5,469,538 and 5,526,475.
4. Malory J. T., Comprehensive Treatise of Electrochemistry, vol.7 (Eds. Conway B. E., Bockris J. O'M., Yeager E., Khan S. U. M., White R. E.) New York, London 1983, p. 417-431.
5. Vilanova X., Llobet E., Brezmes J., Calderer J., Carreig X., Sens. Actuators, 848 (1998) p.21-25.
6. Alden J., Hakoura A. S., Compton R. G., Anal. Chem., 71 (1999) p. 827-830.
7. Adanuvor P. K., White R. E., J. Electrochem. Soc., 134 (1987) p. 1093-1097.
8. Kekedy L., Pica Elena Maria, Rev.Chim., 36 (1985) p.852-855.
9. Pica Elena Maria, Ph. D. Thesis, "Babeş-Bolyai" University, Cluj-Napoca, 1990.
10. Mancy K. H., Okun D. H., Reilley C. N., J. Electroanal. Chem., 4 (1962) p. 65-79.

Simularea ecuatiei de difuzie

În lucrare se prezintă un model de simulare a ecuației de difuzie, care descrie viteza de variație a concentrației particulelor cu timpul într-o regiune neomogenă, utilizând o soluție exactă a ecuației difuziei. Aceasta poate fi utilizată și pentru descrierea cineticii de electrod.

Ecuatia de difuzie fiind o ecuație diferențială de ordinul II, referitor la distanța și ordinul I referitor la timp, pentru rezolvarea ei s-a ținut cont de condițiile la limită și inițiale.

Reader Dr. chem. Elena Maria Pică, Technical University of Cluj-Napoca, Muncii 105, 3400 Cluj-Napoca, RO-3400, ROMANIA.

Assist. prof. Lorentz Jäntschi, Technical University of Cluj-Napoca, Muncii 105, 3400 Cluj-Napoca, RO-3400, ROMANIA.