Physical Chemistry

A. A. Chernenko, Yu. A. Chizmadzhev

1963

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Physical Chemistry

A. A. Chernenko, Yu. A. Chizmadzhev

On the Theory of Capillary Equilibrium in a Porous Body

(Presented by Academician A. N. Frumkin, February 14, 1963)

1. The question of capillary equilibrium in a porous body is of great interest, in particular in connection with calculating the electrochemical activity of a gas porous electrode. As is known ([1]), the geometrical sites at which current arises in such an electrode are portions of the internal surface located near the three-phase boundary, i.e., the electrolyte–gas–solid boundary. It is usually assumed ([1–3]) that gas and electrolyte fill the porous electrode uniformly. In other words, it is assumed that such an electrode may be regarded as a homogeneous system with uniformly distributed volume sources. It is quite obvious that this assumption is not valid at small pressure differences, when practically the entire electrode is filled with electrolyte. In order to determine the range of pressures in which the conditions of homogeneity are satisfied, it is necessary to investigate the properties of the liquid–gas interface, i.e., to find the average depth of gas penetration into the porous electrode and to determine the degree of blurring of this boundary. In general form this problem is very complex and as yet has no solution. It can, however, be simplified by restricting oneself to consideration of the following simple model of a porous body, which in its properties approximates electrodes used in practice. Namely, let us suppose that the porous body consists of two types of pores–wide and narrow. In Fig. 1 the distribution function $f(r)$ of the pores of such a body by radii is shown. We shall consider the pressure interval in which the narrow pores remain flooded. Let us suppose that the wide pores do not intersect one another, but may intersect narrow pores. The narrow pores in such a model are very important, since the regions of their intersection with wide pores filled with gas are the geometrical sites at which current arises. However, in calculating the average depth of gas penetration, the narrow pores may be disregarded altogether.

Fig. 1

2. Let us suppose that an individual pore consists of adjoining cylindrical cavities. Number these cavities by the natural numbers $1, 2, \ldots$, starting from the surface of the porous body in contact with the gas phase. Then, for a given pressure difference in the gas and liquid phases $\Delta p = p_{\mathrm{g}} - p_{\mathrm{l}}$, the gas will displace the liquid successively from ν of the first cavities if all their radii $r_1, r_2, \dots, r_\nu > r_{\mathrm{cr}}$, while $r_{\nu+1} < r_{\mathrm{cr}}$. Denote the corresponding heights of the cylinders by $\xi_1, \xi_2, \dots, \xi_\nu$. Then, at the given moment, the gas penetrates to a depth equal to

$$x_\nu = \xi_1 + \xi_2 + \dots + \xi_\nu. \tag{1}$$

We assume that the porous body is a collection of the parallel pores described above, opening onto the surface in contact with the gas phase. It is then natural to suppose that the quantities $\nu; r_1, r_2, \dots, r_\nu; \xi_1, \xi_2, \dots, \xi_\nu$ vary randomly from pore to pore. Further, having in mind finding the mean depth of penetration of gas into a liquid-filled porous body, we shall understand expression (1) as a sum of a random number of random summands. In [4] it was shown that if, for $n > m$, the random variable ξ_n and the event $\{\nu = m\}$ are independent, the mathematical expectations $M(\xi_n) = a_n$, $M(|\xi_n|) = c_n$ exist, and the series

$$\sum_{n=1}^{\infty} P_n c_n$$

converges, then the mathematical expectation x_ν exists and is equal to

$$M(x_\nu) = \sum_{n=1}^{\infty} p_n A_n, \tag{2}$$

where $A_n = M(x_n) = a_1 + a_2 + \dots + a_n,\ p_n = \mathbf{P}\{\nu = n\},\ P_n = \mathbf{P}\{\nu \geq n\}$.

We shall assume that $\xi_1, \xi_2, \dots, \xi_n$ are mutually independent identically distributed random variables and that the conditions of the theorem stated above are satisfied. Then

$$M(x_\nu) = aM(\nu), \tag{3}$$

where $a = M(\xi_n), \quad M(\nu) = \sum_{n=1}^{\infty} np_n$.

It is of interest to find the variance

$$D(x_\nu) = M(x_\nu^2) - M^2(x_\nu).$$

For this purpose, obviously, it suffices to find $M(x_\nu^2)$. Put

$$\varphi_n = \xi_n^2 + 2\xi_n x_{n-1}. \tag{4}$$

Then we have identically

$$x_n^2 = \varphi_1 + \varphi_2 + \cdots + \varphi_n. \quad (5)$$

From (4), and also from the condition of independence of ξ_n from x_{n-1} (which follows from the mutual independence of the random variables $\xi_1, \xi_2, \ldots$), we obtain

$$M(\varphi_n) = M(\xi_n^2) + 2a^2(n-1) = b_n. \quad (6)$$

Apply the theorem cited above [4]* to the sum

$$x_\nu^2 = \varphi_1 + \varphi_2 + \cdots + \varphi_\nu. \quad (7)$$

Then

$$M(x_\nu^2) = \sum_{n=1}^{\infty} p_n A_n, \qquad \text{where } A_n = \sum_{k=1}^{n} b_k = nM(\xi_n^2) - 2a^2 n + 2a^2 \frac{n(n+1)}{2}$$

or

$$A_n = nM(\xi_n^2) + a^2 n^2 - a^2 n.$$

Consequently,

$$M(x_\nu^2) = [M(\xi_n^2) - a^2]M(\nu) + a^2 M(\nu^2). \quad (8)$$

It follows that

$$D(x_\nu) = [M(\xi_n^2) - a^2]M(\nu) + [M(\nu^2) - M^2(\nu)]a^2. \quad (9)$$

Now suppose that $r_1, r_2, \ldots$ are independent identically distributed random variables. In this case ν has a geometric–

* We do not give the proof that the conditions of the theorem are satisfied for (7), for lack of space.

geometric distribution (5), i.e.

$$p_n = q^n(1-q), \quad (10)$$

where

$$q = \int_{r_{\text{cr}}}^{\infty} f(r)\,dr,$$

$f(r)$ is the distribution density of r.

From (3), (9), and (10) it follows that

$$M(x_\nu) = a\frac{q}{1-q}; \tag{11}$$

$$D(x_\nu) = M(\xi_n^2)\frac{q}{1-q} + a^2\left(\frac{q}{1-q}\right)^2. \tag{12}$$

The ratio of the root-mean-square deviation to the mathematical expectation has the form

$$\frac{\sqrt{D(x_\nu)}}{M(x_\nu)} = \sqrt{1 + \frac{M(\xi_n^2)(1-q)}{a^2 q}}. \tag{13}$$

3. In order to investigate the dependence of the mean depth of gas penetration $M(x_\nu)$ on pressure, suppose that the distribution of pores by radii is normal*

$$f(r) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(r-\bar{r})^2}{2\sigma^2}\right],$$

where σ is the dispersion, $\bar{r}$ is the mean value of the radius. Using formula (11), we obtain

$$M(x_\nu) = \frac{\frac{1}{2}\left[1 - \operatorname{erf}\frac{r_{\text{cr}}-\bar{r}}{\sqrt{2}\,\sigma}\right]}{1 - \frac{1}{2}\left[1 - \operatorname{erf}\frac{r_{\text{cr}}-\bar{r}}{\sqrt{2}\,\sigma}\right]}\,a. \tag{14}$$

As $\Delta p \to 0$, $r_{\text{cr}} \to \infty$ and $\operatorname{erf}\frac{r_{\text{cr}}-\bar{r}}{\sqrt{2}\,\sigma} \to 1$; correspondingly $M(x_\nu) \to 0$, i.e., the gas does not penetrate into the porous body, which is completely filled with liquid. As $\Delta p \to \infty$, $r_{\text{cr}} \to 0$ and

$$M(x_\nu) \to \frac{1 + \operatorname{erf}\bar{r}/\sqrt{2}\sigma}{1 - \frac{1}{2}[\operatorname{erf}\bar{r}/\sqrt{2}\sigma + 1]}\,a.$$

If $\bar{r} \gg \sqrt{2}\sigma$, then practically $M(x_\nu) \to \infty$ as $\Delta p \to \infty$. Thus, with increasing pressure the mean depth of gas penetration into the porous body increases. The character of gas penetration may be judged from Fig. 2. As follows from (14),

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

when $r_{\text{cr}} = \bar{r}$ the quantity $M(x_\nu)$ does not depend on σ and is equal to a. Correspondingly, in Fig. 2 the curves corresponding to different σ intersect at the point $r_{\text{cr}} = \bar{r}$.

Fig. 2

Fig. 3

* Since $r \geq 0$, it would be natural to take as $f(r)$ a truncated Gaussian distribution or a Pearson type III curve; however, for $\sigma \ll \bar{r}$ this difference is apparently immaterial.

Curve a in Fig. 2 corresponds to a broader distribution (function a in Fig. 1), and curve b to a narrower distribution (function b in Fig. 1).

The formulas obtained in Section 2 make it possible to answer the question of whether the liquid-gas interface is sharp or diffuse. As is known, the degree of diffuseness of the boundary is determined by the variance $D(x_\nu)$, which is given by formula (12). Suppose, for simplicity, that $M(\xi_\nu^2) = a^2$. Then

$$\frac{\sqrt{D(x_\nu)}}{M(x_\nu)} = \sqrt{1 + \frac{a}{M(x_\nu)}}$$

and for $M \gg a$ the quantity $\sqrt{D}/M \sim 1$, i.e., the region of diffuseness of the phase boundary is of the same order of magnitude as the mean penetration depth. Hence it follows that the phase boundary is very diffuse (Fig. 3).

The calculations presented do not claim to give a quantitative description of a real porous body, since the pore cross sections may change the results. However, it seems to us that a number of the regularities established will be qualitatively preserved in more realistic models.

We express our gratitude to Corresponding Member of the Academy of Sciences of the USSR V. G. Levich for discussion of the results and useful comments.

Received
12 II 1963

REFERENCES

[1] E. Justi, M. Pilkuhn, V. Scheibe, A. Winsel, *Highly Active Hydrogen Diffusion Electrode*, 1962. [2] A. G. Pshenichnikov, DAN, **148**, No. 5 (1963). [3] V. S. Markin, Yu. A. Chizmadzhev, Yu. G. Chirkov, DAN, **150**, No. 3 (1963). [4] A. N. Kolmogorov, Yu. V. Prokhorov, UMN, **4**, issue 4 (32) (1949). [5] W. Feller, *An Introduction to Probability Theory and Its Applications*, IL, 1952.

Note: Figure translations are in progress. See original paper for figures.