

THE THEORY OF CAPILLARY EQUILIBRIUM IN THE POROUS BODY

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1. The capillary equilibrium in the porous body is of considerable interest, especially in calculating the electrochemical activity of the porous gas electrode. The current in such electrode is known to arise on those portions of the internal surface which are located near three-phase electrolyte-gas-solid interfaces [1]. It is generally assumed [1-3] that the gas and electrolyte fill the porous electrode uniformly. In other words, it is considered that such an electrode can be treated as a homogeneous system of uniformly distributed bulk sources. It is quite obvious, however, that this assumption is not valid when the pressure drop is small since the electrode is then almost completely filled with the electrolyte. In order to mark out the pressure range in which this condition of uniformity is applicable, it is necessary to study the properties of the liquid-gas interface, determining the mean depth of gas penetration and the degree of diffuseness of the interface. In its general form, this is a quite complex problem and one which has not yet been solved. It can, however, be simplified by limiting consideration to a model porous electrode whose properties closely approximate those of actual electrodes. In fact, it will be assumed that the porous body contains just two types of pore, the wide and the narrow. Figure 1 shows pore radius distribution functions, $f(r)$, for such body. We will consider the pressure interval over which the narrow pores remain filled, assuming that the wide pores do not intersect one another but do intersect the narrow pores. The narrow pores are an essential part of this model, the regions of their intersection with the wide gas filled pores being the geometrical sites at which the current originates. These pores can be neglected, however, in calculating the mean depth of gas penetration.

2. We will assume that the individual pore consists of abutting cylindrical cavities which we will number 1, 2, ..., starting from that surface of the body which is in contact with the gaseous phase. For fixed pressured difference between the gaseous and liquid phases, $\Delta p = p_g - p_l$, the gas will displace the liquid from the first ν of these cavities, the radii being such that $r_1, r_2, \dots, r_\nu > r_{cr}$, and $r_{\nu+1} < r_{cr}$. We will designate the respective heights of these cavities by $\xi_1, \xi_2, \dots, \xi_\nu$. The depth of gas penetration in a given pore will then be expressed by

$$x_\nu = \xi_1 + \xi_2 + \dots + \xi_\nu. \quad (1)$$

We will consider the porous body to be an aggregate of pores of this kind which are parallel and open on that one of the surfaces which is in contact with the gas. It is natural to assume that $\nu; r_1, r_2, \dots, r_\nu; \xi_1, \xi_2, \dots, \xi_\nu$ all vary randomly in passing from one pore to another. Since it is a question of finding the mean depth of gas penetration in the liquid filled porous body, Eq. (1) will be considered as the sum of random number of chance variables. It has been shown in [4] that if the chance value ξ_n and the event $\{\nu = m\}$ are independent when $n > m$, the math-

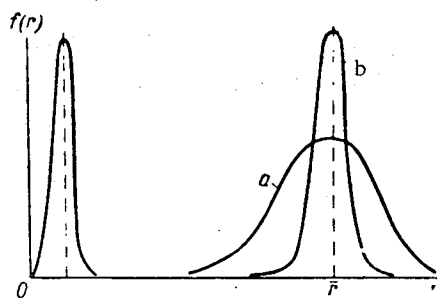


Fig. 1.

ematical expectations $M(\xi_n) = a_n$, $M(|\xi_n|)$ exist, and the series

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

is convergent, a mathematical expectation x_ν will also exist and be given by the expression

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

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

We will assume that $\xi_1, \xi_2, \dots, \xi_n$ are independent uniformly distributed chance variables and that the postulates of the above theory

are applicable. It then follows that

$$M(x_v) = aM(v), \quad (3)$$

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

It is of interest to determine the dispersion

$$D(x_v) = M(x_v^2) - M^2(x_v).$$

To do this it is clearly enough to find $M(x_v^2)$. We will assume that

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

One then has the identity

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

From (4) and the condition that ξ_n be independent of x_{n-1} (this last follows from the mutual independence of the chance variables $\xi_1, \xi_2, \dots$), one obtains

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

We will now apply the above theorem of [4]* to the sum

$$x_v^2 = \varphi_1 + \varphi_2 + \dots + \varphi_v. \quad (7)$$

Then

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

or

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

From this it follows that

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

This yields

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

We will now assume that $r_1, r_2, \dots$ are independent, uniformly distributed, chance variables. The quantity v then has a geometrical distribution [5], which is to say that

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

where $q = \int_{cr}^{\infty} f(r) dr$, $f(r)$ is the distribution function for r .

It follows from (3), (9), and (10) that

$$M(x_v) = a \frac{q}{1-q}; \quad (11)$$

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

The ratio of the mean-square deviation to the mathematical expectation is expressed by

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

* Proof of the fact that (7) fulfills the conditions of this theorem will not be given here because of lack of space.

3. In investigating the pressure dependence of the mean depth of gas penetration, $M(x_v)$, the assumption will be made that the pore radius distribution 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 and $\bar{r}$ is the mean radius. Equation (11) can be used to obtain

$$M(x_v) = \frac{\frac{1}{2} \left[1 - \operatorname{erf} \frac{r_{cr} - \bar{r}}{\sqrt{2}\sigma} \right]}{1 - \frac{1}{2} \left[1 - \operatorname{erf} \frac{r_{cr} - \bar{r}}{\sqrt{2}\sigma} \right]} a. \quad (14)$$

When $\Delta p \rightarrow 0$ $r_{cr} \rightarrow \infty$ and $\operatorname{erf} \frac{r_{cr} - \bar{r}}{\sqrt{2}\sigma} \rightarrow 1$; $M(x_v) \rightarrow 0$, i.e., the gas does not penetrate the porous body

and the latter is completely filled with liquid. When $\Delta p \rightarrow \infty$ $r_{cr} \rightarrow 0$ and $M(x_v) \rightarrow \frac{1 + \operatorname{erf} \bar{r}/\sqrt{2}\sigma}{1 - 1/2 [\operatorname{erf} \bar{r}/\sqrt{2}\sigma + 1]} a$.

If $\bar{r} \gg \sqrt{2}\sigma$, it is then practically so that $M(x_v) \rightarrow \infty$ when $\Delta p \rightarrow \infty$. Thus, the mean depth of gas penetration into the porous body increases with the pressure. Figure 2 gives an idea of the characteristics of the penetration. Equation (14) shows that $M(x_v)$ no longer depends on σ , but is equal to a , when $r_{cr} = \bar{r}$. Thus, the curves of Fig. 2 which correspond to various values of σ must intersect at the point $r_{cr} = \bar{r}$.

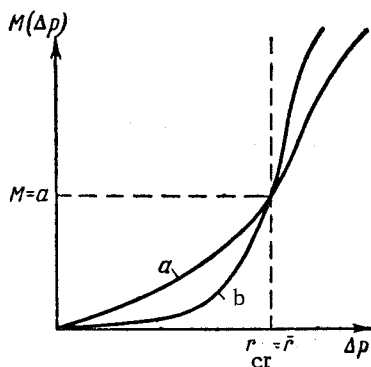


Fig. 2.

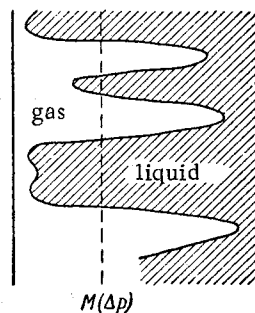


Fig. 3.

Curve a of Fig. 2 corresponds to the wider a distribution function of Fig. 1 and curve b to the more narrow function.

The equations obtained in Section 2 can serve as a basis in answering the question as to whether the liquid-gas interface is sharp or diffuse. The diffuseness of the surface is known to be determined by the dispersion $D(x_v)$, which, in this case, is given by Eq. (12). It will be assumed for simplicity that $M(\xi_v^2) = a^2$. Then

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

and $\sqrt{D/M} \sim 1$ when $M \gg a$, i.e., the region of interfacial diffuseness is of the same order of magnitude as the mean depth of penetration. From this it follows that the phase interface is highly diffuse.

These calculations do not claim to give a quantitative description of the actual porous body since pore intersection could change the results. It seems, however, that some of the relations developed here would be at least qualitatively applicable to more nearly real models.

We wish to express our thanks to V. G. Levich, Corresponding Member, Academy of Sciences, USSR, for a discussion of these results and for valuable remarks.

*It would be more natural to assume a truncate Gaussian distribution or a Type III Pearson distributionsince $r \geq 0$; it is clear that the differences resulting from such choices will be insignificant when $\sigma \ll \bar{r}$.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
