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INFLUENCE OF INHOMOGENEOUS ELECTRIC AND MAGNETIC FIELDS ON INTERNAL MASS TRANSFER IN CAPILLARY-POROUS BODIES

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Equations are derived for mass transfer in inhomogeneous electric and magnetic fields. Experimental results are given in support of the theoretical conclusions.

It has been shown experimentally [1, 2] that inhomogeneous electric and magnetic fields have an appreciable influence on internal mass-transfer processes in porous bodies. We wish to examine some possible physical mechanisms of this phenomenon.

It is generally known that dipolar molecules in an inhomogeneous electric field with gradient ∇E are acted upon by a force

$$f = p_e \nabla E, \text{ dyn.} \tag{1}$$

Under the action of this force dipolar molecules acquire a velocity component in the direction of increasing values of ∇E with a magnitude

$$U = Df/kT, \text{ cm/sec.} \tag{2}$$

To the diffusion flux q_v of vapor molecules in this case is added a convective flux $q_e = UC$. The total flux is then

$$q = q_v + q_e = -D\frac{dC}{dx}\left[1 + \frac{p_e C \nabla E}{kT(-dC/dx)}\right]. \tag{3}$$

It is evident from this equation that for $\nabla E > 0$ the vapor transfer rate increases. The influence of the field is particularly appreciable for small vapor-pressure gradients, such that $q_e \gg q_v$, and for molecules with a large dipole moment.

An inhomogeneous field also affects a liquid dielectric, pulling it into the zone of greater field inhomogeneity. The force acting on unit volume of the dielectric is

$$P_e = \frac{\varepsilon - 1}{8\pi}\nabla(E^2), \text{ dyn/cm}^3. \tag{4}$$

Under the action of the force per unit volume, P_e, viscous flow is analogous to flow at a constant hydrostatic pressure gradient ∇P. For example, in the case of a cylindrical capillary of radius r the mass flux can be written in the form

$$q = q_l + q_e = \frac{\rho r^2}{8\eta}\left[\nabla P + \frac{(\varepsilon - 1)\nabla(E^2)}{8\pi}\right]. \tag{5}$$

Here the first term expresses the mass flux under the influence of the hydrostatic pressure gradient ∇P, and the second term under the influence of the field gradient ∇E.

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For $\nabla(E^2) > 0$ the inhomogeneous field reinforces mass transfer, especially in the case of polar liquids with a high dielectric constant such as water, glycerin, and alcohols. The relative influence of the field is stronger the weaker the contribution of the flux due to the pressure gradient.

As the foregoing discussion indicates, an inhomogeneous electric field can, depending on the sign of ∇E, either accelerate or retard mass transfer. Under certain conditions, however, as when absorption equilibrium is established, the process is always strictly accelerated by an inhomogeneous field of either sign. This result is attributable to the fact that the direction of the convective flux is immaterial for the attainment of equilibrium, much in the same way that, for example, the forcing of a wet gas through a porous body always accelerates the attainment of adsorption equilibrium irrespective of the direction in which it is forced.

Analogous effects take place in inhomogeneous magnetic fields. Instead of Eq. (1) we now have for the force f the equation

$$f = p_m \nabla B, \text{ dyn,} \tag{6}$$

in which ∇B is the gradient of the magnetic field. Accordingly, the force acting on unit volume of the magnetic material is

$$P_m = \frac{\mu - 1}{8\pi\mu} \nabla(B^2), \text{ dyn/cm}^3. \tag{7}$$

Note that $(\mu-1) > 0$ for paramagnets, and $(\mu-1) < 0$ for diamagnets. The latter, unlike paramagnets and dielectrics, are thrust out of the zone of maximum values of the field strength.

Inasmuch as the form of the force equations is identical, from now on we obtain solutions only for the electric field. They can always be adjusted for inhomogeneous magnetic fields by appropriate substitution.

Let us consider the absorption of vapor by a semiinfinite porous body in an inhomogeneous electric field. In the one-dimensional problem the process is described by the familiar adsorption–desorption kinetic equation [4] with terms added to account for the convective transfer UC and surface flux $j(a)$ of adsorbed material:

$$\frac{\partial a}{\partial t} + \frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D \frac{\partial C}{\partial x} - UC - j(a)\right]. \tag{8}$$

the relationship between the local values of $a(x, t)$ and $C(x, t)$ is given by the adsorption isotherm

$$a = F(C). \tag{9}$$

It is assumed that adsorption equilibrium between the vapor and adsorbate can be attained at every point of the pore space.

When the pores are sufficiently wide, it is only meaningful to consider the flow of polymolecular films. The surface transfer process associated with adsorption-film thicknesses equal to or less than monomolecular thickness can be neglected here. On the basis of these assumptions we adopt the following simplified expression for the polymolecular adsorption isotherm [5]:

$$a = F(C) = 0 \quad \text{for} \quad C < C_*; \quad a = F(C) = K(C - C_*) \quad \text{for} \quad C > C_*,$$

where K is a constant.

Let us suppose that the pores are vacant prior to the inception of adsorption ($t = 0$), so that

$$C(0, x) = a(0, x) = 0. \tag{10}$$

At the outer boundary of the porous body ($x = 0$) we maintain a constant vapor concentration

$$C(t, 0) = C_0 = \text{const}. \tag{11}$$

We first examine the case in which $C_0 < C_*$ and only vapor diffusion takes place in the pores. In place of (8), for $D = \text{const}$ we arrive at the equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x}. \tag{12}$$

For a semiinfinite porous body we have

$$C(t, x) = \frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{x - Ut}{2\sqrt{Dt}}\right) + \exp\left(\frac{Ux}{D}\right)\operatorname{erfc}\left(\frac{x + Ut}{2\sqrt{Dt}}\right)\right]. \tag{13}$$

For U = 0 ($\nabla E = 0$) this result goes over to the well-known solution for vapor diffusion [6]:

$$C_v(t,\ x) = C_0 \operatorname{erfc}(x/2\sqrt{Dt}). \tag{14}$$

From Eqs. (13) and (14) we obtain the respective mass fluxes

$$j(t) = -D\frac{\partial C}{\partial x}\bigg|_{x=0} + UC_0 = UC_0\left[1 - \frac{1}{2}\operatorname{erfc}\left(\frac{U\sqrt{t}}{2\sqrt{D}}\right)\right] + C_0\sqrt{\frac{D}{\pi t}}\exp\left(-\frac{U^2 t}{4D}\right) \tag{15}$$

and

$$j_v(t) = -D\frac{\partial C}{\partial x}\bigg|_{x=0} = C_0\sqrt{\frac{D}{\pi t}}\,. \tag{16}$$

As $t \to \infty$ we have $j(t) \to UC_0$ and $j_v(t) \to 0$. As $t \to 0$ we have $j(t) \to j_v(t)$. Consequently, the influence of the flux associated with the inhomogeneous field (for U > 0) increases as the concentration gradient decays, i.e., with increasing t. In the limit $t \to \infty$ the ratio $j(t)/j_v(t) \simeq U\sqrt{\pi t/D}$ tends to infinity.

For U < 0, in which case the field exerts a retarding effect, the redistribution of mass can cease altogether, resulting in a stationary state, for which j(t) = 0. Now in any cross section x of the porous body

$$-D\frac{\partial C}{\partial x} - UC = 0. \tag{17}$$

From this result we infer that for U = const (∇E = const)

$$C = C_0 \exp(-Ux/D). \tag{18}$$

As this equation indicates, the vapor concentration decays exponentially. Despite the fact that the condition $C_0 > 0$ is maintained in the surrounding medium, the vapor cannot fill up the entire porous body, $C \to 0$ as $x \to \infty$, and it penetrates only the surface layers.

For U > 0, in which case the field reinforces the mass flux into the interior of the porous body, it is also possible to arrive at a stationary state. The vapor concentration C in the x direction in this case grows exponentially:

$$C = C_0 \exp(Ux/D). \tag{18'}$$

Here C can become greater than C_*. Then polymolecular adsorption begins, so that it is required to solve Eq. (8). For simplification, however, we can neglect the influence of adsorption. Then the growth of C will be limited by capillary condensation, which sets in as soon as $C = C_k$. From the Kelvin equation we find the value of C_k:

$$C_k = C_s \exp(-2\sigma v_m/rRT);\quad C = Mp_s/RT, \tag{19}$$

where C_s is the vapor concentration corresponding to the saturated vapor pressure p_s of the liquid at a given temperature.

In the stationary state the pores become filled in the zone $x > x_k$ with the capillary condensate, and in the zone $x_k > x > 0$ with vapor, the concentration of which decays exponentially from $C = C_k$ at $x = x_k$ to $C = C_0$ at x = 0. The value of x_k is readily determined from Eq. (18'):

$$x_k = \frac{D}{U}\ln\frac{C_k}{C_0}\,.$$

Thus, for a semiinfinite body or, equivalently, a body of finite dimensions but with dead-end pores, a field inhomogeneous in the x direction can upset the equilibrium of the body with the surrounding medium, preventing material from entering it or, conversely, promoting excess absorption of material by it. As will be shown presently, an inhomogeneous field can also elicit vapor condensation (after a certain supersaturation) in the pores, even when $C_0 < C_k$ in the medium surrounding the body.

The situation changes, however, if the porous body has finite dimensions and the pores run all the way through it. The simplest model of such a system is a capillary of length l, open at both ends. Let a vapor concentration C_0 = const be maintained at the ends of the capillary x = 0 and $x = l$. We first discuss the case $C_0 < C_*$, in which adsorption is disregarded. The corresponding solution of Eq. (12) has the form

$$C(t,\ x) = C_0\left\{1 - \sum_{n=1}^{\infty} A_n \exp\left[-\left(\frac{D\pi^2 n^2}{l^2} + \frac{U^2}{4D}\right)t\right]\exp\left(\frac{Ux}{2D}\right)\sin\left(\frac{\pi n x}{l}\right)\right\}. \tag{20}$$

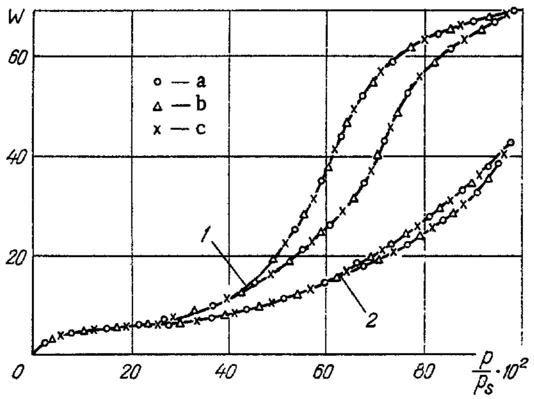

Fig. 1. Adsorption–desorption isotherms of water vapor in KSS-4 silica gel at various temperatures: 1) 293°, 2) 308°K; a) without the field, b) in an inhomogeneous electric field ($\nabla E = 8.5 \cdot 10^8$ V/m^2), c) in an inhomogeneous magnetic field ($\nabla B = 1.2 \cdot 10^6$ A/m^2).

Here $A_n = 4[1 + (-1)^{n+1}\exp(-\alpha\pi n)]/(1 + \alpha^2)$, where $\alpha = Ul/2\pi nD$. In the absence of the field ($U = 0$)

$$C_v(t,\ x) = C_0\left\{1 - \sum_{n=1}^{\infty} B_n \exp\left(-\frac{D\pi^2 n^2 t}{l^2}\right)\sin\left(\frac{\pi n x}{l}\right)\right\}, \tag{21}$$

where $B_n = 2(1 - \cos\pi n)/\pi n$.

For large times t, Eqs. (20) and (21) are simplified:

$$C \simeq C_0\left\{1 - A_1 \exp\left(\frac{Ux}{2D}\right)\sin\left(\frac{\pi x}{l}\right)\exp\left[-\left(\frac{D\pi^2}{l^2} + \frac{U^2}{4D}\right)t\right]\right\}; \tag{22}$$

$$C_v \simeq \left\{1 - B_1 \sin\left(\frac{\pi x}{l}\right)\exp\left[-\frac{\pi^2 D t}{l^2}\right]\right\}. \tag{23}$$

It is evident from Eqs. (20)-(23) that $C(x) \to C_0$ as $t \to \infty$.

Thus, the field does not affect the final state of the system. As $t \to \infty$ a pressure equal to the vapor pressure in the surrounding medium is established in the capillary. The only difference is that without the field the vapor in the capillary is motionless, whereas with the field present the vapor in the capillary moves with the convective flow rate

$$j_{t\to\infty} = UC_0. \tag{24}$$

Let us compare the relaxation time to the final state of the system, using the values of the ratios $y = (C - C_0)/C_0$ and $y_v = (C_v - C_0)/C_0$ as $t \to \infty$ to characterize the degree of deviation of the existing from the final state. From (22) and (23) we obtain

$$\frac{y}{y_v} = \frac{A_1}{B_1}\exp\left(\frac{Ux}{2D}\right)\exp\left(-\frac{U^2 t}{4D}\right) \ll 1. \tag{25}$$

Consequently, the final state of the system (equilibrium without the field, stationary with the field) is attained more rapidly when the porous body is situated in an inhomogeneous field.

These results are in good agreement with the experimental data. Figure 1 gives as an example the adsorption–desorption isotherms of water vapor in KSS-4 silica gel (with a mean pore radius of about 22 Å), obtained on the adsorption apparatus described in [7]. The silica gel, in the form of particles with diameters of 0.35 mm, was placed in the adsorption capsule on a cup with a diameter of $1.6 \cdot 10^{-2}$ m. An inhomogeneous electric field was created by electrodes, one of which was made in the form of a filament running along the axis of support of the cup, while the second was a cylinder 30 mm in diameter encircling the cup with the sample. A potential difference of up to 25 kV from a Pazryad-I dc source was applied to the electrodes. In this field configuration the gradient ∇E varies along the radius of the sample. We characterized the inhomogeneous field in the sample by the mean values of ∇E, which were calculated by the standard procedure [8]. The experiments were carried out for a series of values of ∇E. Figure 1 gives the experimental points for the largest gradient value: $\nabla E = 8.5 \cdot 10^8$ V/m^2. An inhomogeneous magnetic field was created by a special arrangement of pole tips [9] near the cup containing the sample. The largest mean value of ∇B within the limits of the sample in this case was $\nabla B = 1.2 \cdot 10^6$ A/m^2.

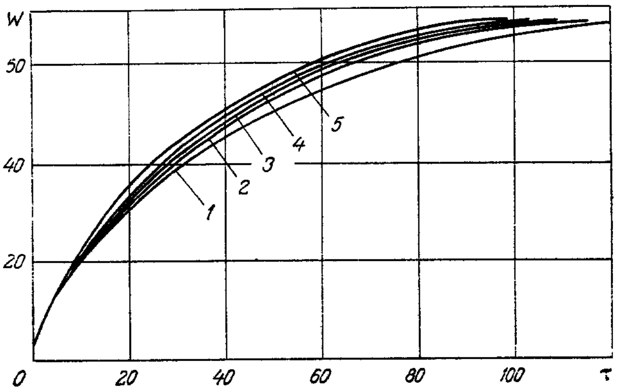

Fig. 2. Percentage adsorption W versus time τ (min) for KSS-4 silica gel at T = 293°K with and without inhomogeneous external electric and magnetic fields. 1) Without any field; 2) in an inhomogeneous magnetic field $\nabla B = 1.2 \cdot 10^6$ A/m^2; 3, 4, 5) in inhomogeneous electric fields: 3) $\nabla E = 0.76 \cdot 10^8$ V/m^2; 4) $2.03 \cdot 10^8$; 5) $8.5 \cdot 10^8$ V/m^2.

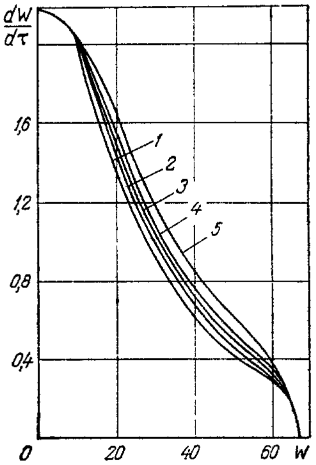

Fig. 3. Adsorption rate dW/dτ (%/min) of water vapor by KSS-4 silica gel versus moisture content W (%). 1) Without any field; 2) in an inhomogeneous magnetic field; 3, 4, 5) in an inhomogeneous electric field: 3) $\nabla E = 0.76 \cdot 10^8$ V/m^2; 4) $2.03 \cdot 10^8$; 5) $8.5 \cdot 10^8$ V/m^2.

It is seen in Fig. 1 that neither the inhomogeneous electric field nor the inhomogeneous magnetic field at the indicated strengths has an appreciable influence on the adsorption–desorption isotherms of samples having finite dimensions and through pores. This result is attributable to the fact that the applied external fields are much less than the internal fields acting in the adsorbate–adsorbent system and governing the molecular bond energy.

Although these fields did not alter the equilibrium of the adsorbate–adsorbent system, they were sufficient to change the adsorption kinetics noticeably. Figure 2 gives results in support of this conclusion. The time is plotted along the horizontal axis, and the mass variation of an initial dry sample of the same KSS-4 silica gel on the vertical. Vapor adsorption proceeded from the surrounding medium, where a relative vapor pressure p/p_s close to unity was maintained. The measurements were performed at T = 293°K.

It is clear from Fig. 2 that the application of an inhomogeneous magnetic field and an inhomogeneous electric field accelerates the attainment of equilibrium through the intensification of internal mass transfer in the sample. Here the final state of the system (i.e., the quantity of water adsorbed) does not depend on ∇B or ∇E. Only the kinetics changes, whereupon the equilibrium relaxation time is shortened 23% relative to the zero-field experiment when $\nabla E = 8.5 \cdot 10^8$ V/m^2. According to Eq. (25) the equilibrium relaxation time is smaller for larger values of ∇E.

It was also shown in the same experiments that, unlike water, an appreciable acceleration of adsorption is not exhibited by nonpolar CCl_4, for which $p_e = 0$ and ε is much smaller than for water.

An analysis of the adsorption-rate curves (Fig. 3) indicates that in the initial stage, when the pressure gradient and adsorption rate are large, the fields accelerate the process only slightly, corroborating the theoretical calculations. The influence of the fields, as we see in Fig. 3, grows as the moisture absorption rate decreases.

The experiments described here therefore lend qualitative support to the developed theory. Quantitative calculations for porous bodies are made difficult by the complex geometry of the pore space. To this end it is proposed that future model experiments be set up with individual capillaries.

We note in conclusion that additional allowance (over and above the vapor flux) for adsorption and surface flow (as is particularly mandatory in the case of fine-pored bodies such as, for example, silica gels) does not change the substance of the foregoing conclusions. The exact solutions involve sizable mathematical difficulties here. However, for a simpler system modeling the influence of surface transfer (capillary with its walls coated with a polymolecular liquid film) we obtain for the flow in the stationary state of the system as $t \to \infty$

$$j_{t\to\infty} = UC_0 + \frac{2\rho h_0^3 P}{3\eta r}, \tag{26}$$

where h_0 is the film thickness at $C = C_0$ and P is the force acting on unit volume of the liquid with values given by Eq. (4) or (7). Equation (26) differs from (24) by the presence of the second term for flow in the liquid phase.

Substituting into Eq. (26) the values of U and P for an inhomogeneous electric field, we obtain

$$j_{t\to\infty} = \left[\frac{Dp_eC_0}{kT} + \frac{\rho h_0^3(\varepsilon_0 - 1)}{6\pi\eta r}E\right]\nabla E. \tag{27}$$

As this equation indicates, the flux $j_{t\to\infty}$ is proportional to ∇E. However, since the flux in the liquid phase also depends on E, in fine pores and in the case of large h_0 the flux becomes strongly dependent now not only on ∇E, but on E as well. Analogous conclusions are obtained for an inhomogeneous magnetic field.

The solutions obtained here, of course, do not exhaust the spectrum of potential problems in which it is required to take account of the influence of an inhomogeneous electric or magnetic field on mass transfer in porous bodies. They are aimed at explicating the physical mechanism of the phenomenon and exhibiting its fundamental laws.

NOTATION

p_e, molecular dipole moment; p_m, molecular magnetic moment; D, vapor diffusion coefficient, cm²/sec; k, Boltzmann constant; T, temperature, °K; ε, static dielectric constant; μ, static permeability; C, concentration of vapor molecules per unit volume of pore space, g/cm³; a, concentration of adsorbed molecules, g/cm³; ρ, density of liquid, g/cm³; η, viscosity of liquid, P; v_m, polar volume of liquid, cm³/mole; σ, surface tension of liquid, dyn/cm; R, gas constant, erg/mole · °K; M, molar mass of adsorbate, g/mole; W, moisture content of sample, g/g.

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