

The dependence of the equilibrium concentration of absorbing centres on pressure of water vapour at constant temperature is at present under investigation.

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¹ Garino-Canina, V., *C.R. Acad. Sci., Paris*, **239**, 705 (1954).

² Harrison, A. J., *J. Amer. Cer. Soc.*, **30**, 362 (1947).

Diffusion of Adsorbed Molecules

IN a recent monograph¹, Carman dismisses the suggestion that the spreading pressure ϕ is the operative force in the diffusion of adsorbed molecules with the statement that the coefficient of resistance of such an equation varies more rapidly with concentration than does the diffusion coefficient of Fick's equation. In presenting his arguments for this view, Carman gives for diffusion under a spreading pressure the equation :

$$-\frac{W_s}{At} = B_\phi \frac{\partial \phi}{\partial x} \quad (1)$$

where W_s/At is the number of moles diffusing across unit area of adsorbent in time t under the influence of a gradient $\partial \phi / \partial x$ of the spreading pressure. $1/B_\phi$ is a two-dimensional resistance constant.

This equation does not represent the theory previously presented by me for the diffusion of adsorbed molecules. In the development of the equations for diffusion², I assumed the fundamental dynamical equation for the diffusion of an adsorbed gas to be :

$$\frac{\partial \phi}{\partial x} + C_r u = 0 \quad (2)$$

where C_r is a coefficient of resistance and u is the resultant velocity of motion of the adsorbed film on the surface. From this equation,

$$u = -\frac{1}{C_r} \frac{\partial \phi}{\partial x} \quad (3)$$

and
$$\frac{W_s}{At} = \frac{Nu}{N_A} = -\frac{N}{C_r N_A} \frac{\partial \phi}{\partial x} \quad (4)$$

where N is the number of adsorbate molecules per unit volume of adsorbent and N_A is Avogadro's number. Equation 4 differs from equation 1 by the factor N and the presence of N destroys Carman's argument.

In these equations it is assumed that C_r , which is equal to the resistance force per unit volume at unit velocity, is a constant independent of N . An alternative assumption is that the resistive force per molecule is independent of N . This second assumption was investigated in a subsequent paper³ and was found to be unsatisfactory. If C_m is the coefficient of resistance per adsorbed molecule :

$$C_r = C_m N \quad (5)$$

and
$$\frac{W_s}{At} = \frac{Nu}{N_A} = -\frac{1}{C_m N_A} \frac{\partial \phi}{\partial x} \quad (6)$$

This equation is equivalent to equation 1 used by Carman. His argument, therefore, applies only to an equation which had already been tested and rejected.

The assumption in equation 2, that the resistive force per unit volume is independent of N , requires that the resistive force per molecule varies as $1/N$. Since it is natural to assume that resistive forces are proportional to the energy with which the molecules are bound to the surface, we should expect equation 2 to be applicable only to adsorptions where the differential heats are inversely proportional to the number of atoms adsorbed. That the equation can be applied to the diffusion of adsorbed gases is undoubtedly due to the fact that most heats of adsorption can be roughly represented by a hyperbolic curve. It follows from these arguments that, when this is not so, or when more precise representation is required, it will be necessary to use an expression for the resistive force that corresponds more closely to the measured heats of adsorption.

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¹ Carman, P. C., "Flow of Gases through Porous Media", 122 (Butterworths Scientific Pub., London, 1956).

² Babbitt, J. D., *Can. J. Research*, A, **28**, 449 (1950).

³ Babbitt, J. D., *Can. J. Phys.*, **29**, 437 (1951).

IN the brief treatment of Babbitt's theory in my book, equation 1 of the above communication was used, and it was pointed out that, with the experimental data available, B_ϕ , instead of being a constant, actually varied more rapidly with surface concentration than the surface diffusion coefficient which arises from Fick's equation. Babbitt now points out that, in the form of the theory which he has advocated, the correct expression is given by equation 4. According to this, the quantity which should be constant is not B_ϕ , but B_ϕ/N , where N is a measure of the surface concentration.

When this was applied to the data of Carman and Raal, it was found that B_ϕ/N in all cases varied much less than the surface diffusion coefficient and sometimes showed a remarkable constancy. Thus, for 'Freon 12' (CF_2Cl_2) on Linde silica, it showed little variation from a surface concentration of about one-half monolayer to about two and one-half monolayers, even though the surface diffusion coefficient passes through a maximum in this range. At higher concentrations it increases, but this could probably be ascribed to the action of capillary forces on capillary condensate. For sulphur dioxide on Linde silica, it is not quite so constant, but increases very little from one-half to two and one-half monolayers. Thereafter it rises fairly rapidly. In the case of 'Freon 12' and of carbon dioxide on 'Carbolac', it is only possible to state that, on the whole, the range of variation is less than for the surface diffusion coefficient; but it is not possible to distinguish any range where B_ϕ/N is even approximately constant.

As explained by Babbitt, a constant value of B_ϕ would result if the coefficient of resistance per adsorbed molecule were independent of surface concentration. This seems a natural assumption to make, but it was rejected by Babbitt because it did not fit the results of King for diffusion of water vapour through horn. He has preferred, therefore, to assume B_ϕ/N or C_r is a constant, and, on this basis,