413. Huttig's Multilayer Isotherm.

By R. M. BARRER.

Huttig's isotherm cannot be interpreted physically in terms of B.E.T. (Brunauer-Emmett-Teller) molecular columns. The Huttig isotherm is thermodynamically consistent with a succession of layers in a potential field, vertical interactions between sorbate molecules in successive layers being omitted. Lateral interactions are, however, allowed. The isotherm is thus complementary to the B.E.T. isotherm where vertical interactions are introduced and lateral interactions are omitted. The Huttig potential normally proves to be the equivalent of a London-van der Waals potential due to the surface together with a potential due to lateral interaction.

HUTTIG (Monatsh., 1948, **78**, 177), using kinetic arguments, derived a multilayer isotherm which Ross (J. Phys. Chem., 1949, **53**, 383) has shown to give as good a fit with experimental isotherms as does that of Brunauer, Emmett, and Teller (B.E.T.) (Brunauer, "Adsorption of Gases and Vapours," Oxford Univ. Press, 1944, Chap. 6). Huttig's isotherm has been the subject of criticism (Hill, J. Amer. Chem. Soc., 1950, **72**, 5347) and the present communication gives some views as to its physical interpretation. In all discussions to date (Huttig, Ross, Hill, locc. cit.; Fergusson and Barrer, Trans. Faraday Soc., 1950, **46**, 400) there has been a failure to evaluate the consequences of an essential physical feature which is indicated in the next paragraph, and neglect of which has led to confusion.

Interpretation of the Isotherm.-The equation

defines for Huttig's isotherm the relative number of molecules N_i and N_{i-1} $(N_i/N_{i-1} = \theta'_i)$ in the *i*th and the (i - 1)th layer respectively; a_i and b_i in equation (1) are constants. This equation is *not* compatible with the B.E.T. type of linear molecular column, for when one considers such a column one finds that no two kinetic mechanisms can be devised for evaporation and condensation which are the reverse of one another and at the same time lead to equation (1). The principle of microscopic reversibility thus shows that equation (1) cannot follow from B.E.T. molecular columns.

It is not yet clear therefore with what physical picture Huttig's isotherm is thermodynamically consistent, and what physical limitations this picture involves. It is accordingly of value to consider Huttig's isotherm again, because of its undoubted usefulness in correlating adsorption data and determining surface areas.

We first show that the isotherm is consistent with a distribution of adsorbed molecules in successive layers in a field of sorption potential, emanating from the sorbent. There may be and usually is a contribution to the potential owing to lateral interaction (see next section), but vertical interactions between sorbate molecules in successive layers must not be counted [in order that *i*th-layer molecules may become independent of (i - 1)th or (i + 1)th layer molecules]. If equation (1) is to be satisfied, this model gives :

$$N_i/N_{i-1} = \gamma_i p/(1 + \gamma_i p) \text{ (where } \gamma_i = a_i/b_i) \quad . \quad . \quad . \quad (1a)$$

Thus the field of sorption potential caused by the sorbate-sorbent interaction, and by *lateral* sorbate-sorbate interaction must be such that

$$\theta_i = \frac{N_i}{N_s} = \prod_{\gamma_1,\ldots,\gamma_i} \left(\frac{\gamma_i p}{1 + \gamma_i p} \right) \cdot \ldots \cdot \ldots \cdot (2)$$

where θ is the degree of filling of the *i*th layer and N_s the number of molecules needed to saturate that (and on a plane surface any other) layer. For a vapour equation (2) may be written :

where $C_i = \gamma_i p_0$, $x = p/p_0$, and p_0 is the vapour pressure of liquid sorbate. The resultant isotherm is:

$$v/v_m = \Sigma \theta_i \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

where v and v_m have their usual significance (Ross, *loc. cit.*). Equations (3) and (4) lead easily to all variants of Huttig's isotherm (Fergusson and Barrer, *loc. cit.*).

When each layer is thus made independent of other layers the thermodynamic equilibrium condition is $M_i = M_g$ where M_i is defined by $\frac{M_i}{kT} = -\frac{\partial}{\partial N_i} (\ln Q_i)$ and $Q_i = F(N_i, N_s, T, \phi)$. Here M_i and M_g are the chemical potential in any *i*th layer and in the gas phase respectively; Q_i denotes the partition function, and ϕ is the sorption potential. With M_i thus defined this is a different equilibrium condition from that obtained by using the B.E.T. model (Hill, *loc. cit.*). The condition $M_i = M_g$ corresponding to Huttig's isotherm is satisfied by any gas obeying the equation p(V - Nb) = NkT in any field of potential due to the surface. It will likewise be followed by a van der Waals gas in the field of sorption potential provided that we omit vertical

Some distributions of molecules near a surface, in presence of various fields of sorption potential.



Curves 1, 2, and 3: $\frac{\theta}{1-\theta} \exp \frac{\theta}{1-\theta} = \theta_{\theta} \exp \beta$, where $\beta = \frac{3000}{RT} \left(\frac{r_0}{r}\right)^n$; $r_0 = 4.0$ A.; $T = 90^{\circ}$ K.; p = 1 atm. so that $\theta_{\theta} = 0.00051$; and n = 1, 2, and 3 respectively. Equation of state : p(V - Nb) = NkT, with b as for nitrogen.

Curve 4: $\frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta}-a\theta\right) = \theta_{\theta} \exp\left(\frac{\theta}{1-\theta}-a\theta\right) = \theta_{\theta} \exp\left(\frac{\theta}{1-\theta}-a\theta\right) = \theta_{\theta} \exp\left(\frac{\theta}{1-\theta}-a\theta\right) = \theta_{\theta} \exp\left(\frac{\theta}{1-\theta}-a\theta\right) = 0$; n = 3; a = 9.97; and all other constants as for curves 1, 2, and 3. Equation of state: $(p + aN^2/V^2)(V - Nb) = NkT$, for nitrogen gas. The simple B.E.T. distribution with $\theta_1 = 0.90_3$, $C_2 = C_3 = \ldots = 1$, and the corresponding Huttig distribution with $\theta_1 = 0.90_3$, $C_2 = C_3 = \ldots = 1$ are also shown as dotted curves.

sorbate-sorbate interactions between molecules in different layers, while counting lateral interactions. This is complementary to the B.E.T. model which counts vertical and omits lateral interactions.

In accord with the idea of such a distribution the sorption volume is divided parallel to the surface into layers one molecule thick. Any molecular centre falling within one such region belongs to that layer. Molecular centres may be, but are not necessarily, regarded as concentrated at the mid-plane of the layer. All that is necessary for the independence of layers is that interaction between molecules in different layers be omitted. This omission may be one reason why Huttig's isotherm understates sorption at higher p/p_0 , for at higher relative pressures the self-potential of sorbate becomes dominant in building layers beyond the first (Barrer and Robins, *Trans. Faraday Soc.*, in the press).

The Huttig Distribution.—One must also consider further the magnitude and character of the potential which will give rise to the Huttig type of isotherm. This can be done by comparing the distribution of a gas obeying the equations

$$p(V - Nb) = NkT$$
 and $\left(p + \frac{a^2N^2}{V^2}\right)(V - Nb) = NkT$

in a London-van der Waals potential due to the sorbent with the distribution required by Huttig's isotherm.

The figure gives the distribution

$$\theta_{g} \exp \beta_{i} = \frac{\theta_{i}}{1 - \theta_{i}} \exp \left(\frac{\theta_{i}}{1 - \theta_{i}}\right).$$
(5)

corresponding to p(V - Nb) = NkT. For a molecule with the dimensions of nitrogen at 90° K., we have $\theta_g = N/N_s = pb/VkT = 0.00051$, when p = 1 atm. Also $\beta_i = E_i/RT = \text{const.}/r_i^n RT$, where r_i denotes the distance of the mid-plane of the *i*th layer from the surface, E_i is the energy of interaction between an Avogadro number of molecules in this *i*th layer and the substrate. E_i when n = 3 corresponds to London disperision forces (De Boer and Custers, Z. physikal. Chem., 1934, 25, B, 225; Verwey and Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, 1948, Chap. 6). In curves 1, 2, and 3, E_1 for the molecule in the first layer is taken to be 3000 cals./g.-mol., and n = 1, 2, and 3 respectively. The co-volume and molecular dimensions of the sorbate are taken to be those of nitrogen and the mid-plane of successive layers to lie at 4, 8, 12, 16, etc., A. from the mid-plane of the surface layer of sorbent atoms.

The distribution corresponding to the Huttig isotherm in its simplest form $\frac{v}{v_m} = \frac{C_1 x}{1 + C_1 x} (1 + x)$ is also given, and follows quite closely the curve 2 of the figure (n = 2), when $C_1 = 33.08$ and x = 0.281 (as for nitrogen at 90° K.). The Huttig isotherm in its general form (Fergusson and Barrer, *loc. cit.*), *viz.*:

$$\frac{v}{v_m} = \frac{C_1 x}{1 + C_1 x} \left(1 + \frac{C_2 x}{1 + C_2 x} + \frac{C_2 C_3 x^2}{(1 + C_2 x)(1 + C_3 x)} + \dots \right) \quad . \qquad . \qquad (6)$$

coincides with the curve for n = 1, and with x = 0.281, when $C_1 = 33.08$, $C_2 = 11.5$, $C_3 = 4.63$, $C_4 = 3.95$, a very reasonable sequence of values.

The Huttig distribution thus normally falls off less rapidly than corresponds to London-van der Waals forces between substrate and sorbate when *all* molecular interactions between sorbate molecules are omitted (curve 3, figure). This slower decrease is then formally equivalent to the empirical introduction of *lateral* interactions, just as the still slower decrease corresponding to the B.E.T. distribution (curve 4) is formally the equivalent of introducing *vertical* intermolecular interactions. The empirical nature of Huttig and B.E.T. distributions is shown by calculating θ vs. r for a van der Waals gas where $(p + aN^2/V^2)(V - Nb) = NkT$. In this case one may approximate the actual distribution by using the relation *:

$$\theta_{g} \exp \beta = \frac{\theta}{1-\theta} \exp \left(\frac{\theta}{1-\theta} - \alpha \theta \right).$$
(7)

where $\alpha = 2a/bkT$ with a and b defined by van der Waals's equation for nitrogen, $\beta = \text{const.}/r^3 RT$, and $E_1 = 3000$ cals./g.-mol. for a molecule in the first layer. The appropriate value of α for nitrogen gas at 90° K. is 9.97 (Barrer and Robins, *loc. cit.*). The artificiality of the B E.T. and Huttig distributions near the surface, compared with distribution of nitrogen at 90° K., is made clear from these curves.

In conclusion one may say that Huttig's isotherm has limitations comparable with those of the B.E.T. isotherm. Both isotherms may be used in obtaining surface areas and in correlating adsorption data, but in these uses a large element of empiricism must be accepted.

I am indebted to Mr. J. A. Barrie, B.Sc., of this Department for the calculations recorded in the figure.

MARISCHAL COLLEGE, ABERDEEN.

[Received, March 28th, 1951.]

* More exact calculation, allowance being made for the effect of concentration gradient and of the limited extent of the sorbed film on the sorbate-sorbate self potential, shows that the discontinuity in Curve 4 often, but not always, disappears (Barrer and Robins, paper in preparation).