

Hüttig's Adsorption Isotherm

THREE years ago, Hüttig¹ derived a multilayer adsorption isotherm which in most cases agrees with experiment up to higher relative pressures $x = p/p_0$ (where p_0 is vapour pressure of the liquid adsorbate) than the Brunauer-Emmett-Teller² isotherm. Hüttig's formula, however, is not in accord with the kinetic assumptions implied in the derivation and does not explain the entire failure of the theory at very high pressures (x greater than 0.8).

The kinetic assumption underlying Hüttig's theory is that all molecules of each layer may evaporate, whereas in the Brunauer-Emmett-Teller theory only uncovered molecules are allowed to do so. Hüttig's mechanism of desorption is rather unrealistic from the point of view of the multilayer model in which the adsorbed molecules are arranged in vertical chains. To permit a lateral evaporation of covered molecules, these vertical chains must be arranged rather loosely, and one can scarcely assume that such an arrangement would be in a stable equilibrium. Further, if a covered molecule evaporated from the lower part of a vertical chain, this chain would collapse or at least re-arrange itself, so that the net result would again be evaporation from the top of the chain.

This difficulty can be removed in the following way. We consider a surface on which adsorption occurs only at localized centres separated from each other by surface regions with negligible attractive power for the adsorbate. The distance between the centres should be at least one or two molecular diameters. Then the vertical chains of the multilayer model turn over into the surface, where they form essentially two-dimensional clusters around the localized centres. In this model the concept of several layers loses its meaning. We can distinguish only between the molecules adsorbed on the localized centres (first layer) and additional molecules (higher layers). We shall, however, retain Hüttig's formalism in which the different layers are distinguished. It appears that for this model Hüttig's mechanism of evaporation is quite satisfactory. A proof of this assumption can be derived, however, only from a rigorous statistical treatment of the model. The statistical equivalent to Hüttig's formalism will be investigated elsewhere.

Quite independent of the special condition of desorption, there is still another, much more general, argument for the proposed cluster model. It has been shown by Halsey³ that two-dimensional condensation within the first layer occurs earlier than the formation of higher layers in all cases where the surface centres are close enough together to exclude the cluster model suggested here. Hence it appears that this latter model is the only one which fits the formalism of Brunauer-Emmett-Teller or Hüttig.

Concerning the failure of Hüttig's isotherm for very high pressures, we assume that this failure is the result of the simplification that the affinity constants K_1 and K (see equation 1) or, in other words, the conditions of evaporation, do not depend on the number of adsorbed molecules. This simplifying assumption can be modified in a semi-empirical way by the following considerations. The clusters, which are essentially two-dimensional at low pressures, will gradually overlap and grow vertically to the surface if the pressure is increased. The result will be that a certain fraction n' of the n adsorbed molecules will be entirely enveloped by other molecules, and

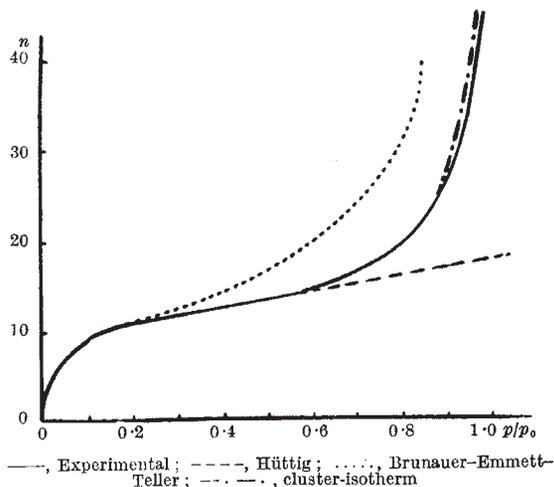
hence unable to evaporate. If we put $n = nx^s$, Hüttig's velocity of desorption $K_i''n$ is transformed to $K_i''n(1-x^s)$ and the affinity constant $K_i = K_i'/K_i''$ is transformed to $K_i/(1-x^s)$. Introducing this expression into Hüttig's formula (1) (where n_0 is number of surface centres),

$$\Theta = \frac{n}{n_0} = \frac{K_1 p}{1 + K_1 p} (1 + Kp); \quad (1)$$

and putting $K_1 p = Cx$ and $Kp = x$, we obtain:

$$\Theta = \frac{Cx}{1 + Cx - x^s} \cdot \frac{1 + x - x^s}{1 - x^s}. \quad (2)$$

Equation 2 is the formula for the cluster isotherm in the notation of the Brunauer-Emmett-Teller theory. It is a generalization of formulae which are the limiting cases for $s = 1$ (Brunauer-Emmett-Teller) and $s = \infty$ (Hüttig). Since in Hüttig's theory the number of chains containing s adsorbed molecules is about $n_1 x^s$ (n_1 is number of molecules in the first layer), s can be interpreted as the average number of molecules necessary to envelop entirely a molecule of the first layer. Hence the reciprocal of s measures the tendency of the essentially two-dimensional clusters partly to grow vertically to the surface. $1/s$ is zero for Hüttig's isotherm; this involves restriction to entirely two-dimensional clusters and the finite number $2n_0$ of adsorbed molecules for $p = p_0$.



Adsorption isotherms for the system $\text{H}_2\text{O}-\text{BaSO}_4$ at 273°K .

The agreement between formula (2) and experiment is found to be very satisfactory. This can be seen from the accompanying graph, which is characteristic of a large number of cases. The parameter s , which is 5 in this case, has been found to assume values between 2 and 12 in other systems and to increase with temperature.

Details of this work will be published elsewhere.

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¹ Hüttig, G. F., *Monatsh. Chem.*, **78**, 177 (1948).

² Brunauer, S., Emmett, P. H., and Teller, E., *J. Amer. Chem. Soc.*, **60**, 309 (1938).

³ Halsey, G., *J. Chem. Phys.*, **16**, 931 (1948).