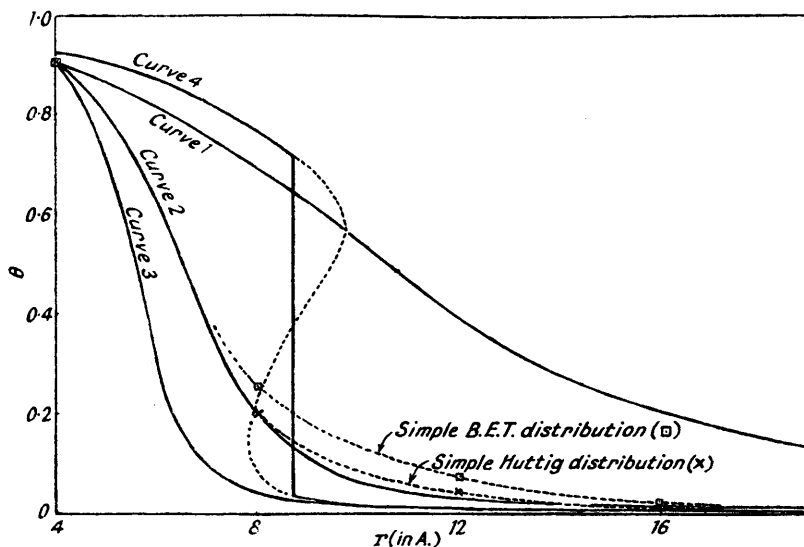




where  $v$  and  $v_m$  have their usual significance (Ross, *loc. cit.*). Equations (3) and (4) lead easily to all variants of Huttig's isotherm (Fergusson and Barrer, *loc. cit.*).

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  $\phi$  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:  $\frac{\theta}{1-\theta} \exp. \frac{\theta}{1-\theta} = \theta_0 \exp. \beta$ , where  $\beta = \frac{3000}{RT} \left(\frac{r_0}{r}\right)^n$ ;  $r_0 = 4.0 \text{ \AA.}$ ;  $T = 90^\circ \text{ K.}$ ;  $p = 1 \text{ atm.}$  so that  $\theta_0 = 0.00051$ ; and  $n = 1, 2,$  and  $3$  respectively. Equation of state:  $p(V - Nb) = NkT$ , with  $b$  as for nitrogen.

Curve 4:  $\frac{\theta}{1-\theta} \exp. \left(\frac{\theta}{1-\theta} - a\theta\right) = \theta_0 \exp. \beta$ ;  $n = 3$ ;  $a = 9.97$ ; 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  $\theta_1 = 0.90_3$ ,  $C_2 = C_3 = \dots = 1$ , and the corresponding Huttig distribution with  $\theta_1 = 0.90_3$ ,  $C_2 = C_3 = \dots = 1$  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

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

