A STATISTICAL DERIVATION OF LANGMUIR'S ADSORPTION ISOTHERM

By Prof. R. H. FOWLER, Trinity College

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I. Introduction

The commonest form of Langmuir's adsorption isotherm is

$$\theta = \frac{Ap}{1+Ap}, \tag{1}$$

where θ is the fraction of the surface of the solid covered by adsorbed molecules, p the gas pressure in equilibrium with the adsorbed layer and $A = A\ (T)$ a function of the temperature alone. This formula is usually derived by a kinetic argument which balances the rates of deposition and re-evaporation. It is perhaps not without interest to show that formula (1) and similar formulae can be obtained directly by the usual statistical methods which evaluate all the properties of the equilibrium state of any assembly. The ordinary derivation is apt to obscure the essentially thermodynamic character of (1) and to lead one to think that its form depends on the precise mechanisms of deposition and re-evaporation, whereas in fact it depends only on the whole set of states, adsorbed and free, accessible to the molecules in question. By suitable use of the usual technique for handling assemblies obeying the Fermi-Dirac statistics the saturation effect can be naturally incorporated in the theory *ab initio*.

II. Molecular adsorption

Let us suppose that the states accessible to the adsorbable systems are (i) the ordinary states of free atoms or molecules in a gas, a set of states of weight ϖ_r and energy ϵ_r, and (ii) states of attachment to any one of the surface atoms of the adsorbing solid. We suppose in this section that the atom or molecule is attached as a whole to the surface atom of the adsorber and that in this state of attachment it possesses a series of possible states of weights ρ_r and energies η_r leading to the partition function $v_s(T) = \Sigma_r \rho_r e^{-\eta_r/kT}$ for the adsorbed states attached to a specified surface atom. We suppose further that there are N_s surface atoms in the assembly capable of serving as points of attachment and that only one adsorbed molecule can be attached to any one surface atom. The adsorbed states belonging to any one surface atom are assumed to be independent of whether surrounding surface atoms are holding adsorbed molecules or not. It will be sufficient to use classical statistics for the gas, but since in the classical limit it is a matter of indifference what statistics are used we shall actually use Fermi-Dirac statistics as a matter of convenience. The energy zero for an absorbable molecule may be defined to be the energy of the molecule in its lowest adsorbed state.

Following standard procedure* we now form for the gas states the product

$$\prod_{r=0}^{\infty}(1+xz^{\epsilon_r})^{\varpi_r}, \tag{2}$$

and for the adsorbed states the product

$$[1+x(\Sigma_r \rho_r z^{\eta_r})]^{N_s}. \tag{3}$$

If the assembly consists of M adsorbable systems in all, with a total energy E, then the total number C of accessible states of the assembly is given by the coefficient of $z^E x^M$ in the product of (2) and (3), that is by

$$C=\left(\frac{1}{2\pi i}\right)^2\iint\frac{dx}{x^{M+1}}\frac{dz}{z^{E+1}}\prod_{r=0}^{\infty}(1+xz^{\epsilon_r})^{\varpi_r}[1+x(\Sigma_r \rho_r z^{\eta_r})]^{N_s}, \tag{4}$$

the integrals being taken round suitable contours. Note the manner in which the sum $\Sigma_r \rho_r z^{\eta_r}$, for each point of attachment, enters with a single common factor x, since the occupation of any state on any point of attachment puts out of action all states on that point of attachment. The proposed form makes precisely this condition hold.

Having composed C, the rest of the derivation is standard. The integrand of C possesses a unique stationary value, $z=\vartheta=e^{-1/kT}$, $x=\lambda$, determined by

$$\lambda\frac{\partial}{\partial\lambda}\sum_{r=0}^{\infty}\varpi_r\log(1+\lambda e^{-\epsilon_r/kT})+\lambda\frac{\partial}{\partial\lambda}N_s\log(1+\lambda v_s(T))=M, \tag{5}$$

$$kT^2\frac{\partial}{\partial T}\sum_{r=0}^{\infty}\varpi_r\log(1+\lambda e^{-\epsilon_r/kT})+kT^2\frac{\partial}{\partial T}N_s\log(1+\lambda v_s(T))=E. \tag{6}$$

If $\overline{M}_g$ and $\overline{M}_s$ are the equilibrium numbers of molecules free and adsorbed respectively, then it follows further that

$$\overline{M}_g=\lambda\frac{\partial}{\partial\lambda}\sum_{r=0}^{\infty}\varpi_r\log(1+\lambda e^{-\epsilon_r/kT}), \tag{7}$$

$$\overline{M}_s=\lambda\frac{\partial}{\partial\lambda}N_s\log(1+\lambda v_s(T))=\frac{N_s\lambda v_s(T)}{1+\lambda v_s(T)}. \tag{8}$$

In the classical limit we can now simplify (7) and it becomes

$$\begin{aligned}\overline{M}_g&=\lambda\sum_{r=0}^{\infty}\varpi_r e^{-\epsilon_r/kT}\\&=\lambda\frac{(2\pi mkT)^{\frac{3}{2}}V}{h^3}b_g(T)\,e^{-\chi/kT}.\end{aligned} \tag{9}$$

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* See for example, Fowler, *Statistical Mechanics* (1929), § 21·4.

In (9), χ is the energy step from the lowest adsorbed state to the lowest free state in the gas, $b_g(T)$ the partition function for the rotations and vibrations of the free molecule, and the remaining factor the usual partition function for the free motion of its centre of gravity in a volume V.

In the problem proposed in this section

$$\overline{M}_s/N_s=\theta, \quad \overline{M}_g/V=p/kT. \tag{10}$$

Combining (8), (9) and (10) we find at once

$$p=\frac{\theta}{1-\theta}\,\frac{(2\pi m)^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{h^3}\,\frac{b_g(T)}{v_s(T)}\,e^{-\chi/kT}, \tag{11}$$

which is the explicit form of Langmuir's isotherm (1).

III. ATOMIC ADSORPTION OF A DIATOMIC MOLECULE X_2

It is not always realized that a somewhat different isotherm must be obtained if the adsorbable systems are atoms X, while the gas phase consists overwhelmingly of molecules X_2. All the work of the preceding paragraph stands with atoms for the adsorbable systems and free systems in the gas, except that an extra set of states, the molecular gas states, is accessible to the assembly. These states lead to an extra factor

$$\prod_{r=0}^{\infty}(1+x^2z^{\zeta_r})^{\sigma_r}$$

in (4) with corresponding terms in (5) and (6). Besides (7) and (8) there is now the extra equation

$$\overline{(M_2)_g}=\lambda^2\frac{\partial}{\partial\lambda^2}\sum_{r=0}^{\infty}\sigma_r\log\left(1+\lambda^2e^{-\zeta_r/kT}\right) \tag{12}$$

$$=\lambda^2\frac{(2\pi m'kT)^{\frac{3}{2}}V}{h^3}\,b'_g(T)\,e^{-\chi'/kT}. \tag{13}$$

In (13) m' and $b'_g(T)$ refer to the free molecule X_2 and χ' is the energy step from the lowest adsorbed states for two atoms X to the lowest state for the pair as a molecule X_2 in the gas. Since the free atoms are negligible we now have

$$\overline{(M_2)_g}/V=p/kT. \tag{14}$$

Combining (8), (13) and (14) we find at once

$$p=\left(\frac{\theta}{1-\theta}\right)^2\frac{(2\pi m')^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{h^3}\,\frac{b'_g(T)}{v_s^2(T)}\,e^{-\chi'/kT}. \tag{15}$$

This isotherm has the form

$$\theta=\frac{(Ap)^{\frac{1}{2}}}{1+(Ap)^{\frac{1}{2}}} \tag{16}$$

in place of (1). Whatever the mechanism, if the systems are adsorbed as separate atoms X, requiring therefore two points of attachment, and present in the gas overwhelmingly as molecules X_2, the isotherm must have the form (16) and not (1).

It should be remembered that all these formulae have the weakness that they must assume that the fields holding the adsorbed molecules, and therefore $v_s(T)$ and χ, are temperature independent, whereas being fields of solid surfaces they may actually depend on the temperature, and also on the presence of adsorbed neighbours.

IV. ADSORPTION OF COMPETING MOLECULES

It is simple to discuss by the same methods the case of an adsorbed layer in equilibrium with two (or more) gases of adsorbable atoms or molecules, which can attach themselves to surface atoms but in so doing exclude all others of either kind. For definiteness let us confine attention to the conditions of § II, generalized to two competing gases. The generalization is obvious. We have to use selector variables x_1 and x_2 for each type of gaseous system and find

$$C=\left(\frac{1}{2\pi i}\right)^3\iiint\frac{dx_1}{x_1^{M_1+1}}\frac{dx_2}{x_2^{M_2+1}}\frac{dz}{z^{E+1}}\prod_{r=0}^{\infty}(1+x_1z^{\epsilon_r^1})^{\varpi_r^1}\prod_{r=0}^{\infty}(1+x_2z^{\epsilon_r^2})^{\varpi_r^2}$$

$$\times[1+x_1(\Sigma_r\rho_r^1z^{\eta_r^1})+x_2(\Sigma_r\rho_r^2z^{\eta_r^2})]^{N_s}. \quad (17)$$

The factor in square brackets allows for no system or one system of either type but no more to be attached to each surface atom. From (17) it follows that*

$$\overline{M_g^1}=\lambda_1\frac{(2\pi m_1kT)^{\frac{3}{2}}V}{h^3}b_g^1(T)\,e^{-\chi_1/kT}, \quad (18)$$

$$\overline{M_g^2}=\lambda_2\frac{(2\pi m_2kT)^{\frac{3}{2}}V}{h^3}b_g^2(T)\,e^{-\chi_2/kT}, \quad (19)$$

$$\overline{M_s^1}=\frac{N_s\lambda_1v_s^1(T)}{1+\lambda_1v_s^1(T)+\lambda_2v_s^2(T)}, \quad (20)$$

$$\overline{M_s^2}=\frac{N_s\lambda_2v_s^2(T)}{1+\lambda_1v_s^1(T)+\lambda_2v_s^2(T)}. \quad (21)$$

If $\theta_1=\overline{M_s^1}/N_s$, $\theta_2=\overline{M_s^2}/N_s$, $p_1=\overline{M_g^1}kT/V$, $p_2=\overline{M_g^2}kT/V$, then†

$$p_1=\frac{\theta_1}{1-\theta_1-\theta_2}\frac{(2\pi m_1)^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{h^3}\frac{b_g^1(T)}{v_s^1(T)}e^{-\chi_1/kT}, \quad (22)$$

$$p_2=\frac{\theta_2}{1-\theta_1-\theta_2}\frac{(2\pi m_2)^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{h^3}\frac{b_g^2(T)}{v_s^2(T)}e^{-\chi_2/kT}. \quad (23)$$

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* It will be sufficiently obvious that in this section the superior affix 2 refers to the second type of system and does not denote a square.

† Equations equivalent to these or their generalizations were first given by kinetic arguments by Henry, *Phil. Mag.* 44 (1922), 689.

These equations lead to the two isotherms

$$\theta_1 = \frac{A_1 p_1}{1 + A_1 p_1 + A_2 p_2}, \quad \theta_2 = \frac{A_2 p_2}{1 + A_1 p_1 + A_2 p_2}, \tag{24}$$

with explicit values for A_1 and A_2.

Equations (24) can be extended to the conditions of § III and so apply for example to the competing adsorption of H_2 and D_2. Equations (24) then hold with p_1 and p_2 denoting the atomic partial pressures. These can then be converted into molecular partial pressures by the ordinary equations of dissociative equilibrium.

Still more complicated cases can be handled in which the second system can also be attached to an already adsorbed first system and so on. This particular case is dealt with by using in C the factor

$$[1 + x_1 (\Sigma_r \rho_r^1 z^{\eta_r^1}) \{1 + x_2 (\Sigma_s \sigma_s z^{\zeta_s})\} + x_2 (\Sigma_r \rho_r^2 z^{\eta_r^2})]^{N_s}. \tag{25}$$

Further elaboration of these formulae is however probably not worth while since the conditions postulated hardly correspond sufficiently closely to those of actual adsorbed systems.