144. *Monolayers on Solids.*

By J. K. ROBERTS.

Certain statements by Langmuir (Faraday Lecture, this vol., p. 533) are discussed or corrected, and numerical calculations are given based on the author's work.

LANGMUIR (*loc. cit.*) makes the following statement : " A more detailed analysis of the condensation of atoms to form an immobile adsorbed film for the case $\gamma = 2$, $E = 5$ has recently been published by Roberts (*Proc. Camb. Phil. Soc.*, 1940, **36**, 53). The adsorption isotherm obtained by Roberts and others for this case is essentially different from that given in the present paper. The derivations of the adsorption isotherms for the cases $\gamma = 2, E = 5$ and $\gamma = 4, E = 9$ are contained in a paper by Tonks, which was recently submitted to the *Journal of Chemical Physics*. He shows that Roberts' application of Bethe's statistical method to this problem is incorrect."

The last sentence in this statement cannot be dealt with because no justification of it is given and the paper by Tonks is not yet available.

In the author's paper, cited above, no numerical calculations of the isotherm were given because the object of the paper was to discuss the properties of immobile films in which each adsorbed atom remains permanently fixed on the site on which it is first adsorbed and in which, in Langmuir's notation, $\gamma = 2$ and $E = 5$. From the calculations on which the results given in it were based the isotherm can, however, be immediately obtained and, in view of Langmuir's statement, it seems desirable to give a comparison of it with Tonks's isotherm as quoted by Langmuir in equations (44)

$$\theta_L = 2Ap(1 - 2{\cdot}5\theta_L + 1{\cdot}5\theta_L{}^2 + 0{\cdot}75\theta_L{}^3 + \ldots) \quad . \quad . \quad . \quad . \quad (1)$$

and (49)

$$\theta_L = Ap(1 - \theta_L)[1 - 3(1 - \theta_L)^2 + 5(1 - \theta_L)^3] \quad . \quad . \quad . \quad . \quad (2)$$

The former equation is stated to be valid from $\theta_L = 0$ to $\theta_L = 0{\cdot}3$ and the latter from $\theta_L = 0{\cdot}7$ to $\theta_L = 1$. The intermediate region from 0·3 to 0·7 is not covered by Tonks's equations. θ_L is used to denote the θ defined by Langmuir to distinguish it from the θ (or rather θ') defined by the author, which is denoted by θ_R. Actually

$$\theta_L = 2\theta_R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is easy to show that the form of the isotherm given by Bethe's method is [see equation (7) of the author's paper cited above, and compare with the treatment of a similar problem (Roberts, *Proc. Camb. Phil. Soc.*, 1938, **34**, 585)]

$$\xi = \frac{\theta_R}{1 - \theta_R} \frac{\mathrm{D}(\theta_R)}{(1 + \varepsilon_2)^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\mathrm{D}(\theta_R)$ and ε_2 are functions of θ_R defined by the author (*loc. cit.*). At constant temperature, ξ is proportional to the pressure and is, in fact, the same as Langmuir's Ap.

In Table I values of Ap from the appropriate one of equations (1) and (2) and of ξ from equation (4) are given for various values of θ_L. The two intermediate values of θ_L are not covered by either of the formulæ given by Langmuir. It will be seen immediately that in the range $\theta_L = 0$—0·3 covered by Langmuir's equation (44) the Tonks formula for the isotherm and the Bethe isotherm give practically identical results, while in the range $\theta_L = 0{\cdot}7$—1 covered by Langmuir's equation (49) the calculated pressures for a given θ_L differ by only about 50% throughout. Considering that each is based on an approximation, this must be regarded as satisfactory agreement and there is nothing in the figures to justify Langmuir's statement that the isotherms are " essentially different."

TABLE I.

θ_L	0·1452	0·2652	0·4962	0·6128	0·7252	0·8234	0·9132
Ap	0·1083	0·2904	—	—	3·007	4·994	10·20
ξ	0·1083	0·2909	1·286	2·463	4·456	7·625	14·73

The Bethe method of treating problems of the type we are considering depends on the detailed discussion of a small group of sites and on the introduction of suitable parameters which take account of the effect of the occupation of sites outside the group on those inside it and *vice versa.* The more sites there are in the group, the behaviour of which is discussed in detail, the more accurate is the final result obtained. In the paper cited by Langmuir, on which the results in Table I are based, a group of nine sites on a simple quadratic lattice was considered in detail. These consisted of a central site and the eight sites nearest to it. In his 1938 paper, the author considered from a different point of view, and using Bethe's method, the lattice shown in the figure. In it the sites are arranged like the atoms in the 110 plane of tungsten. For this lattice and for a film in which, in Langmuir's notation, $\gamma = 2$ and $E = 5$, and in addition there is a repulsive force between adsorbed particles which need not be specified in detail, it was desired to bring out an interesting point in connection with the variation of the heat of adsorption with θ. For this purpose it was sufficient to consider in detail the group of seven numbered sites shown in the figure. In the limiting case of no additional repulsive force between adsorbed particles, a first approximation to the isotherm with which we are now concerned was derived. The values obtained for ξ', which is proportional to p and corresponds to Langmuir's Ap or to the ξ used earlier, at various values of θ_L are given in Table II. Corresponding values of ξ deduced, apart from the first value, by graphical interpolation from those given in Table I are also included. It will be seen that for small values of θ_L the values of ξ' are the same as the more accurate ξ, and even this (for the present purpose) comparatively crude application of Bethe's method gives results that are not seriously in error until θ_L is greater than, say, 0·6.

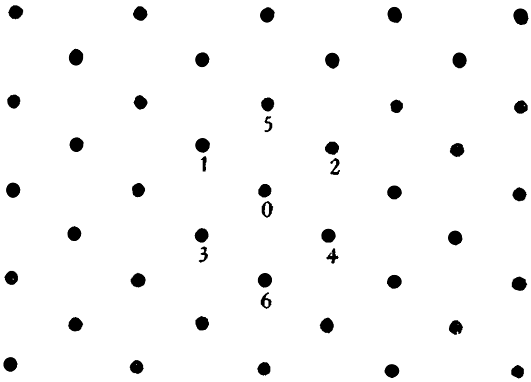

TABLE II.

θ_L	0·1550	0·4330	0·5714	0·7058	0·8164
ξ'	0·1192	0·917	2·5	7·3	23·2
ξ	0·119	0·92	2·0	4·1	7·4

Another point may be mentioned as it concerns the foundation of the theory of adsorption. Langmuir (*loc. cit.*, p. 532) states the basis of the theory in the following form (σ_f is the number of free sites) : " Consider a gas of pressure p in equilibrium with an adsorbed film of gas on the surface of a crystal. Select a particular atom of gas and follow its history as it moves back and forth between the gas and the surface phases. Since this atom, when it condenses on the surface, can go only into free sites, the total probability that it is on the surface is proportional to σ_f . . . . " There are difficulties in the way of accepting this version of the method used by Hückel (" Adsorption und Kapillar-Kondensation," Akad. Verlagsgesellschaft, Leipzig, 1928, p. 157) for, if w_a is the probability that a given atom is on the surface at a given time, and w_g is the probability that it is in the gas phase, it is not w_a but, as Hückel shows, w_a/w_g or $w_a/(1 - w_a)$ that is proportional to σ_f, provided the volume of the gas phase is constant.

Immediately preceding the paragraph on p. 533 under discussion is one which, although noting that in 1935 the author considered the case where $E = 2$ (in Langmuir's notation), yet omits to refer to his statements (*Nature*, 1935, **135**, 1037; *Proc. Roy. Soc.*, 1935, *A*, **152**, 473) pointing out that structural discontinuities, gaps, or holes arise whenever the spacing of the adsorbed particles is greater than that of the sites for adsorption, and that such discontinuities are of particular importance in considering immobile films.

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