

Statistical Mechanics of Multimolecular Adsorption II. Localized and Mobile Adsorption and Absorption

Terrell L. Hill

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Statistical Mechanics of Multimolecular Adsorption

II. Localized and Mobile Adsorption and Absorption

TERRELL L. HILL

Department of Chemistry, University of Rochester, Rochester, New York

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It is shown that the transition from localized to mobile adsorption (in the first adsorbed layer) takes place at rather low temperatures for potential barriers of around 1000 cal./mole or less, so that localized physical adsorption should be a very rare phenomenon at the temperatures usually employed in adsorption experiments. Since the BET (and Langmuir) isotherm actually assumes localized adsorption, a new approximate isotherm equation is derived here on the basis of a mobile first layer obeying a two-dimensional van der Waals' equation. This isotherm is in semiquantitative agreement with the two-dimensional phase changes observed by Jura and co-workers, and by earlier workers, at very low pressures. The localized-mobile transition in the absorption of hydrogen by metals is mentioned briefly. The relationships between (1) the two-dimensional equation of state of a monolayer, (2) the adsorption isotherm of the monolayer, and (3) the ordinary three-dimensional equation of state of the gas being adsorbed are discussed in some detail.

I. INTRODUCTION

IN most cases at ordinary temperatures, a molecule which is held to the surface of a solid by van der Waals forces is able to migrate rather freely over the surface.^{1a} In order to do this the molecule must, in general, be able to pass over potential barriers (of the order of 400 cal./mole^{1a} in physical adsorption) which arise because of the periodic structure of the surface of the solid and the resulting periodic variation (in two dimensions) of the energy of adsorption. However, at sufficiently low temperatures, such a molecule will be restricted to a localized^{1b} site at a potential minimum, with vibrations about the equilibrium point replacing translational motion in two dimensions. At intermediate temperatures, the situation is rather more complicated.

We have been referring above to molecules in the first adsorbed layer. Whether these molecules

are localized or mobile, the behavior of molecules (if any) in second and higher adsorbed layers is generally assumed to resemble the behavior of molecules in the liquid state, and hence these latter molecules are not localized. However, at temperatures below the melting point of the adsorbed phase, this would naturally not be the case.

As is well known, mobile monolayers exhibit a phase change which is analogous to ordinary condensation. This phase change is usually studied experimentally on the surface of a liquid, but there have been a few studies of two-dimensional condensation on the surface of a solid.² Presumably these experiments involving solid surfaces have always dealt with mobile rather than localized monolayers. The theoretical problem involved in studying the condensation of a mobile surface layer is essentially the same as for the usual type of condensation. A completely rigorous treatment has not been accomplished because of mathematical complications, but certain semi-empirical methods are quite useful.

It is clear from theoretical considerations³ that "condensation" of a localized monolayer is also possible. The theory of the phase change in this case is a good deal simpler (though still requiring

^{1a} For a recent discussion of this point, see S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, 1943), pp. 448-454.

^{1b} The term "localized" will be used here to refer to molecules whose motions in the two surface dimensions can be described as primarily vibrational, with only relatively infrequent shifts from one potential minimum to another. These shifts can of course occur in any case by the process of evaporation and condensation. By "mobile" molecules will be meant molecules whose motions in the two surface dimensions are essentially those of a two-dimensional gas or liquid, with no effective constraint due to the periodic variation of the energy of adsorption over the surface. The energy of adsorption itself of course constrains the motion to two dimensions.

² See reference 1a, pp. 437-440. Also, see reference 10.

³ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (University Press, Cambridge, England, 1939), pp. 429-443.

approximations) than for a mobile monolayer, essentially because of the restriction to discrete sites which makes it somewhat easier to enumerate possible states and energies of the system. A statistical treatment leads to Langmuir's isotherm if interactions between adsorbed molecules are neglected, and to a sudden phase change, at temperatures below a critical temperature, if interactions are not neglected. As far as the writer is aware, the condensation of a localized monolayer has never been studied experimentally.

The general problem is thus rather complicated. Not only are different phases possible for an adsorbed layer (for example, gas, liquid expanded, liquid condensed, solid), but one must also consider (1) the low temperature localized-mobile transition, (2) the possibility of multimolecular adsorption at higher pressures, and, in this case, (3) the properties of second and higher layers.

In Section II we shall consider the transition from localized to mobile adsorption when the adsorbed phase is quite dilute. A few remarks will also be made about the absorption of hydrogen by metals, since this is a closely related problem in some respects. In Section III we derive an approximate adsorption isotherm for multimolecular adsorption when the first layer is mobile. Relations between the two-dimensional equation of state and the adsorption isotherm and between the two- and three-dimensional equations of state are discussed in Sections IV and V, respectively.

II. THE LOCALIZED-MOBILE TRANSITION

Adsorption

We consider in this paper only the simplest case. Several possible generalizations will be obvious. We assume that: (1) The potential energy function restricting free migration of an adsorbed molecule over the surface is of the form^{4a}

$$U = \frac{1}{2}V \left(1 - \cos \frac{2\pi x}{d} \right) + \frac{1}{2}V \left(1 - \cos \frac{2\pi y}{d} \right), \\ = \frac{1}{2}V \left(2 - \cos \frac{2\pi x}{d} - \cos \frac{2\pi y}{d} \right), \quad (1)$$

^{4a} If the dimensions of the molecule are large compared to d , the situation is more complicated. But there will still

where the maximum potential barrier is $V_0 = 2V$, and d is the distance between potential minima along both x and y axes (the surface lattice is thus assumed to be simple cubic); and (2) the number of molecules, N , adsorbed in the area $\mathcal{A} = l^2$ is sufficiently small so that (a) interactions between adsorbed molecules may be neglected (the mobile case may then be treated as a perfect gas and the two-dimensional gas pressure will be less than the two-dimensional vapor pressure of the condensed phase—solid or liquid—so condensation will not take place when mobility is acquired, as will ordinarily be the case), and (b) the number of sites available to each of the N adsorbed molecules in the localized case is essentially $n^2 = l^2/d^2$. That is, the probability of any two molecules being in the same site is assumed negligible, and it is not necessary to invoke a special "exclusion principle" restricting the number of molecules per site to one. Although the following discussion will be based on the above simplifications, the general conclusions arrived at should not be affected by further refinements.

It is easy to see that under assumption (2), above, a partition function for the system of the form

$$Q = \frac{1}{N!} f^N, \quad (2)$$

where f is the partition function for a single molecule over the entire area \mathcal{A} , is correct not only for the mobile case but also for the localized case. In the latter case we would ordinarily write

$$Q = \frac{n^2!}{N!(n^2 - N)!} f_v^N, \quad (3)$$

where f_v is the partition function for a single molecule in a single site. Since we are assuming $n^2 \gg N$, Eq. (3) becomes

$$Q = \frac{(n^2)^N}{N!} f_v^N = \frac{1}{N!} (n^2 f_v)^N, \quad (4)$$

which is the same as Eq. (2) with $f = n^2 f_v$, thus taking into account correctly the degeneracy (n^2) in the localized case.

be a periodic potential function. Other things being equal, the potential barrier should be smaller the larger the molecule.

We proceed now to formulate f for the two degrees of freedom of interest here. In order to do this, a study must first be made of the possible energy levels of the system, the system being a single molecule of mass m in the area $\mathcal{A} = l^2$ with the potential energy given by Eq. (1). The two-dimensional quantum-mechanical problem here is essentially equivalent to the one-dimensional problem encountered in studying restricted rotation in molecules such as ethane. This makes it possible to use some of the results and tables obtained by Pitzer and Gwinn,^{4b} after a suitable correlation of parameters. Also, it appears that a rather accurate method of approximation suggested by Pitzer and Gwinn should be quite adequate and very convenient for adsorption studies, so we shall consider it in some detail as applied to the present problem rather than discuss further the more exact results obtained by these authors. The approximation consists of using the following partition function:

$$f = f_{\text{classical}} \times \frac{f_{\text{harmonic osc-quantal}}}{f_{\text{harmonic osc-classical}}} \quad (8)$$

The classical partition function here is

$$f_{\text{class}} = \frac{1}{h^2} \int_{-\infty}^{\infty} \int_0^l \int_0^l \int_0^l \times \exp(-H/kT) dx dy dp_x dp_y, \quad (9)$$

where

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2}V \left(2 - \cos \frac{2\pi x}{d} - \cos \frac{2\pi y}{d} \right). \quad (10)$$

On performing the integrations over the momenta, we have

$$f_{\text{class}} = \frac{2\pi mkT}{h^2} \exp(-V/kT) \times \left[\int_0^l \exp\left(\frac{1}{2} \frac{V}{kT} \cos \frac{2\pi x}{d}\right) dx \right]^2, \quad (11)$$

$$= \frac{2\pi mkT}{h^2} l^2 \exp(-V/kT) I_0^2\left(\frac{V}{2kT}\right), \quad (12)$$

^{4b} K. S. Pitzer, J. Chem. Phys. 5, 469 (1937); K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. 10, 428 (1942).

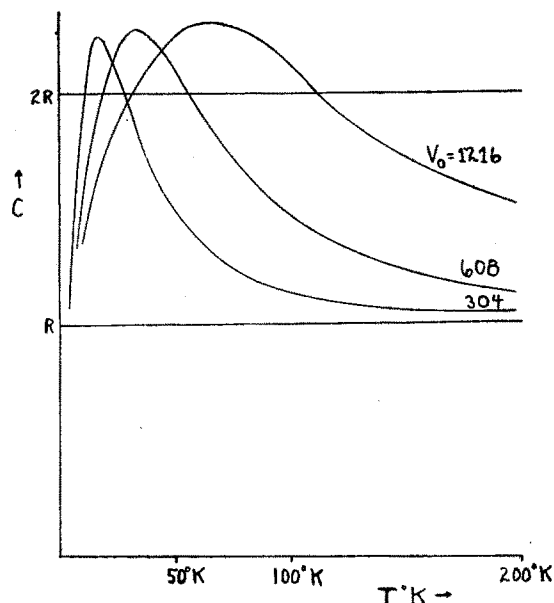


FIG. 1. Heat capacity of adsorbed argon.

where $I_0(u)$ is a modified Bessel function of the first kind. Also,

$$f_{\text{har osc-quant}} = n^2 / [1 - \exp(-h\nu/kT)]^2, \quad (13)$$

$$f_{\text{har osc-class}} = n^2 (kT/h\nu)^2, \quad (14)$$

with

$$\nu = (V/2md^2)^{1/2}. \quad (15)$$

Substituting Eqs. (12)–(14) into Eq. (8) gives

$$f = \frac{2\pi n^2 u e^{-2u} I_0^2(u)}{(1 - e^{-Ku})^2}, \quad (16)$$

$$u = V/2kT, \quad K = (2h^2/md^2V)^{1/2}. \quad (17)$$

The two limiting expressions are, as expected:

$$u \text{ large: } f = n^2 / (1 - e^{-Ku})^2, \quad (18)$$

$$u \text{ small: } f = \frac{2\pi mkT}{h^2} l^2. \quad (19)$$

Equation (18) follows from

$$\lim_{u \rightarrow \infty} I_0(u) = \frac{e^u}{(2\pi u)^{1/2}}, \quad (20)$$

and we have used $n^2 d^2 = l^2$ to obtain Eq. (19).

Finally, the complete partition function for the

two degrees of freedom is

$$Q = \frac{1}{N!} f^N. \quad (21)$$

The contribution of these degrees of freedom to the thermodynamic functions may be obtained in the usual way. For example, for the heat capacity, one finds

$$C = Nk \left\{ -1 + 2u \left[u - \frac{I_1(u)}{I_0(u)} - u \frac{I_1^2(u)}{I_0^2(u)} \right] + \frac{2K^2 u^2 e^{-Ku}}{(1 - e^{-Ku})^2} \right\}. \quad (22)$$

As an illustration we have plotted C against T , in Fig. 1, for different values of $V_0 = 2V$, for argon adsorbed on potassium chloride. The true value of V_0 is probably about 400 cal./mole.⁵ Actually, to save labor, Table IV of Pitzer's^{4b} paper was used instead of Eq. (22). The connection between our notation and his is found by putting

$$I \text{ (moment of inertia)} = mr^2 = ml^2/4\pi^2,$$

since $l = 2\pi r$. This becomes clear if one considers the problem of a particle constrained to move in a circular path. The motion can be thought of either as rotation or translation (even if a perfectly reflecting barrier is introduced, blocking the path). One finds that K is related to the variable n^2/IV used by Pitzer by

$$10^{-36} n^2/IV = 31.25 K^2, \quad (23)$$

where V is in cal./mole.

The theoretical form of the heat capacity curve, as given in Fig. 1, has apparently not been observed experimentally. In fact the only work of this type seems to be that of Simon and Swain¹⁸ in which the heat capacity of adsorbed argon on charcoal was measured. This experimental heat capacity curve resembles that of a one-dimensional harmonic oscillator. There have been several conflicting interpretations of this result. In any case, this example is unsatisfactory from our point of view because of the high porosity of the adsorbent and the large amount of argon

adsorbed, leading to complications not taken into account in the present theory.

The transition from vibration to translation is continuous and takes place over an appreciable temperature range. However, one may indicate the general temperature region in which the transition occurs by noting that the heat capacity for the two degrees of freedom passes through a maximum at about $T = V_0/10R$, this temperature being fairly insensitive to K (values of K of interest here will correspond in general to $10^{-36} n^2/IV < 8$). It is therefore clear, since V_0 is generally of the order of 500 cal./mole or less, that the transition is in progress at quite low temperatures and that true localized physical adsorption should be a very rare phenomenon indeed at temperatures ordinarily used in adsorption work, although intermediate cases should be somewhat more common (e.g., around 90°K). Certainly the mobile case is the rule and not the exception. Thus the above analysis tends to confirm the similar view expressed by Brunauer^{1a} concerning the mobility of physically adsorbed molecules. In chemical adsorption the situation is, of course, radically different because of much higher potential barriers (see the discussion of absorption below).

At the low pressures being considered here the adsorption isotherm is linear, the amount adsorbed being proportional to the pressure. The constant of proportionality is in turn proportional to the partition function f , Eq. (16). It is through the partition function f that the amount of adsorption at low pressures and temperatures will depend on the localized-mobile transition.

Absorption

As is made clear by Fowler and Guggenheim,⁶ the absorption of hydrogen by certain metals bears some resemblance to the adsorption of molecules on the surface of a solid. Both localized and mobile absorption are to be expected and both are found experimentally. We should merely like to point out here that there is an analogous localized-mobile transition problem in absorption, but in three dimensions instead of two. Since localized absorption is very common, the

⁵ W. J. C. Orr, Trans. Faraday Soc. **35**, 1247 (1939). The curves given are not exact, of course, since the theoretical potential function used is more symmetrical than the actual (potassium chloride) one.

⁶ See reference 3, pp. 554-563.

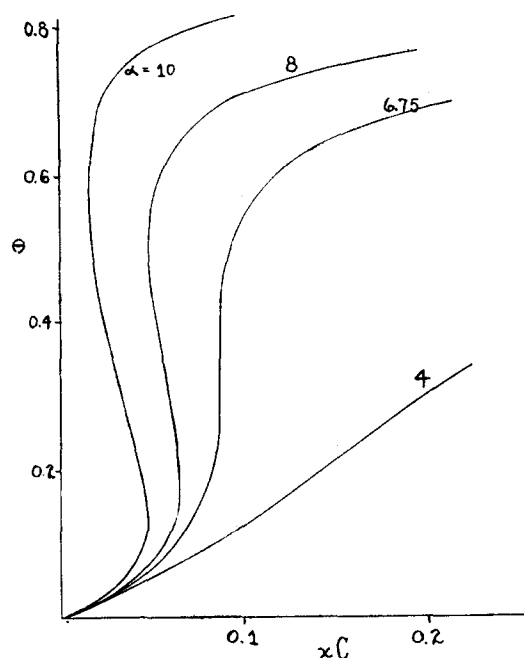


FIG. 2.

potential barriers must be much greater in this case. This is caused, at least in some cases, by chemical absorption—the formation of metal hydrides, MH_n , at the absorption sites (metal atoms).

III. MULTIMOLECULAR ADSORPTION ON A MOBILE FIRST LAYER

The Brunauer-Emmett-Teller⁷ theory of multimolecular adsorption is a generalization of Langmuir's theory of unimolecular adsorption. As is pointed out in the statistical versions,^{8,9} these theories are based on the assumption of localized sites. Since localized physical adsorption is really rather uncommon, it would seem worthwhile to derive a multimolecular adsorption isotherm on the assumption of a mobile first layer. We shall confine ourselves in this paper to a treatment which is only slightly more general than the corresponding statistical treatment⁹ for a localized first layer, which leads to the BET equation. The BET model neglects interactions between molecules in the same layer. We shall also neglect these interactions, except in the first

layer where they will be taken into account in an approximate manner (by the use of Eq. (24)).

We assume for simplicity that the X molecules in the first layer obey van der Waals' equation in two dimensions. It should be recognized at the outset that the choice (there seems to be no satisfactory alternative at the present time) of such a crude equation of state will give the resulting theory only semi-quantitative significance. However, the theory should still be useful in contributing to an understanding of the problem. We also neglect the existence of more than one liquid phase in using this equation of state. Thus we shall write

$$(\varphi + a'X^2/\mathfrak{A}^2)(\mathfrak{A} - Xb') = XkT, \quad (24)$$

where φ is the two-dimensional pressure, \mathfrak{A} is the area, and a' and b' are constants. The associated partition function (for these two degrees of freedom) which leads to this equation of state is

$$\frac{1}{X!} \left[\frac{2\pi mkT}{h^2} (\mathfrak{A} - Xb') \exp(a'X/\mathfrak{A}kT) \right]^X. \quad (25)$$

We therefore write for the separate partition functions of the X molecules in the first adsorbed layer and the $N-X$ molecules in higher layers, respectively,

$$Q_S = \frac{1}{X!} \left[j j_n \exp(\epsilon_1/kT) \times \frac{2\pi mkT}{h^2} (\mathfrak{A} - Xb') \exp(a'X/\mathfrak{A}kT) \right]^X, \quad (26)$$

$$Q_L = \frac{(N-1)!}{(N-X)!(X-1)!} [j_L \exp(\epsilon_L/kT)]^{N-X}, \quad (27)$$

in which j is the internal partition function, j_n the partition function for vibrations normal to the surface, $-\epsilon_1$ the potential energy of a molecule in the first layer due to interaction between the molecule and the surface, and j_L and $-\epsilon_L$ the partition function and potential energy of molecules in higher layers (assumed to be liquid-like). Equation (27) is the same as Eq. (4) in the first paper of reference 9, while Eq. (26) is the analog of Eq. (3) in that paper. We are thus assuming that molecules in the first layer behave like a two-dimensional van der Waals' gas and that addi-

⁷ See reference 1a, Chapter VI.

⁸ R. H. Fowler, Proc. Camb. Phil. Soc. **31**, 260 (1935).

⁹ T. L. Hill, J. Chem. Phys. **14**, 263 (1946); A. B. D. Cassie, Trans. Faraday Soc. **41**, 450 (1945).

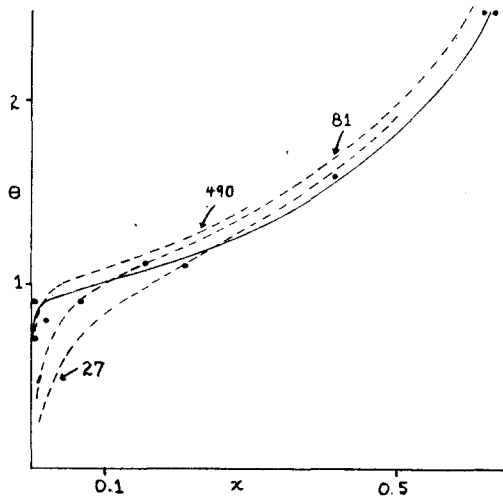


FIG. 3.

tional molecules may build up higher layers on top of the X sites presented by the first layer.

The equilibrium value of X is found from

$$\frac{\partial \log Q_s Q_L}{\partial X} = 0. \quad (28)$$

We neglect unity compared to N and X in Eq. (27) and find, from Eq. (28),

$$\frac{(N-X)(\mathfrak{A}-Xb')}{X^2} \exp\left(-\frac{Xb'}{\mathfrak{A}-Xb'} + \frac{2a'X}{\mathfrak{A}kT}\right) = \frac{j_L \exp[(\epsilon_L - \epsilon_1)/kT]}{jj_n 2\pi m kT/h^2}. \quad (29)$$

The chemical potential of the adsorbed phase is

$$\begin{aligned} \frac{\mu_A}{kT} &= -\frac{\partial \log Q_s Q_L}{\partial N} \\ &= \log \frac{N-X}{N} - \log j_L - \frac{\epsilon_L}{kT}. \end{aligned} \quad (30)$$

For the gas phase,

$$\frac{\mu_G}{kT} = \frac{\mu_0(T)}{kT} + \log p, \quad (31)$$

where p is the gas pressure and $\mu_0(T)$ need not be specified further for our purposes. At equilibrium, $\mu_A = \mu_G$:

$$\log \frac{N-X}{N} - \log j_L - \frac{\epsilon_L}{kT} = \frac{\mu_0(T)}{kT} + \log p. \quad (32)$$

For the pure liquid

$$-\log j_L - \frac{\epsilon_L}{kT} = \frac{\mu_0(T)}{kT} + \log p_0, \quad (33)$$

where p_0 is the vapor pressure of the liquid at T . Subtracting Eq. (33) from Eq. (32) gives

$$(N-X)/N = p/p_0 = x \quad (34)$$

or

$$X = N(1-x). \quad (35)$$

If we now substitute Eq. (35) into Eq. (29) to eliminate X , there results

$$\begin{aligned} C &= \frac{\theta(1-x)^2}{x(1-\theta+\theta x)} \\ &\times \exp\left[\frac{\theta(1-x)}{1-\theta+\theta x} - \alpha\theta(1-x)\right], \end{aligned} \quad (36)$$

$$C = \frac{b'jj_n 2\pi m kT}{j_L h^2} \exp[(\epsilon_1 - \epsilon_L)/kT], \quad (37)$$

$$\theta = Nb'/\mathfrak{A}, \quad \alpha = 2a'/b'kT.$$

The quantity θ corresponds to v/v_m in the BET theory. It is not possible to solve Eq. (36) for θ or x explicitly. In order to calculate an isotherm, for given values of C and α , one must find by trial the value of x which satisfies Eq. (36) for each value of θ chosen.

There are several special cases of interest:

(1) At low pressures ($x \ll 1$), Eq. (36) simplifies to

$$x = \frac{1}{C} \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \alpha\theta\right). \quad (38)$$

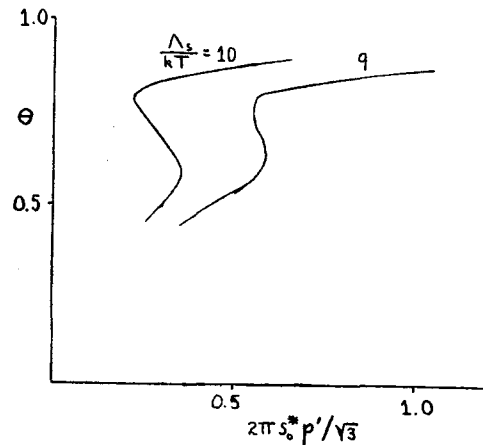


FIG. 4.

It should be emphasized that this equation can also be derived directly from Eq. (26) alone, if only unimolecular adsorption is allowed. That is, it follows from Eq. (24) and does not depend on any of the assumptions concerning the behavior of layers other than the first. In most cases of interest, Eq. (38) is an excellent approximation to Eq. (36) up to values of θ of about 0.7 or 0.8. Then second and higher layers begin to build up and θ becomes increasingly larger than Eq. (38) would predict. We have plotted, in Fig. 2, θ against Cx for several values of α , using Eq. (38). The critical value of α is $\alpha_c = 27/4$, or $T_c = 8a'/27b'k$. This is, of course, also the critical temperature of the equation of state, Eq. (24). The other critical values are $\theta_c = \frac{1}{3}$ and $x_c = 0.0869/C$. These results are of interest in connection with the recent communication of Jura, Loeser, Basford, and Harkins¹⁰ reporting a first-order phase change for *n*-heptane on the surface of silver at 15°C and $p = 0.019$ mm ($x = 0.00070$). Clearly, the present theoretical treatment is in semiquantitative agreement with their results (see also reference 2). As we have arbitrarily chosen van der Waals' equation as the equation of state, one should not expect more than this. Since C will generally be of the order of 100 or more, x_c is in the neighborhood of 10^{-3} – 10^{-4} . Hence this phase change is to be expected at quite low pressures ordinarily, as is emphasized by Jura and co-workers on the basis of their experimental work.

(2) If we set $a' = 0$ and $b' = 0$, the first layer is a perfect gas. Equation (36) then reduces to

$$N = \frac{\alpha C}{b'} \frac{x}{(1-x)^2}, \quad (39)$$

a result obtained by Cassie¹¹ by an incorrect argument.⁹

(3) If the exponential factor in Eq. (36) is ignored, one obtains, on solving for θ ,

$$\theta = Cx/(1-x)(1-x+Cx), \quad (40)$$

which is the BET equation.

Returning now to the general isotherm, Eq. (36), we have plotted in Fig. 3 as an illustration

the isotherm for $C=490$ and $\alpha=8$. The dotted curves are ordinary BET curves for comparison, with $c=490$, 81, and 27. The solid points above the $\alpha=8$ curve are for $\alpha=12$ and those below are for $\alpha=4$. It will be observed that Eq. (36) is not very sensitive to α (except at low pressures). It is also not very sensitive to C , when $x > 0.1$. For example, in this region the points for $\alpha=4$ and $C=490$ are also approximately the points for $\alpha=8$ and C equal to about 10. However, the sensitivity to C at low pressures is considerable, as is indicated in Fig. 2.

Perhaps the most noticeable difference between the mobile isotherm, Eq. (36), and the BET isotherm is that the former associates much lower pressures with values of θ less than, say, 0.8. In general this is in the direction of a correction of a well-known fault of the BET equation, but unfortunately Eq. (36) seems to over correct considerably. It should be remarked that this property (low pressures) of Eq. (36) is caused primarily by the fact that we are taking into account interactions between molecules in the first layer and not to the fact that the molecules are mobile. As will be seen in a later paper of this series, if one takes these interactions into account in a localized first layer a condensation can take place³ at pressures which are also very low. But in this localized condensation θ jumps from almost zero to almost unity, and $\theta_c = \frac{1}{3}$.

While the equations of this section should not be expected to provide a really satisfactory agreement with experiment, it is of some interest to know to what extent they are actually applicable and useful. In a paper to be published at a later date, Dr. George Jura will discuss this question, using experimental data obtained at the University of Chicago.

Finally, the question arises as to whether a more satisfactory equation of state might be used. A possibility that suggests itself is the equation of Devonshire.¹² Actually, the general form (Fig. 4) of the adsorption isotherm thus obtained at low pressures (corresponding to Eq. (38)) is not nearly as satisfactory as Eq. (38) itself, obtained from van der Waals' equation, judging from the experimental curves of Jura and

¹⁰ G. Jura, *et al.*, J. Chem. Phys. **13**, 535 (1945). See also reference 20.

¹¹ A. B. D. Cassie, Trans. Faraday Soc. **41**, 450 (1945).

¹² A. F. Devonshire, Proc. Roy. Soc. **163A**, 132 (1937).

co-workers (which are the only ones available up to the present time). For example, θ_c (Devonshire) = 0.71, which appears to be much too high. The adsorption isotherm is derived in Appendix I.

IV. RELATIONS BETWEEN THE TWO-DIMENSIONAL EQUATION OF STATE AND THE ADSORPTION ISOTHERM

The equation of state of an adsorbed phase can be related thermodynamically to the adsorption isotherm through the Gibbs equations (Appendix II). However, thermodynamics can tell us only very little about the equation of state and adsorption isotherm separately. The following equations represent the best that can be done (the notation is summarized in Appendix II):

$$p(\Gamma, T) = \exp \left\{ \left[\left(\frac{\partial A}{\partial N} \right)_{\mathfrak{A}, T} - \mu^0(T) \right] / kT \right\}, \quad (41)$$

$$\varphi(\Gamma, T) = -(\partial A / \partial \mathfrak{A})_{N, T}. \quad (42)$$

Thermodynamics does not provide $A(\mathfrak{A}, N, T)$ or $\mu^0(T)$. In order to proceed we must turn to statistical mechanics.

We shall confine the discussion to mobile monolayers as this is the case in which φ is of most interest. A corresponding treatment can be given for other systems, using the appropriate partition function. We have,

$$A = -kT \log Q, \quad (43)$$

where Q is the partition function. The problem thus becomes one of finding Q . In analogy with Eq. (26), we employ here

$$Q = \frac{1}{N!} \left[j j_n \exp(\epsilon_1/kT) \frac{2\pi m k T}{h^2} \right]^N Q_r = \frac{1}{N!} Q_1^N Q_r, \quad (44)$$

where Q_r is the usual configuration integral

$$Q_r = \int \cdots \int e^{-W/kT} dx_1 dy_1 \cdots dx_N dy_N, \quad (45)$$

and $W(x_1, \cdots, y_N)$ is the potential energy of interaction between the N adsorbed molecules.

In Eq. (44), Q_1 is independent of \mathfrak{A} so that

$$\varphi = -\frac{\partial A}{\partial \mathfrak{A}} = kT \frac{\partial \log Q}{\partial \mathfrak{A}}, \quad (46)$$

$$= kT \frac{\partial \log Q_r}{\partial \mathfrak{A}}. \quad (47)$$

We now express p in terms of Q_r . In Eq. (41),

$$\frac{\partial A}{\partial N} = -kT \frac{\partial \log Q}{\partial N}, \quad (48)$$

$$= kT \left(\log N - \log Q_1 - \frac{\partial \log Q_r}{\partial N} \right) \quad (49)$$

(assuming that Q_1 is independent of N) and, as is well known,³

$$\frac{\mu^0(T)}{kT} = -\log \left[\frac{(2\pi m k T)^{3/2} k T j_g}{h^3} \right], \quad (50)$$

where j_g is the internal partition function of a molecule in the gas phase. Substituting Eqs. (49) and (50) in Eq. (41), there results

$$p' = p \left\{ \frac{j}{j_g} \frac{h j_n \exp(\epsilon_1/kT)}{(2\pi m k T)^{3/2} k T} \right\} = N \exp \left(-\frac{\partial \log Q_r}{\partial N} \right), \quad (51)$$

which defines p' . When the internal degrees of freedom of adsorbed molecules are not appreciably influenced by interactions with the surface, $j = j_g$. It is often convenient to rewrite Eq. (51) in the form (compare Eqs. (36) and (37)):

$$p' = \frac{p}{p_0} \left\{ \frac{j j_n}{j_L} \frac{2\pi m k T}{h^2} \exp[(\epsilon_1 - \epsilon_L)/kT] \right\} = N \exp \left(-\frac{\partial \log Q_r}{\partial N} \right), \quad (52)$$

in which we have made use of Eq. (33).

Equations (47) and (51) give φ and p in terms of Q_r . Q_r depends on N and \mathfrak{A} and on the intermolecular forces between the N adsorbed molecules. If the nature of these forces is known, it is possible in principle to derive Q_r from Eq. (45).

However, because of mathematical difficulties, approximations¹³ must be resorted to in practice.

When the surface does not effectively influence the intermolecular forces between adsorbed molecules, the right-hand members of Eqs. (47) and (51) are independent of the properties of the surface and depend only on Γ , T , and the properties of the gas being adsorbed. If the adsorption of a given gas is studied on several different surfaces, all of which satisfy the above condition, it is clear that $\varphi(\Gamma, T)$ and $p'(\Gamma, T)$ should be the same for all the surfaces. That is, for surfaces of this type, the two-dimensional equation of state of a given gas is independent of the surface, and the adsorption isotherm $\Gamma(p, T)$ depends on the surface only to the extent that in plotting Γ against p , p must be multiplied by an appropriate constant (which depends on the surface) for each surface in order to make the different adsorption isotherms coincide. This might be the basis of an approximate method of determining the surface area of a solid from the known surface area of another solid¹⁴ (or of determining the relative surface areas of several solids). For, if both surfaces are in the class being discussed, any unusual features of the adsorption isotherms (e.g., phase changes) will occur at the same value of $\Gamma = N/\mathcal{A}$. Hence if $N_1/\mathcal{A}_1 = N_2/\mathcal{A}_2$ and if N_1 , N_2 and \mathcal{A}_1 are known, \mathcal{A}_2 may be calculated.

The question naturally arises as to what combinations of adsorbents and adsorbates are likely to exhibit the phenomenon, discussed above, of the independence of $\varphi(\Gamma, T)$ and $\Gamma(p', T)$ on the adsorbent. There will obviously be a wide range of examples, depending primarily on the polar properties of adsorbent and adsorbate.¹⁵ The most unfavorable case, from the present point of view, would be the adsorption of a substance with a strong permanent dipole moment on a plane of an ionic crystal having all ions of the same type (e.g., the 100 plane in caesium iodide). The permanent dipoles of the adsorbed molecules will all be oriented approximately in the same direction thus introducing a repulsive orientation

effect between them. There will be an additional and similar effect because of a further dipole induced by the ions of the crystal. The attractive dispersion forces and the short range repulsive forces between adsorbed molecules should be relatively unaffected by the surface. But the over-all effect of the adsorbent on the forces between the adsorbed molecules would be considerable in this case. On the other hand, the most favorable combination would be the adsorption of a gas without permanent moments (dipole, quadrupole, etc.) on a non-polar surface (e.g., argon on graphite, charcoal, metals, mercury). In such a case the dispersion and repulsive forces between the adsorbed molecules should be essentially the same as in the gas phase. Without an experimental or a detailed theoretical study of the question, it is rather difficult to say very much about intermediate cases. However, it is clear that the most important criterion for the independence of $\varphi(\Gamma, T)$ and $\Gamma(p', T)$ on the adsorbent is that the adsorbent be non-polar (non-ionic, no oriented dipoles). This is perhaps more crucial than the presence or absence of permanent moments in the adsorbed molecules.

The above argument implies that the most suitable gases would be those that are small and spherically symmetrical. There is another reason for this. Regardless of whether or not the surface is polar, a large or non-spherical molecule will tend to be oriented on the surface in such a way as to give a large "contact" between the surface and the adsorbed molecule (e.g., heptane molecules would lie flat on the surface rather than assume all possible orientations with the same probabilities as in the gas phase). This will clearly lead to a different intermolecular potential function for adsorbed molecules as compared to molecules in the gas phase. Also, the extent to which a molecule is flattened by a surface will be a function of the nature of the surface (even if the surfaces considered are non-polar). Hence, not only will the intermolecular potential function be different (in this case), for adsorbed molecules and molecules in the gas phase but the potential function will also be different for adsorbed molecules on different surfaces, because of varying degrees of flattening.

A further complication is that the most desirable molecules, such as argon, may not be

¹³ See pp. 423-426 of reference 3. For a van der Waals gas $Q_T = (\mathcal{A} - Nb')^N \exp(a'N^2/\mathcal{A}kT)$.

For a perfect gas, $Q_T = \mathcal{A}^N$.

¹⁴ See also D. H. Bangham, Proc. Roy. Soc. A147, 175 (1934).

¹⁵ See Chapters VII and VIII of reference 1a.

TABLE I. Two-dimensional critical constants for *n*-heptane.

	Experimental			Theoretical	
	Silver	Ferric oxide	Graphite	Lennard-Jones and Devonshire	Van der Waals
T_{2c}	$14.9^\circ\text{C} < T_{2c} < 25^\circ\text{C}$	29°C	31°C	13°C	-3°C
$\frac{q_c}{N}$	$310A^2 < \frac{q_c}{N} < 2200A^2$	$900A^2$	$400A^2$	$82A^2$	$110A^2$
φ_c	$\varphi_c > 0.18 \text{ erg/cm}^2$	0.45 erg/cm^2	1.05 erg/cm^2	1.9 erg/cm^2	0.87 erg/cm^2

completely mobile at temperatures sufficiently low to study two-dimensional condensation.

In view of the above restrictions there is naturally some question as to just how many, if any, actual systems will satisfy the various requirements (to some reasonable degree of accuracy). This question must be settled by experiment. At the present time, experimental data do not exist for a suitable test of this point. Practically all of the work in this field (phase changes on solids) has been done at the University of Chicago by Harkins, Jura, and co-workers, but the systems studied so far are not suitable, for the reasons discussed above, to test the arguments of this or the following section.

V. RELATIONS BETWEEN THE TWO- AND THREE-DIMENSIONAL EQUATIONS OF STATE

In this section also we shall only consider mobile monomolecular adsorption. There has been some interest in the past in the relation between the two- and three-dimensional critical temperatures but there has not been as much discussion of the more general problem of the relations between the two- and three-dimensional equations of state. The two equations are obviously closely connected. In the ideal case (discussed at the end of Section IV), the law of force between molecules is essentially the same, but the two equations of state differ in that: (1) in the adsorbed phase, the configuration integral Q_τ (Eq. (45)) is over x_1, \dots, y_N as compared to x_1, \dots, z_N ; and (2) in the adsorbed phase,

$$\varphi = kT \frac{\partial \log Q_\tau}{\partial \mathfrak{A}}, \quad (53)$$

as compared to

$$P = kT \frac{\partial \log Q_\tau}{\partial V}. \quad (54)$$

Experimental evidence on the ratio of the two-dimensional critical temperature to the three-dimensional critical temperature, T_{2c}/T_{3c} , is not at all plentiful. There is a certain amount of indirect evidence¹⁶ which is contradictory. The best (until recently) direct evidence^{12,17,18} indicates that two-dimensional condensation does not occur at temperatures well below T_{3c} , but the ratio T_{2c}/T_{3c} was not actually measured.

On the theoretical side, using the method (for spherical molecules) which Lennard-Jones and Devonshire¹⁹ applied successfully to three-dimensional condensation, Devonshire¹² found that, according to the theory, $T_{2c}/T_{3c} = 0.53$. As pointed out by Devonshire, this value agrees qualitatively with the experimental work mentioned above^{17,18} (as far as that work goes). Of considerably more interest is the fact that, in the condensation of *n*-heptane on silver recently reported by Jura and co-workers,¹⁰ the critical temperature was found to lie between 14.9°C and 25°C . As will be clear from the discussion at the end of the preceding section, heptane is not a very satisfactory molecule for this type of comparison; but it is still interesting that, using the known value of $T_{3c} = 266.8^\circ\text{C}$, the temperatures 14.9°C and 25°C lead to a value of T_{2c}/T_{3c} between 0.53 and 0.55, in excellent agreement (somewhat fortuitous, no doubt) with Devonshire's prediction.²⁰

¹⁶ See pp. 440–444 of reference 1a.

¹⁷ H. Cassel and K. Neugeberger, *J. Phys. Chem.* **40**, 523 (1936).

¹⁸ F. Simon and R. L. Swain, *Zeits. f. physik. Chemie* **B28**, 189 (1935).

¹⁹ J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.* **163A**, 53 (1937).

²⁰ After the present manuscript was submitted, a paper appeared by Jura, Loeser, Basford, and Harkins (*J. Chem. Phys.* **14**, 117 (1946)) in which this agreement is also discussed. In a private communication, Dr. Jura has kindly supplied me with the critical constants for heptane on ferric oxide and on graphite. These values are given in Table I. They are somewhat more exact than the values published in the above reference. The T_{2c}/T_{3c} ratio for

Although the theory of Lennard-Jones and Devonshire¹⁹ is quite successful in predicting critical temperatures of gases, it is not very successful in predicting critical volumes and pressures. Hence, it is perhaps not surprising to find that the theoretical critical two-dimensional pressure φ_c and area \mathfrak{A}_c , calculated (see below) from the theory and the experimental three dimensional values for *n*-heptane, do not seem to agree very well with the two-dimensional experimental values. This may be seen in Table I²⁰ and in the curves given by Jura and co-workers.^{10,20} We also include in Table I, for purposes of comparison, the corresponding theoretical values (also based on the three-dimensional experimental values) obtained if one uses the appropriate two- and three-dimensional van der Waals' equations (see below). In the critical region one should not, of course, take van der Waals' equation very seriously, but these results are still of some interest. Although neither Devonshire's theory nor van der Waals' equation should lead to very good values of the critical area, it is probably true that the large discrepancy between the theories and experiment is owing at least in part to some special cause. That is, as mentioned by Jura and co-workers,²⁰ the experimental critical areas are really much higher than one would expect.

The van der Waals values in Table I were obtained by carrying through the two-dimensional statistical treatment of the hard sphere model with an attractive energy proportional to r^{-6} for $r > r_0$. The approximations made were the same as in the corresponding three-dimensional treatment given by Mayer and Mayer.²¹ This leads to the evaluation of the two-dimensional van der Waals constants. If the two- and three-dimensional equations of state are

$$\left(\varphi + \frac{a'N^2}{\mathfrak{A}^2}\right)(\mathfrak{A} - Nb') = NkT, \quad (55)$$

both ferric oxide and graphite is 0.56. The critical areas and pressures for heptane on the three surfaces are not in agreement. This is certainly not surprising (see the discussion at the end of Section IV). One gets the impression that T_{2c} is not nearly so sensitive to varying conditions as \mathfrak{A}_c and φ_c .

²¹ J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), pp. 262-269. As Mayer and Mayer point out, the correct results are obtained here by a convenient but slightly incorrect argument (cancellation of errors).

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT, \quad (56)$$

one finds

$$b' = 2\left[\pi\left(\frac{r_0}{2}\right)^2\right] = 2\alpha_0 = \frac{\pi}{2}\left(\frac{3b}{2\pi}\right)^{\frac{2}{3}}, \quad (57)$$

$$a' = \frac{\pi u_0 r_0^2}{4} = \frac{\pi a}{4b}\left(\frac{3b}{2\pi}\right)^{\frac{2}{3}}, \quad (58)$$

where α_0 is the projected area of a hard sphere of radius $r_0/2$ and $-u_0$ is taken as the potential energy of interaction between two molecules practically in contact ($r \rightarrow r_0$). Using the expressions for the critical constants in terms of the van der Waals constants, one obtains the following relations between the two- and three-dimensional critical constants:

$$T_{2c} = 0.50T_{3c}, \quad (59)$$

$$\frac{\mathfrak{A}_c}{N} = \frac{3\pi}{2}\left(\frac{V_c}{N}\right)^{\frac{2}{3}} = 1.38\left(\frac{V_c}{N}\right)^{\frac{2}{3}}, \quad (60)$$

$$\varphi_c = \frac{P_c\left(\frac{V_c}{N}\right)^{\frac{2}{3}}}{\pi\left(\frac{3}{2\pi}\right)^{\frac{2}{3}}} = 0.361P_c\left(\frac{V_c}{N}\right)^{\frac{2}{3}}. \quad (61)$$

It will be noted in particular that $T_{2c}/T_{3c} = 0.50$, according to this model.

The corresponding equations for the theory of Lennard-Jones and Devonshire are approximately:

$$T_{2c} = 0.53T_{3c}, \quad (62)$$

$$\mathfrak{A}_c/N = 1.03(V_c/N)^{\frac{2}{3}}, \quad (63)$$

$$\varphi_c = 0.79P_c(V_c/N)^{\frac{2}{3}}. \quad (64)$$

These are based on the following approximate values estimated from the data and curves given by Lennard-Jones and Devonshire (in their notation except for T_{2c} and T_{3c}):

$$\left. \begin{aligned} p_c v_0 / NkT_{3c} &= 0.36, & p_{sc} s_0 / NkT_{2c} &= 0.71; \\ \Lambda / kT_{3c} &= 9, & \Lambda_s / kT_{2c} &= 8.6; \\ v_c / v_0 &= 1.8, & s_c / s_0 &= 1.4. \end{aligned} \right\} \quad (65)$$

It should be of considerable interest to find experimental values of the numerical constants²² appearing in Eqs. (62)–(64) and in Eqs. (59)–(61). The question is, will these experimental constants, in suitable cases, be independent of the adsorbent and adsorbate? If, as there is some reason to expect, constant “constants” are indeed found, say, for small spherical non-polar adsorbates on non-porous non-polar adsorbents, the values of these constants should be useful in providing an additional check on theories of the liquid state and condensation. That is, if both two- and three-dimensional versions of a theory are worked out, as was done by Lennard-Jones and Devonshire, the theoretical constants of Eqs. (62)–(64) may be calculated and compared with experiment.

It is planned to carry out in this laboratory some experimental work in connection with the theoretical problems discussed in Sections III, IV, and V.

The author is indebted to Professor K. S. Pitzer, Dr. George Jura, and Dr. P. H. Emmett for their helpful comments.

APPENDIX I

We use the notation of Devonshire in this Appendix. For Devonshire's model the configuration integral Q_r is

$$Q_r = \left\{ \pi a^2 N g \exp \left[\frac{\Lambda_s}{kT} (1.06\theta^3 - 0.5\theta^6) \right] \right\}^N, \quad (69)$$

with

$$\theta = s_0/s, \quad (70)$$

$$g = \int_0^1 \exp \left[\frac{\Lambda_s}{kT} \{ -\theta^2 \epsilon_s(y) + 2\theta^3 m_s(y) \} \right] dy. \quad (71)$$

The θ defined above has approximately the same physical significance as the θ in Section III. Using $a^2 = 2s/\sqrt{3}N$,

²² The fact that constants are expected which are independent of the gas (if the intermolecular potential function is of the same form for different gases, and is identical for a given gas in two and three dimensions) follows from the law of corresponding states, especially as discussed by Fowler and Guggenheim (reference 3, pp. 342–345). Partly in their notation we have

$$\begin{aligned} kT_{3c} &= \text{const.} \times \Lambda^*, \\ V_c/N &= \text{const.} \times r^{*3}, \\ P_c &= \text{const.} \times \Lambda^*/r^{*3}; \end{aligned} \quad (66)$$

and also

$$\begin{aligned} kT_{2c} &= \text{const.} \times \Lambda^*, \\ \mathfrak{A}_c/N &= \text{const.} \times r^{*2}, \\ \varphi_c &= \text{const.} \times \Lambda^*/r^{*2}. \end{aligned} \quad (67)$$

Combining these equations,

$$\begin{aligned} T_{2c}/T_{3c} &= \text{const.}, \\ \mathfrak{A}_c/N &= \text{const.} \times (V_c/N)^{1/3}, \\ \varphi_c &= \text{const.} \times P_c (V_c/N)^{1/3}. \end{aligned} \quad (68)$$

Eq. (69) becomes

$$Q_r = \left\{ \frac{2\pi s g}{\sqrt{3}} \exp \left[\frac{\Lambda_s}{kT} (1.06\theta^3 - 0.5\theta^6) \right] \right\}^N. \quad (72)$$

This gives Q_r as a function of s and N . After obtaining $\frac{\partial \log Q_r}{\partial N}$, as required by Eq. (51), there results finally

$$p' = \frac{\sqrt{3}}{2\pi s_0^*} \cdot \frac{\theta}{g} \cdot \exp \left[-\frac{\Lambda_s}{kT} \left\{ \theta^3 \left(4.24 + 6 \frac{g_m}{g} \right) - \theta^6 \left(3.5 + 6 \frac{g_l}{g} \right) \right\} \right] \quad (73)$$

or, in a form which is more convenient for calculations,

$$p' = \frac{\sqrt{3}}{2\pi s_0^*} \cdot \frac{\theta}{g} \cdot \exp \left[\frac{ps}{NkT} - 1 - \frac{\Lambda_s}{kT} (1.06\theta^3 - 0.5\theta^6) \right]. \quad (74)$$

The tables given by Devonshire for $\Lambda_s/kT = 9$ and 10 were used to calculate $2\pi s_0^*/\sqrt{3}$, as plotted in Fig. 4.

The critical values of Λ_s/kT and s/s_0 are estimated by Devonshire to be approximately 8.6 and 1.4, respectively. Hence, $\theta_c = 1/1.4 = 0.71$.

APPENDIX II

In studying an adsorbed insoluble surface phase of a single substance which is in equilibrium with the same substance in gaseous form, there are certain thermodynamic variables which are most useful: the surface area \mathfrak{A} , the equilibrium number of adsorbed molecules N (in the area \mathfrak{A}), the absolute temperature T , the pressure p of the gas phase in equilibrium with the adsorbed phase, the two-dimensional (spreading) pressure φ of the adsorbed phase, and the Helmholtz free energy A of the adsorbed phase. \mathfrak{A} , N , and T may most conveniently be thought of as independent variables and p , φ , and A as dependent variables. Also, \mathfrak{A} , N , and $A(\mathfrak{A}, N, T)$ are extensive properties while T , $p(\mathfrak{A}, N, T)$, and $\varphi(\mathfrak{A}, N, T)$ are intensive properties. Hence p and φ may be written $p(\Gamma, T)$ and $\varphi(\Gamma, T)$ and the same is true of A/\mathfrak{A} , where $\Gamma = N/\mathfrak{A}$, the surface concentration.

We wish to consider the relations between the adsorption isotherm, which is obtained experimentally in the form $p(\Gamma, T)$ or $\Gamma(p, T)$, and the equation of state $\varphi(\Gamma, T)$. We assume for convenience that the gas phase is a perfect gas so that μ_G , the chemical potential of this phase, may be written

$$\mu_G = \mu^0(T) + kT \log p. \quad (75)$$

In an exact treatment, we would replace p by the fugacity. The chemical potential μ_A of the adsorbed phase is, by definition,

$$\mu_A = (\partial A / \partial N)_{\mathfrak{A}, T}. \quad (76)$$

At equilibrium,

$$\mu_A = \mu_G, \quad (77)$$

$$(\partial A / \partial N)_{\mathfrak{A}, T} = \mu^0(T) + kT \log p. \quad (78)$$

This equation relates A and p . The corresponding relation between A and φ is contained in the thermodynamic definition of φ :

$$\varphi = -(\partial A / \partial \mathfrak{A})_{N, T}. \quad (79)$$

The next step is to eliminate A from Eqs. (78) and (79).

Integrating Eq. (78) for fixed values of \mathfrak{A} and T ,

$$A(\mathfrak{A}, N, T) = \int_0^N [\mu^0(T) + kT \log p] dN, \quad (80)$$

since $A(\mathfrak{A}, 0, T) = 0$. Therefore, using Eqs. (79) and (80), and keeping T constant in the following,

$$-\varphi = \int_0^N \frac{\partial}{\partial \mathfrak{A}} [\mu^0(T) + kT \log p] dN, \quad (81)$$

$$= kT \int_0^N \left(\frac{\partial \log p}{\partial \mathfrak{A}} \right)_N dN. \quad (82)$$

Now, since $p = p(\Gamma)$,

$$\left(\frac{\partial \log p}{\partial \mathfrak{A}} \right)_N = \left(\frac{\partial \Gamma}{\partial \mathfrak{A}} \right)_N \frac{d \log p}{d\Gamma} = -\frac{\Gamma}{\mathfrak{A}} \frac{d \log p}{d\Gamma}. \quad (83)$$

Equation (82) becomes

$$\varphi = kT \int_0^\Gamma \Gamma \frac{d \log p}{d\Gamma} d\Gamma \quad (84)$$

or

$$\varphi = kT \int_0^p \Gamma d \log p. \quad (85)$$

In differential form, Eq. (85) is

$$d\varphi = \Gamma kT d \log p. \quad (86)$$

Equations (85) and (86) are the familiar Gibbs equations as applied to this type of adsorption. The derivation given here proves helpful in relating the thermodynamic and statistical aspects of the problem. It will be noted from the derivation that Eqs. (85) and (86) are thermodynamically exact, except for the assumption that the gas phase behaves like a perfect gas. These equations are also general, applying to monomolecular, multimolecular, mobile, and localized adsorption on a solid or liquid. Of course φ is not of much physical interest except for the case of mobile monomolecular adsorption.

The usual procedure in obtaining the equation of state from the experimentally determined adsorption isotherm $\Gamma(p)$ is to evaluate $\varphi(p)$ from Eq. (85), and then, by combining $\Gamma(p)$ and $\varphi(p)$, find $\varphi(\Gamma)$ at the given temperature.

Time-Dependence of Boundary Tensions of Solutions

I. The Role of Diffusion in Time-Effects

A. F. H. WARD AND L. TORDAI

Faculty of Technology, University of Manchester, Manchester, England

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The variation of surface tension of solutions with time has in some cases, where the change is over within a few seconds or less, been explained on the basis of diffusion. This paper attempts a rigorous mathematical analysis of the role that diffusion might play in such time-effects. The limitations of diffusion theories which have been proposed previously are discussed. A general theory of diffusion to the surface is derived, which allows for back-diffusion and which makes no special assumptions of a physical nature. It is possible to use Fick's equation to calculate the total amount of solute which diffuses from a semi-infinite bulk solution into the surface if the concentration immediately under the surface is known at various times throughout the process. It is shown how the latter information may be deduced from the variation of surface tension with time together with final equilibrium values of surface tension. The methods of this theory are applied to analyze recent data on time-effects of short duration. It is concluded that even in cases where the variation of the surface tension is over in less than a second the rate-determining process is not diffusion. Even for these very rapid changes one is therefore led to assume the existence of an activation barrier which determines the rate of adsorption.

INTRODUCTION

MANY instances have been reported of the surface tension of solutions being a function of time. In some cases this has been ascribed to slow chemical changes in the bulk of the solution.¹ But many observed time-variations cannot be explained in this way. The change in surface tension may occur very slowly, over a

period of several days.^{2,3} On the other hand, variations of an apparently similar kind may be complete in a few hours or within an hour.⁴⁻⁶ In some cases the time-effect may last only for a

² N. K. Adam and H. L. Shute, *Trans. Faraday Soc.* **31**, 205 (1935).

³ N. K. Adam and H. L. Shute, *Trans. Faraday Soc.* **34**, 758 (1938).

⁴ K. S. G. Doss, *Kolloid Zeits.* **84**, 138 (1938).

⁵ K. S. G. Doss, *Kolloid Zeits.* **86**, 205 (1939).

⁶ H. V. Tartar, V. Sivertz, and R. E. Reitmeier, *J. Am. Chem. Soc.* **62**, 2375 (1940).

¹ A. Lottermoser and B. Baumgürtel, *Trans. Faraday Soc.* **31**, 200 (1935).