Surfaces of Solids. XIV. A Unitary Thermodynamic Theory of the Adsorption of Vapors on Solids and of Insoluble Films on Liquid Subphases

By George Jura and William D. Harkins

I. Introduction

When a gas or vapor is adsorbed on the surface of a solid, a film is formed. If the vapor pressure is sufficiently high, the films thus formed are almost always polymolecular. Films that remain monomolecular to very high relative pressures are usually those on a porous material, such as charcoal, where the fineness of the pores limits a large portion of the film to a thickness of one layer. Until recently, films on the surfaces of solids have received little attention from the standpoint of their behavior as surface layers, since nearly all of the emphasis has been directed toward the determination and interpretation of the pressure–volume relations observed in the adsorption process.

The greatest part of the knowledge and understanding of films has been obtained from insoluble monolayers on water or on aqueous solutions. These, when stable, are always monomolecular. The most important properties of such insoluble films have been obtained by the determination and study of the film pressure (π); area (σ) of the surface available per molecule, as defined later; and temperature (T). Monolayers on water exhibit several phases and in an isothermal compression the transitions observed are both first and second order: more often the latter. Some phase changes seem to be of the third order.

If the π–σ curves and, when data at different temperatures are available, the π–σ–T curves are constructed for films formed on solids, it becomes evident that the behavior is qualitatively the same as on a liquid subphase. The following questions are raised by this similarity: (1) can the comparison be made quantitative as well as qualitative; (2) in what specific respects are the films on solid subphases similar to those on liquids; and (3) how are they different?

In this paper the writers show that the available evidence indicates that films on the surfaces of solids, which are monomolecular at low and polymolecular at high vapor pressures, exhibit phases which are analogous to those of insoluble films on water and that the transitions between the phases are practically the same on both. In the comparison, the behavior of insoluble films on water is used as a model.

On various occasions in the past other investigators have pointed out some similarity between the films on solid and liquid subphases. The two most recent suggestions of such a nature are those of Armbruster and Austin,[1] who

based their result on the behavior of the π–σ curves of nitrogen, while the film is monomolecular at liquid nitrogen temperatures, and of Gregg,[2] who compared $\pi\sigma$ vs. π curves for films on charcoal with those on water.

Later, it is shown that, though Gregg's conclusion agrees with that of the writers, the data used by him are not suitable to show this. Neither of the above, however, extended their treatment to include the polymolecular films found on solids.

II. Fundamental Concepts and Definitions

The comparison between films on liquid and solid subphases is based on the π–σ and, where possible, on the π–σ–T relationships. Before π and σ can be evaluated, the specific area of the solid must be known. This (Σ) can be obtained from an adsorption isotherm by a calculation according to (1) the method of Brunauer, Emmett and Teller[3] (BET), or (2) the relative method of Harkins and Jura[4] (HJ), (3), in rare instances, by that of Langmuir.[5]

The area of the surface available per molecule, x, is obtained by dividing the area by the number of molecules. The film pressure, π, is obtained from an adsorption isotherm by the integration of the Gibbs adsorption equation as suggested by Bangham.[6,7,8]

The expression for π is

$$\pi = \gamma_S - \gamma_{Sf} = \frac{TR}{V_M \Sigma} \int_0^f v \, d \ln f \qquad (1)$$

where γ_S is the free surface energy of the clean surface in equilibrium with its own vapor; γ_{Sf} is the free surface energy of the surface when v cc. is adsorbed per gram; R the gas constant; T the temperature; V_M the molar gas volume; and Σ the specific area. Innes and Rowley[9] showed that the integral exists if the film behaves as a two-dimensional gas as p and v approach zero. Jura and Harkins[10] have pointed out the necessary experimental requirements for a satisfactory numerical evaluation of the integral.

Thus, a sufficiently detailed determination of

(2) S. J. Gregg, J. Chem. Soc., 696 (1942).

(3) S. Brunauer, P. H. Emmett and E. Teller, This Journal, 60, 309 (1938).

(4) W. D. Harkins and G. Jura, ibid., 66, 1366 (1944).

(5) I. Langmuir, ibid., 40, 1361 (1918).

(6) D. H. Bangham, Trans. Faraday Soc., 33, 805 (1937).

(7) D. H. Bangham and R. I. Razouk, ibid., 33, 1463 (1937).

(8) D. H. Bangham and R. I. Razouk, Proc. Royal Soc. (London), A166, 572 (1938).

(9) W. B. Innes and H. H. Rowley, J. Phys. Chem., 45, 158 (1944).

(10) G. Jura and W. D. Harkins, This Journal, 66, 1356 (1944).

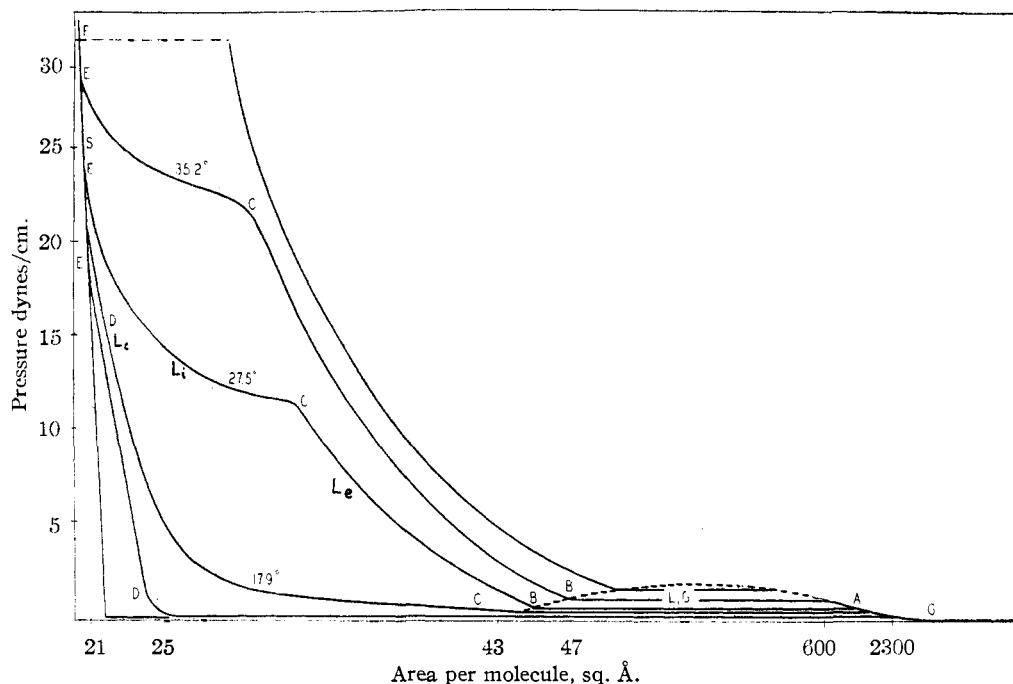(1) M. H. Armbruster and J. B. Austin, This Journal, 66, 159 (1944).

Fig. 1A.—General phase diagram for monolayers below the critical temperature for the liquid expanded phase, L_e: G = gas region; L-G, two phase region, gas and liquid expanded; L_e, liquid expanded; L_i, liquid intermediate; L_c, liquid condensed; and S, "solid" condensed. The curves are the composite of several workers for myristic acid.

the isotherm yields the π–σ relationships at the given temperature, and at several temperatures give the π–σ–T relations.

The concepts of film pressure and molecular area were developed initially for monomolecular films. The use of π for polymolecular films causes no difficulty, but σ no longer represents the mean area per molecule but merely the total area (Σ) divided by the number of molecules adsorbed on this area (N) i.e., Σ/N the inverse of the surface concentration.

In the use of this equation it should be kept in mind that surfaces are two-dimensional only with respect to the variables which are necessary for a description of the phenomena. Perhaps the best illustrative example of this fact is to be found in soluble films on liquids. In these the excess number of molecules adsorbed in the surface region can be calculated, but an accurate π–σ curve cannot be obtained because there is no way of determining the total number of molecules present in this region, since the calculation of this value entails a knowledge of the thickness of the region. All of the available estimates of σ for these films are based on the assumption that the region is monomolecular, even though it is known that this is incorrect.

With the proper understanding of σ, there is no difficulty in using π, σ, and T as the variables that describe the system. Any relation between these variables is an equation of state of the film, and if the film exists in different phases then in

general each phase will be described by a specific equation. Also, if the film exists in different phases, then the problem of finding a single equation that will satisfactorily represent the entire region under consideration is comparable to the task of finding a single equation to adequately and simultaneously represent the pressure–volume relations of a substance in the gas, liquid, and solid states in three dimensions. This has not as yet been accomplished. The BET theory, however, may apply to two adjacent phases, provided there is only a third order change between them (see Section V).

III. Phases and Phase Transitions of Insoluble Films on Liquid Subphases

The existence of different phases of insoluble films on water has been discussed by Adam,[11] Dervichian,[12] and in several papers by Harkins, especially by Harkins and Boyd.[13] There are differences with respect to the exact number and nomenclature of the phases which may exist. For the present treatment these differences are unimportant, and the classification of Harkins and his co-workers, in which there are six phases, is used: (1) gas, G; (2) liquid expanded, L_e; (3) liquid intermediate, L_i; (4) liquid condensed, L_c; (5) superliquid condensed, L_{sc}; (6) "solid" condensed, S_c. Whereas this phase is commonly

(11) N. K. Adam, "Physics and Chemistry of Surfaces," 2nd edition. Oxford, 1938, p. 40 and following.
(12) D. G. Dervichian, J. Chem. Phys., 1, 931 (1939).
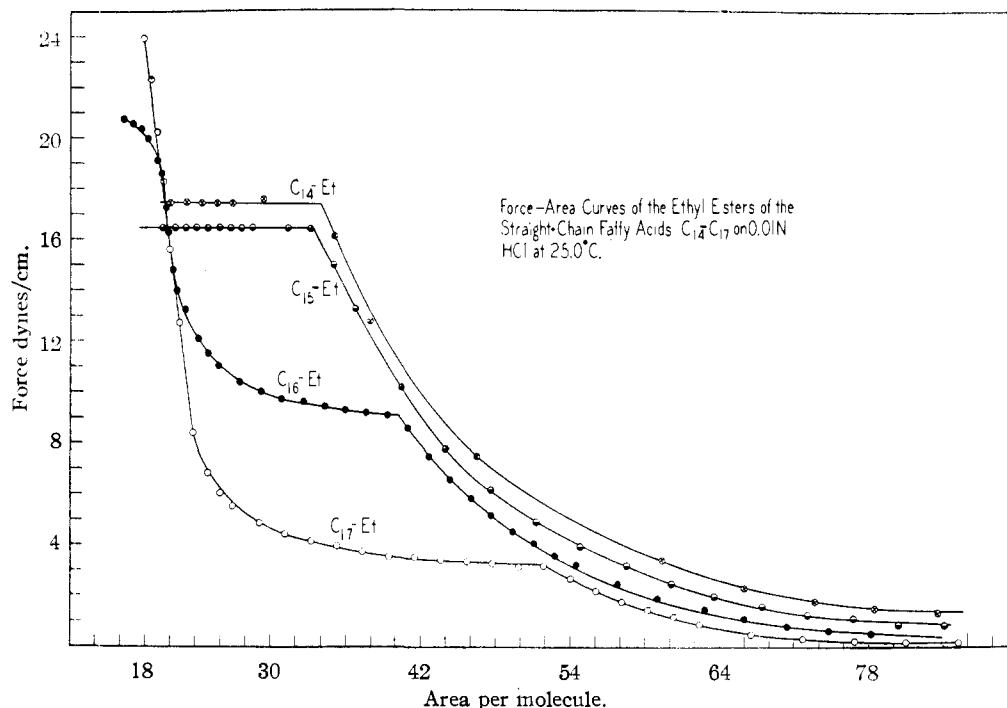(13) W. D. Harkins and G. E. Boyd, ibid., 45, 20 (1941).

Fig. 1B.—Exhibits the pressure–area relations observed for monolayers above the critical temperature for the expanded phase. The effect of decreasing the carbon chain by one CH_2 group is, in general, equivalent to an increase of approximately 5° in temperature. Thus, at 40° the C_{17} ester would occupy the position of the C_{14} ester.

designated as a "solid" it is usually, merely plastic." If all of the phases were to be exhibited by a single film, they would appear in the above order as the pressure is increased.

Dervichian[12] and Harkins[13] have discussed the nature of the transition between the various phases as the film is compressed isothermally as based on the theory of higher order phase changes of Ehrenfest.[14] They show that for films the behavior of the compressibility is sufficient to determine (1) whether or not a phase transition occurs, and (2) the order of the transition. If a first order transition occurs, the compressibility becomes infinite; for a second order transition there is a finite discontinuity in the compressibility, whereas if a third order change occurs, the discontinuity is finite in the derivative of the compressibility with respect to the area.

The order of transitions observed between the various phases of insoluble films on aqueous subphases is: gas to liquid expanded, 1st order; gas to liquid intermediate, 2nd order; liquid expanded to liquid intermediate, 2nd order; liquid intermediate to liquid or "solid" condensed seems to simulate third order; liquid condensed to superliquid, 1st or 2nd order, depending upon the subphase; liquid condensed to solid condensed, 2nd order; and superliquid to solid condensed, 2nd order.

Unfortunately, no single insoluble film has been

investigated over a sufficiently wide temperature and area range to develop all of the possible phases and transformations. None of the published general phase diagrams incorporate all the known facts. Fig. 1A is general for the behavior of myristic acid to the critical temperature, while Fig. 1B illustrates the behavior above the critical temperature. The general feature of the behavior of insoluble films as outlined in the preceding paragraphs appears to be substantially correct. Illustrative examples of all the known phenomena are given in reference 13, with the exception of the superliquid phase.[15]

IV. Equations of State for Insoluble Films

The only valid theoretical equation of state for insoluble films is that for the perfect gas. Langmuir,[16] it is true, has developed a theoretical equation which he considers to represent the behavior of the "liquid expanded phase," as follows

$$(\pi - \pi_0) (\sigma - \sigma_0) = kT$$

However, this does not reproduce the data at all well *for any one of the hundreds of isotherms for this phase as obtained in this Laboratory*, and is, therefore, useless for the present purpose.

The equation of state for a perfect two-dimensional gas as derived by Adam and Jessop[17] $\pi\sigma$

(12) P. Ehrenfest, *Proc. Koninkl. Akad. Wetenschappen, Amsterdam*, **36**, 115 (1933).

(15) W. D. Harkins and L. E. Copeland, *J. Chem. Phys.*, **10**, 272 (1942).

(16) I. Langmuir, *ibid.*, **1**, 762 (1933).

(17) N. K. Adam and G. Jessop, *Proc. Roy. Soc.* (London), **A110**, 423 (1926).

$= kT$ (Eq. 2) is usually valid for only large molecular areas: the film deviates more and more from the relation as the pressure is increased. For the higher pressures the equation is modified in the same way as that for three-dimensional gases. Unfortunately, very little work has been done with insoluble films in the gas region.

It is found empirically that the liquid expanded and intermediate phases are uniquely and adequately represented if the compressibility for these phases is assumed to be given by the following relations:

$$\kappa = -\frac{a}{\sigma + b} \quad \text{(liquid expanded)} \qquad (3)$$

and

$$\kappa = -\left(\frac{a}{\sigma} + b\right) \quad \text{(intermediate)} \qquad (4)$$

respectively, where

$$\kappa = -\frac{1}{\sigma}\left(\frac{\partial \sigma}{\partial \pi}\right)_T \qquad (5)$$

and a and b are unknown functions of the temperature.

Integration of eqs. 3 and 4 gives the desired π–σ equation for the expanded phase

$$\pi = c + \frac{\sigma}{a} + \frac{b}{a} \ln \sigma \qquad (6)$$

and for the intermediate phase

$$\pi = c + 1/b \ln (b\sigma + a) \qquad (7)$$

The constant of integration (c) is also an unknown function of the temperature. The application of Eqs. 6 and 7 to the data of Harkins and Boyd[13] for pentadecylic acid on 0.01 N sulfuric acid is shown in Fig. 2. The solid lines marked L_i and L_e are those calculated for the intermediate and expanded phases by Eqs. 6 and 7, while the circles represent the observed data. The calculated and
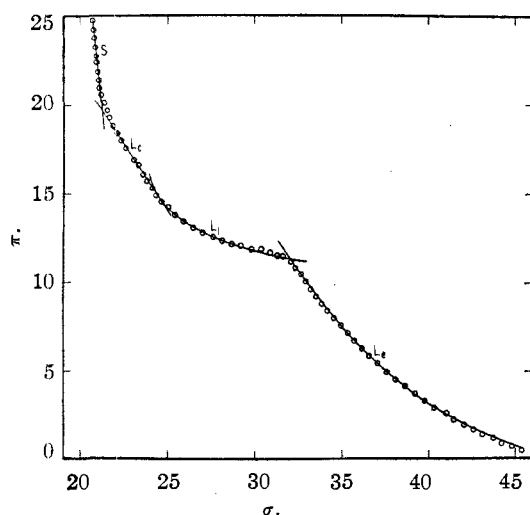
observed values are in excellent agreement, except for the very lowest pressures of the expanded phase. Also, the liquid and solid condensed phases are represented. Eqs. 6 and 7 have been applied with equal success to the data for these (expanded and intermediate) phases at other temperatures for the monolayers of octadecanitrile[18] and for several esters.

The equations of state for the three condensed films are obvious, since the π–σ relation is linear. Except at the highest pressures, the π–σ data are accurately represented by the equation

$$\pi = b - a\sigma \qquad (8)$$

where b and a are unknown functions of the temperature and are different for each condensed phase. The liquid condensed phase shows an increase in compressibility at high pressures. This is especially noticeable with the film of octadecyl alcohol. Recent accurate work by Harkins and Copeland[19] exhibits this effect in a similar but less marked form with stearic acid monolayers. The liquid condensed and solid condensed phases are also shown in Fig. 2. This behavior here is not, however, typical of the behavior of the two condensed films, which is shown much better in work by Adam,[11] Dervichian,[12] and Harkins and Boyd.[13]
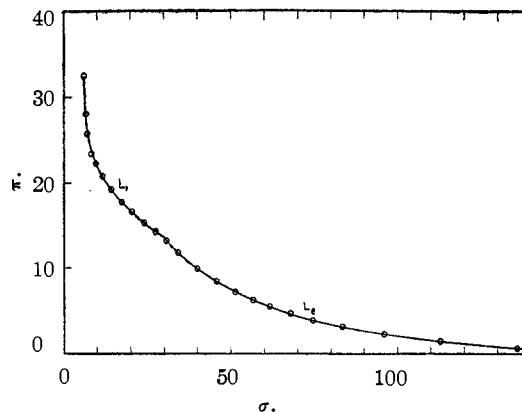
Fig. 3.—The pressure (π)–area (σ) isotherm of n-butane at 0° on a fluid cracking catalyst. The circles represent the experimental points, while the lines are calculated by the equations representing each phase. Note the second order transition between the two phases.

Fig. 3 exhibits the π–σ isotherm of n-butane at 0° on an alumina–silica catalyst whose area is 118 m.^{2}g.$^{-1}$. The regions marked L_i and L_e give curves which in appearance are analogous to those for the liquid intermediate and liquid expanded phases of pentadecyclic acid. The circles are the experimentally determined points, while the lines are calculated by the use of Eqs. 6 and

(18) L. E. Copeland and W. D. Harkins, THIS JOURNAL, 64, 1600 (1942).

(19) W. D. Harkins, The Surfaces of Solids and Liquids and the Films that Form upon Them, Part I, "Liquids in Colloid Chemistry," J. Alexander, Vol. V, Reinhold Publishing Company, New York. N. Y., 1944, p. 60.

Fig. 2.—Monolayer of pentadecyclic acid at 27.5° on water (0.01 N hydrochloric acid). The circles represent the experimental data, while the lines are calculated from the appropriate equation.

7. The film on the solid obeys exactly the same relationships as that on water. This particular system was chosen to illustrate the behavior, since both the L_i and L_2 phases appear and exist over comparable regions. This same type of behavior has been obtained with non-porous as well as with porous solids. (With porous solids the data used are well below the pressure at which the structure begins to determine the course of the isotherm.) The same type of behavior has been observed with other gases, for example, with triptane at $0°$, and n-heptane at $25°$ on copper and water at $25°$ on graphite containing 0.46% ash.

Figure 4 exhibits the π–σ isotherms of nitrogen at $-195.6°$ and n-heptane at $25°$ on titanium dioxide, in the form of anatase (area, 13.8 m.^{2}-g.$^{-1}$). The feature of interest in these isotherms is the long linear region. The nitrogen isotherm shows one such region and at high pressures exhibits the same increase of compressibility found in alcohol films, except that on the surface of the solid the increase of compressibility is much more marked. The n-heptane isotherm exhibits two such linear relations, each of which represents a different condensed phase. In this behavior a difference between the films on the surfaces of solids and liquids becomes apparent. On solids, when two condensed phases appear, the phase at lower areas is the more compressible, while on the surface of water the opposite is true. This is unquestionably due to the difference in the thickness of the films. This behavior (*i.e.*, two linear regions with the higher pressure condensed phase the more compressible) has been found by the writers with nitrogen at $-195.8°$ on both porous and non-porous solids and for non-porous solids with triptane, n-hexane, and n-butane at $0°$; n-heptane at 15 and $25°$, and water at $25°$. Recently, Beebe and co-workers[20] reported for krypton at $-195.0°$ a linear relation between log p/p_1 and $1/v^2$. This represents the existence of a condensed phase. Also reported are ammonia at $-40°$[21] and ethane and ethylene at $-195°$.[22]

The discussion of the gaseous region is deferred until a later section, but it is generally agreed that all films at high dilutions behave as two-dimensional gases.

V. Phase Transitions in Films on the Surfaces of Solids

If at constant temperature more than one phase is developed with change of pressure, it is evident that at least one transition occurs between phases. Conversely, if there are phase transitions, the film must of necessity exhibit different phases. In an earlier paper[23] it was shown

(20) R. A. Beebe, J. B. Beckwith and J. M. Honig, This Journal, 67, 1554 (1945).

(21) H. Ries, private communication.

(22) C. Brown, private communication.

(23) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, J. Chem. Phys., 14, 117 (1946).

that the compressibility, of the film is given by

$$\kappa = \frac{V_M \Sigma p}{RTv^2} \left(\frac{\partial v}{\partial p}\right)_{T,\,\Sigma} \qquad (9)$$

and that for a first order phase change $(\partial v/\partial p)_{T,\,\epsilon}$ becomes infinite, for a second order change a finite discontinuity is exhibited in this function, while for a third order change there is a finite discontinuity in $(\partial^2 v/\partial p^2)_{T,\,\Sigma}$. Thus, to prove that phase transitions exist in films formed by adsorption on the surfaces of solids, all that is necessary to demonstrate is that the derivatives are discontinuous. If the data for the isotherm are sufficiently accurate and extensive, then this problem is relatively simple. A study of the data shows that such discontinuities are common.
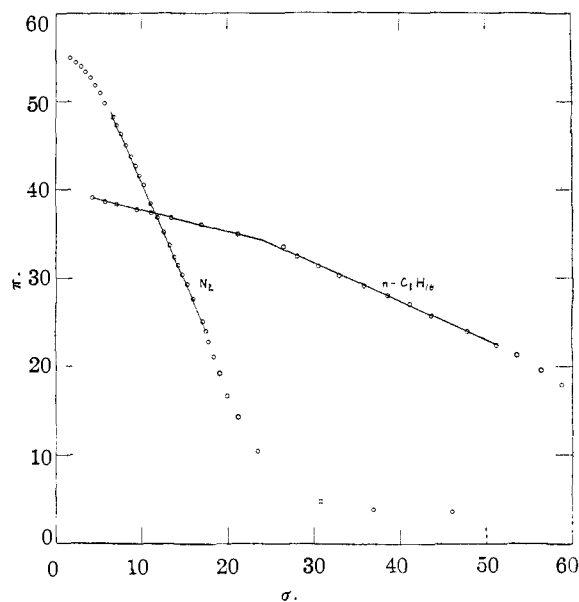

Fig. 4.—The condensed phases formed by the adsorption of nitrogen and n-heptane on titanium dioxide. The film of n-heptane forms two condensed phases. The transition is of the second order and is represented by the intersection of the two straight lines. The nitrogen film at the high pressures shows an increase of the compressibility.

Thus, first order phase changes are characterized by a discontinuity of the volume adsorbed as a function of the pressure. Data for two such systems have already been published.[23,24] The π–σ–T relations for the adsorption of n-heptane on ferric oxide are exhibited in Fig. 5. This exhibits a first-order change.

Second order changes are more difficult to demonstrate from the adsorption data: it is essential to determine a derivative. However, if enough experimental points are taken with sufficient accuracy, it is almost always possible to determine whether or not a discontinuity exists.

(24) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, J. Chem. Phys., 13, 535 (1945); G. Jura, W. D. Hawkins and P. R. Basford, ibid., 14, 344 (1946).
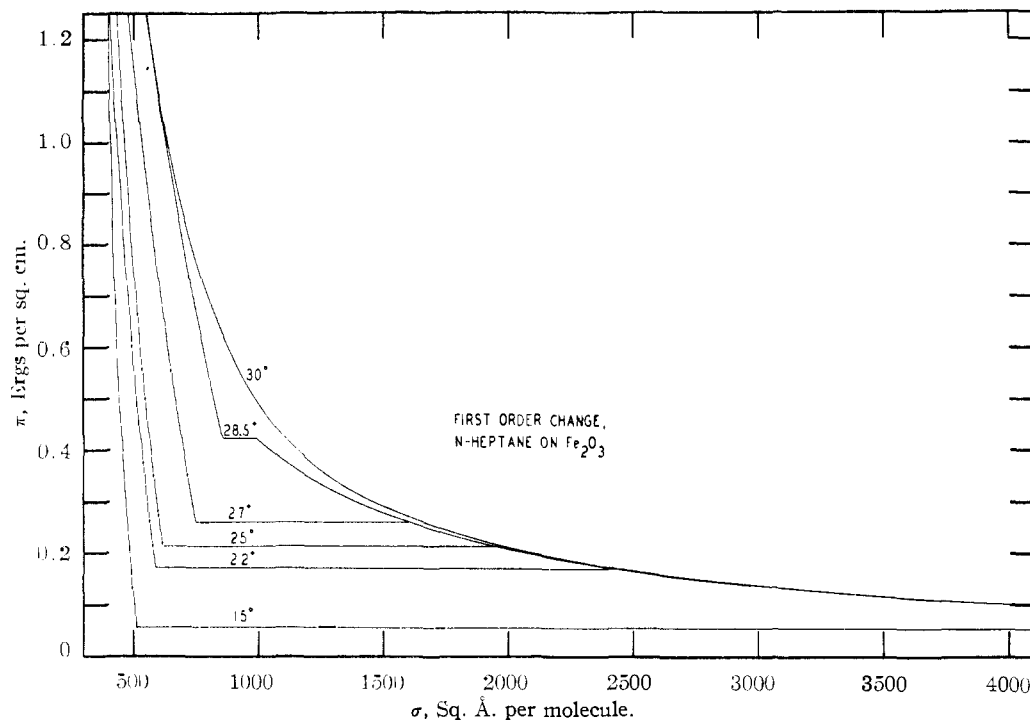
Fig. 5.—The pressure–area–temperature relationship in the low pressure region of the film of n-heptane on ferric oxide, illustrating a first-order phase change in films on the surfaces of solids.

If a second order phase change occurs at a low value of p/p_0, then the discontinuity usually can be observed by inspection of the p–v data. Such an example is shown in Fig. 6, where such data are shown for the adsorption of n-butane on a "fluid" cracking catalyst whose area is 475 m.²g.⁻¹ at 25°. This discontinuity represents the
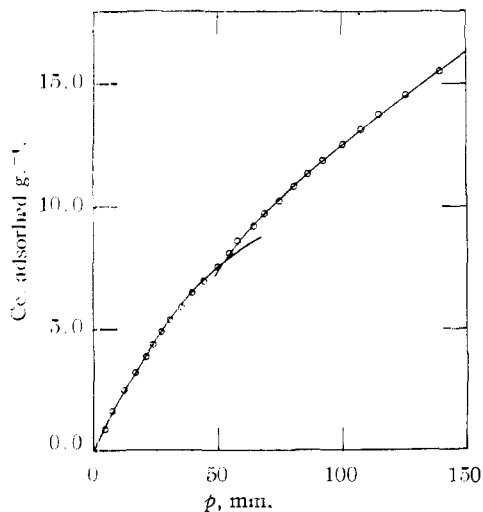

Fig. 6.—The adsorption isotherm of n-butane on an alumina–silica cracking catalyst at 25°. This illustrates a second order change of phase from the gas to the liquid intermediate above the critical temperature of the liquid expanded phase. v_m for this sample is 20.2 cc.

transition from an imperfect gas to the liquid intermediate phase.

Similar discontinuities at these low relative pressures have been observed with triptane and n-heptane at 0° and n-heptane at 15 to 40°.

At relative pressures above 0.05 it is only in exceptional cases that a discontinuity in the derivative can be observed by inspection. Usually, it is necessary to apply the chord–area method to the data, which must of necessity be extensive.

That discontinuities actually exist in the high pressure region is best shown when two condensed films are present, i.e., the data are represented by two straight lines when log p is plotted against $1/v^2$. The compressibility of this film is

$$k = N_0 v / V_M \Sigma a$$

In six systems in which nitrogen is the adsorbate at temperature of $-195.8°$ an experimental point determined by adsorption lies *exactly* at the intersection of two lines. Since the value of the constant a is different for the two lines, it is apparent that there is a discontinuity in the derivative and, consequently, a phase transition.

The most striking evidence of a change of this kind is to be found in the work of Harkins, Basford and Jura,[25] who found two discontinuities in the calorimetric study of the adsorption of water on graphite. These discontinuities agree in position with the discontinuities in the adsorption isotherm of water on the same sample, one of

(25) W. D. Harkins, P. R. Basford and G. Jura, accepted for publication in THIS JOURNAL.

which occurs in the film while monomolecular, and the other in the polymolecular region. The derivative and the change in total surface energy are exhibited in Fig. 7.

Third order changes are difficult, if not impossible, to demonstrate with certainty, since the second derivative is required. However, there are many instances in which it appears almost certain that changes of this order take place. In general, the above phase changes appear to become more marked when the data are represented in terms of film pressure and area available per molecule (σ). The cause of this can be seen by an examination of eq. 9. To relative pressures of about 0.8 the change in $(\partial v/\partial p)_{T,\epsilon}$ becomes smaller for a given change in K. This is due to the fact that v^2/p decreases as v and p increase to about a relative pressure of 0.8.

Over one hundred isotherms have been determined by the writers in much detail to high relative pressures: with water at $25°$, n-heptane at temperatures ranging from 15 to $40°$, triptane at $0°$, n-hexane at $0°$, n-butane at temperatures of 0 to $25°$ and of nitrogen at $-195.8°$. In every one of these, at least one change of phase was found. Many isotherms exhibit three such changes. If third order changes are included, four transformations are often found, for example, in the adsorption of n-heptane on titanium dioxide of area 13.8 m.^{2}g.$^{-1}$ at $25°$. At a pressure of 0.015 mm. there is a first order change, at 0.038 mm. a second order change, at 4.7 mm. what seems to be a third order change, and at 32.1 mm. a second order change.

Note on the Region of Applicability of the Theory of Brunauer, Emmett and Teller

The most successful general theory of adsorption, that of Brunauer, Emmett and Teller, is usually applicable between relative pressures (p/p_0) of the general order of 0.05 to 0.35. According to this theory, the volume adsorbed as a function of the pressure is continuous and the derivative of the volume with respect to the pressure is also continuous. Wherever this is not true the theory is *inapplicable*.

The region in which the BET isotherm is applicable is highly dependent upon the nature of the surface of the solid, upon that of the vapor, and upon the temperature. Thus, the outline which follows cannot be expected to give a complete description of the relations involved.

1. The applicability of the BET isotherm is often restricted, at a certain temperature, to one phase only; for example, with n-heptane on copper at $25°$ to the gaseous phase of the film which exists up to $p/p_0 = 0.4$. In this special case the *area* given by the application of the theory is only about 50% of that obtained from the usual nitrogen isotherm. Also, in another case, the theoretical BET isotherm gives a good fit for *only* the gaseous film phase: *i.e.*, with n-
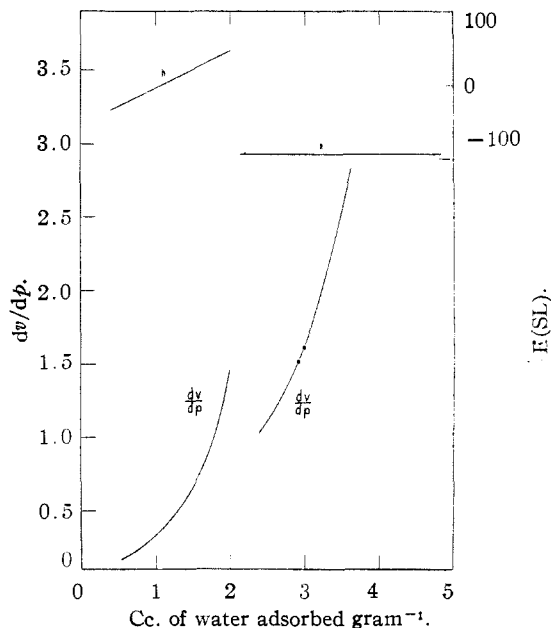

Fig. 7.—The heat of emersion of graphite from water and the derivative of the volume of water adsorbed with respect to the pressure. There should be a finite discontinuity in both functions at the volume adsorbed at which the transition occurs. Both functions meet this requirement.

butane at $50°$ on a silica–alumina cracking catalyst of an area of 485 sq. meters per g.

2. The BET isotherm was found to be valid for *only* the expanded liquid phase of a film of n-butane at $0°$ on a silica–alumina cracking catalyst of an area of 118 sq. meters per g.

3. However, n-butane at $0°$ on a cracking catalyst of an area of 475 sq. meters per g. was found to exhibit validity of the BET relation for only the intermediate liquid phase of the film.

4. It is not uncommon for the BET relation to exhibit validity over both the lower pressure region of a lower pressure condensed phase of the film and the upper pressure region of the phase just below it (commonly the intermediate phase) but this is *impossible* if the change of phase is of the first or second order. It becomes possible only if the change is of the third order.

Only one example of a second order transition in the relative pressure range, 0.05 to 0.35, is known to the writers. This is for the adsorption of nitrogen on graphite at $-195.8°$, where there is a second order transition at a relative pressure of 0.28. From $p/p_0 = 0.05$ up to 0.28 the BET theory fits the data, but above this pressure the data and theory are in disagreement.

Also, a first order transition occurs at a relative pressure of 0.073 when water is adsorbed on a sample of graphite containing 0.46% ash. The writers cannot offer an explanation for the relatively few transitions of first or second order which appear in this region of relative pressures.

In contrast with the above, the relations of the isotherm of Harkins and Jura[26] (H.J.) are ex- extremely simple: the equation of the isotherm is that for a condensed phase, so the region of ap- plicability is that of the existence of a condensed phase. Notwithstanding this limitation, the re- gion over which the H.J. relation is valid is com- monly much more extensive than that of the BET relation.

The *lower pressure condensed phase exists* over a vapor pressure region which is so highly dependent upon the temperature and the vapor involved, as well as on the solid that it is difficult to state any limits. However, this phase seldom exists under conditions usually employed at pres- sures below $p/p_0 = 0.05$ nor above $p/p_0 = 0.4$.
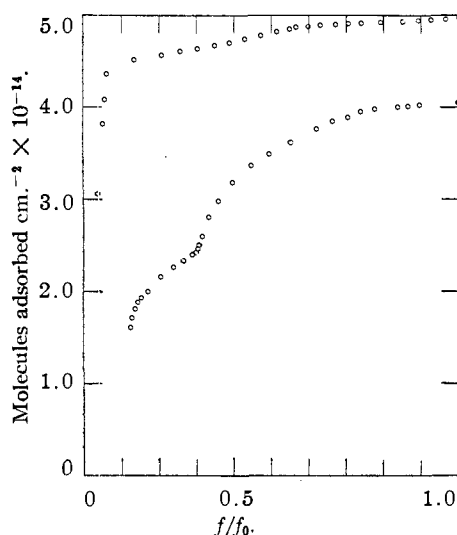

Fig. 8.—The adsorption isotherms of octadecyl alcohol and pentadecylic acid on water. The S-shaped isotherm is that of pentadecylic acid. The kinks which are so marked in the π-σ representation are not very marked. With fewer experimental observations continuous curves would be drawn through the points.

VI. Transformation of π-π Equations to p-v Equations

Since film pressure–molecular area $(\pi$-$\sigma)$ equa- tions are used for insoluble films on water and pressure–volume $(p$-$v)$ relations for films on solids, it is essential to give the relation between the two sets of variables. The simplest procedure is to start with the identity

$$\left(\frac{\partial \ln f}{\partial v}\right)_T = \left(\frac{\partial \ln f}{\partial \pi}\right)_T \left(\frac{\partial \pi}{\partial v}\right)_T \tag{10}$$

where f is the fugacity when the equilibrium pres- sure of the film is p. If the relationship between π and σ is known, then eq. 10 can be transformed into a differential equation involving only f and v. The following relations are used in obtaining the proper expression in f and v

$$\pi = \gamma_s - \gamma_{s_f} \tag{11}$$

(26) G. Jura and W. D. Harkins, *J. Chem. Phys.*, **11**, 430 (1943).

The Gibbs adsorption equation is

$$\Gamma = \frac{1}{RT}\left(\frac{\partial \gamma_{s_f}}{\partial \ln f}\right)_{T,\Sigma} \tag{12}$$

where

$$\Gamma = v/V_M \Sigma \tag{13}$$

If σ is expressed in sq. cm. per molecule, then

$$\sigma = V_M \Sigma / v N_0 \tag{14}$$

where N_0 is Avogadro's number. Finally

$$\left(\frac{\partial \pi}{\partial v}\right) = -\frac{V_M \Sigma}{v^2 N_0}\left(\frac{\partial \pi}{\partial \sigma}\right)_T \tag{15}$$

From Eqs. 11, 12 and 13 it is found that

$$\left(\frac{\partial \ln f}{\partial \pi}\right)_{T,\Sigma} = -\frac{V_M \Sigma}{RTv} \tag{16}$$

The substitution of eqs. 15 and 16 in eq. 10 gives

$$\left(\frac{\partial \ln f}{\partial v}\right)_T = -\frac{(V_M \epsilon)^2}{RTN_0 v^3}\left(\frac{\partial \pi}{\partial \sigma}\right)_T \tag{17}$$

Since, in general

$$\pi = \phi(\sigma) \tag{18}$$

Eq. 17 becomes

$$\left(\frac{\partial \ln f}{\partial v}\right)_T = -\frac{(V_M \epsilon)^2}{RTN_0 v^3} \phi'\left(\frac{V_M \epsilon}{v N_0}\right) \tag{19}$$

Eq. 19 is now only a function of f, the fugacity, and of v, the volume of gas adsorbed per gram. Since the form of ϕ' is known, the integration is a simple matter. If the gas obeys the perfect gas law, then the fugacity may be replaced by the pressure. Similarly, for each equation in p-v, there is a corresponding single equation in π-σ.

Thus, though it has been customary to repre- sent the results of the adsorption of gases on the surfaces of solids *only* in terms of pressure and volume and those for the study of insoluble films on liquids in terms of π and σ, *it is possible to ex- press the relations in either case by either set of variables.* Figure 8 exhibits the adsorption iso- therms of pentadecylic acid and octadecyl alcohol at 25° on a 0.01 N aqueous solution of hydrogen chloride. In Fig. 8 the number of molecules ad- sorbed per sq. cm. is plotted as a function of the relative fugacity f/f_0, where f_0 is the fugacity of the film at the pressure at which the film collapses. The data used for pentadecylic acid and for octadecyl alcohol are those of Harkins and Cope- land.[15] This figure represents the results that would be obtained if the films were formed by adsorption from the gas phase instead of by spreading a solution of the material. It should be noted in Fig. 8, that the kinks which are very marked in the π-σ curves are here barely notice- able with pentadecylic acid and not noticeable at all for octadecyl alcohol. It has been found by the writers that, in general, the representation of data or a film in terms of p and v tends to mask discontinuities or discontinuous derivatives much more than when expressed in terms of π and σ. The reason for this has already been given. If the data for insoluble films on water had always been expressed in terms of p and v with as few

experimental points as most investigators have taken in studying the adsorption of gases on solids, it is practically certain that our knowledge of the relations of insoluble films on water would be small.

There are two points that should be considered when Eq. 19 is applied to the adsorption of gases on the surfaces of solids, both of which are associated with the nature of the surface of the solid. If more than one type of surface is present, it is highly probable that for each type present a different form of Eq. 19 is applicable: (1) if the film is in a different phase on each of the surfaces, then the form of ϕ will be different; or (2) if the film exists in the same phase on all of the surfaces, the coefficients of σ in ϕ will be different. In the determination of the isotherm the statistical average of the ϕ function is observed. If the film exists in different phases on the different surfaces, then this approach fails, except in the eventuality that the film is the same on nearly the whole of the surface. The work of the writers indicates that this situation is not serious. If future work should prove that "stepwise" adsorption is a real phenomena, then the preceding might be a possible, or partial, explanation of the observed facts.

The second point in the application of Eq. 19 is that the specific area, Σ, enters as a parameter in any usable equation. Therefore, if only p and v are considered, the area must be constant. If the solid has an internal area, *i.e.*, is porous, then, as the adsorption proceeds to higher pressures, the pores are gradually filled and, concomitantly, the area which was originally available for adsorbing gas is decreased, so p becomes a function of both Σ and v. Unless the variation of Σ with v is known, Eq. 11 loses its significance. In a later paper it will be shown that in some instances the methods in this paper may be used for approximating the variation of Σ. It is not meant ·to imply that eq. 11 is not applicable to porous solids, but that it is applicable only within certain limits.

Gregg came to the same general conclusion as that of the writers, that the phases of films on solids are analogous to those of insoluble films on water. However, the evidence he used in support of this idea is incapable of showing it to be valid. First, he plotted $\pi\sigma$ against π, which clearly differentiates the gaseous and non-gaseous phases only. Second, he considered adsorption only on charcoal where the area is also a variable.

When eqs. 2 (perfect gas), 6 (liquid expanded), 7 (liquid intermediate), and 8 (condensed) are transformed by eq. 19 to p–v equations (it is assumed that the fugacity is equal to the pressure) it is found that the equation for the perfect gas is

$$p = Kv \tag{20}$$

for the liquid expanded phase

$$\ln p = K + \frac{C}{2aDv^2} + \frac{b}{aDv} \tag{21}$$

for the liquid intermediate phase

$$\ln p = K - \frac{1}{bDv} + \frac{a}{b^2DC} \ln \frac{bC + av}{v} \tag{22}$$

and for the condensed phase

$$\ln p = K - \frac{(V_M\Sigma)^2a}{2RTN_0v^2} \tag{23}$$

where

$$C = V_M/N_0$$

and

$$D = RT/V_M\Sigma$$

Figure 9 exhibits the application of Eqs. 21, and 22 to the data used for Fig. 3. The good agreement between the observed p–v values and Eq. 23 has been shown in another paper.[26] Since the π–σ equations represent the data so well, the agreement in the p–v data is to be expected. In the very high pressure region of Fig. 9, the deviation is unquestionably due to the pore structure of the solid. All of the many isotherms available to the writers can be described completely by the equations given in this section.
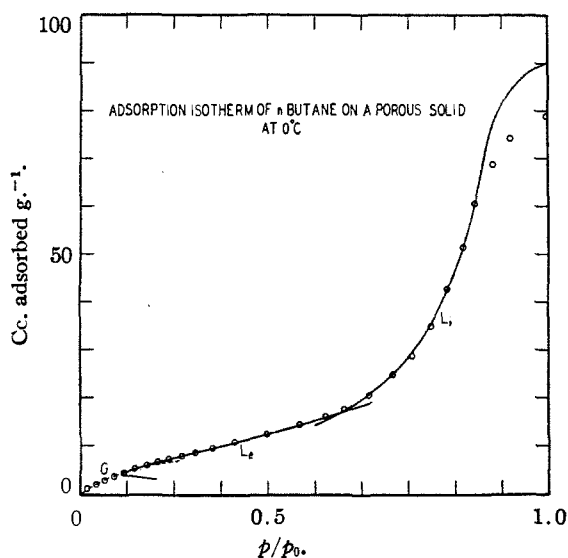

Fig. 9.—The lines give the amount of vapor adsorbed as a function of the relative pressure as calculated from the equations for the three phases. The circles represent the experimental data. The deviation at the high relative pressures is due to the porosity of the solid.

It is of interest to see the effect on the shapes of the isotherms introduced by a variation of the parameters a, b and K. For the condensed film this effect is exhibited in Fig. 5 of an earlier paper by the writers.[4] Figures 10 and 11 illustrate the effect of the variation of b in the equations of the liquid expanded and intermediate phases. The simultaneous variation of K can be obtained if $p/p_0 = 1.0$ is placed anywhere on the x-axis. These curves, especially that for the intermediate phase, may have any shape whatever. In spite of these variations, if a phase exists over a rela-

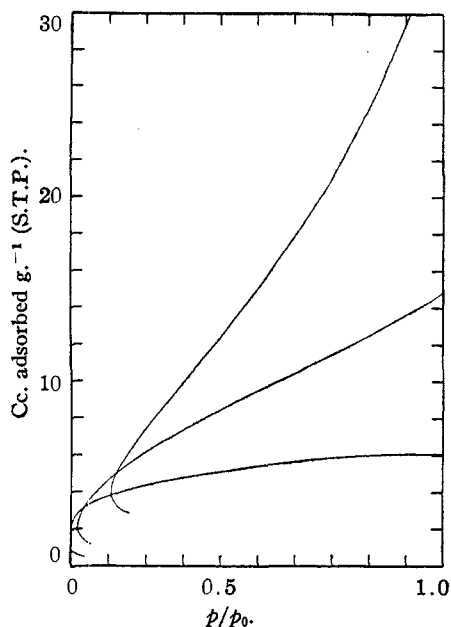tive pressure region of about 0.25, only one specific equation reproduces the data in a satisfactory way.

Fig. 10.—Three calculated shapes of the adsorption isotherm for the liquid expanded phase. The area of the subphase is constant. $p/p_0 = 1$ can be placed at any position of this axis. At the lower pressures where the curves turn toward the right no difficulty is found, since the film is still gaseous.
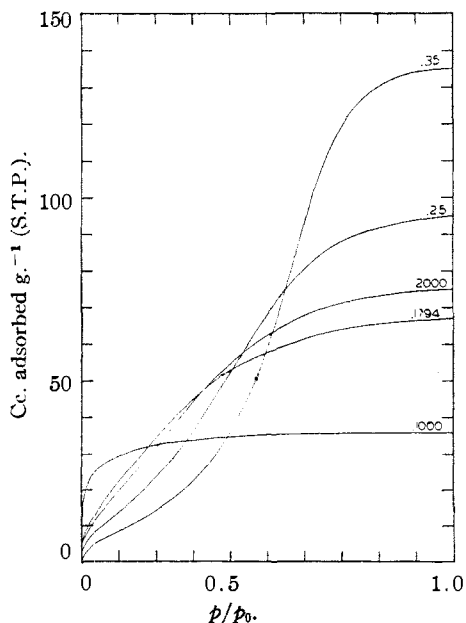

Fig. 11.—Possible shapes of the absorption isotherm for the liquid intermediate phase for constant area. As in Fig. 10, the saturation pressure may be moved anywhere on the p-axis.

VII. Discussion

In the previous sections it is indicated that at constant temperature the film formed by adsorption on a solid may undergo phase transitions as the pressure is increased and that each of the phases may be described by an equation, which also represents accurately a single phase of an insoluble film on a subphase of water. The data available to the writers show (1) that a given equation is *applicable only between two phase transitions;* (2) the order in which various phases appear is gas, liquid expanded, liquid intermediate, and one or more condensed phases; and (3) the transitions observed between the various phases is gas to liquid expanded, first order; gas to intermediate, second order; liquid expanded to intermediate, second order; intermediate to condensed, presumably third order; and condensed to condensed, second order. This general behavior is so characteristic of insoluble films on aqueous subphases that the conclusion seems inevitable that the phase relations of films are the same on both subphases.

That this conclusion is also borne out by the available temperature data is indicated by the following facts:

First order transitions from the gas phase have been observed with all of the vapors used by the writers. Two systems have been extensively studied with respect to temperature: n-heptane and ferric oxide[24] and n-heptane on graphite.[27] Both of these systems exhibit in the π-σ-T relations all the phenomena associated with the critical temperature region of three-dimensional systems. In the study of the system with graphite as the subphase the transition from the liquid expanded to the intermediate phases was also obtained. In this work the triple point of the gas–liquid expanded–liquid intermediate phase was located, and it was shown that transitions from the gas phase are possible even above the critical temperature.

One further point may be mentioned concerning the gas phase. Devonshire[28] calculated the ratio of the critical temperature of the films of the rare gases to the three-dimensional critical temperature to be 0.53. The maximum value of this ratio thus far found by the writers for a first-order change is 0.62. From the data available from our own experiments the ratio to the critical temperature would be 0.63. Considering the assumption involved in Devonshire's calculation, the agreement with the observed results is remarkable. It should be borne in mind that the critical temperature is only critical for the existence of the liquid expanded phase. Similar phenomena are known to occur in three dimensions, for example, helium can be solidified above its critical temperature. Also, even above the

(27) W. D. Harkins, G. Jura and E. H. Loeser, THIS JOURNAL, **68**, 554 (1946); G. Jura, W. D. Harkins and E. H. Loeser, *J. Chem. Phys.*, **14**, 344 (1946).

(28) A. F. Devonshire, *Proc. Roy. Soc. London.* **A163**, 132 (1937).

critical temperature the film pressure increases and the molecular area decreases when the film transforms from the gas. This behavior is exactly that which would be expected. This behavior has been observed with n-butane as well as n-heptane.

Similar results have been observed for the formation of condensed films. For six solids, which we are not allowed to identify at present, it was found that at 15° a condensed film is formed at lower film pressures and higher molecular areas than at 25°. This is the behavior to be expected on the premise of the existence of different phases. Thus, all the available data on the effect of temperature supports the concept of the existence of various phases. More data of this type are needed.

Wooten and Brown[29] obtained results with oxide-coated cathodes which strongly suggest that adsorbed films of ethylene exhibit a phase transition. With this concept there is apparently no difficulty.

Negative evidence which indicates that the film undergoes phase transitions can be obtained in the following manner. The previous attempts to explain the nature of the adsorbed film from the point of view of the equation of state have all assumed that the film behaves as a more or less imperfect gas. The equations in no case gave a satisfactory explanation of the observed facts. Thus, it seems that the film at the higher pressures is not gaseous, and, if not, then a phase transition must occur if the pressure is increased from very low to high pressures at constant temperature.

Since all the available evidence indicates that at temperatures below 0.7 of the three-dimensional critical temperature of the gas phase transitions occur, it is evident that non-gaseous phases must exist, unless the assumption is made that a gas may have allotropic forms. This is so unreasonable with gases that it is necessary to assume the existence of a non-gaseous state (or states) of the film.

The question naturally arises as to the number and nature of these phases. The writers have presented an analysis of this problem, but, it may be asked, (1) are the equations presented unique; and (2) is the set complete? The reply to the first of these is given by experimental results. Figure 12 exhibits the application of Eqs. 21 and 22 (L_e and L_i phases) to the adsorption of nitrogen on titanium dioxide at −195.8°. The equation for the condensed state reproduces accurately the data from $p/p_0 = 0.05$ to 0.7 (see ref. 23, Fig. 1). It can be seen that neither Eq. 21 nor 22 applies to this (or any other) condensed film. It has been found that, in general except for the gaseous region, if a phase exists over a relative pressure region of 0.25, it is possible to reproduce the data by only one of the equations that represent non-gaseous phases. Thus, within these limits, the representation is unique.

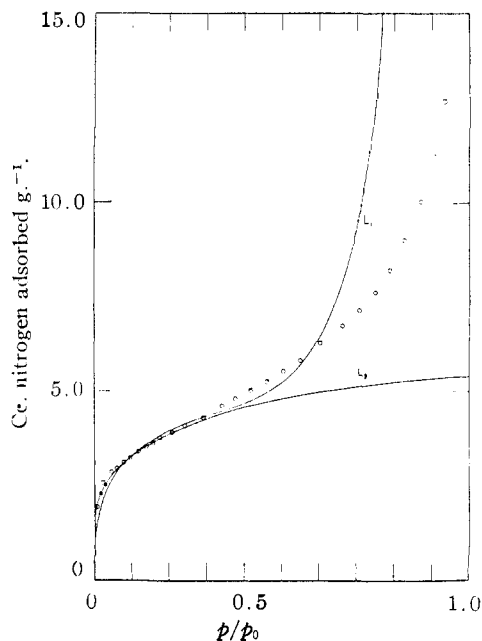(29) L. A. Wooten and C. Brown, This Journal, 65, 113 (1943).

Fig. 12.—The application of the equations of state for the liquid expanded (L_e) and intermediate (L_i) states for the adsorption of nitrogen on anatase ($\Sigma = 13.8$ m.² g.⁻¹). This film obeys the simple equation of state for a condensed film from $p/p_0 = 0.05$ to 0.70. The calculated isotherms for the L_e and L_i phases do not agree well with the experimental points (circles). The calculated isotherms for the L_e and L_i phases are not unique. A whole series of such curves for each phase can be drawn which will represent the experimental data as well as those drawn. It is not possible, however, to obtain agreement over a longer region of relative pressure than represented in this figure.

The question of completeness cannot be answered without many more data than are now available. The model used is that of a monomolecular film. It would indeed be surprising if more new phenomena were not found with polymolecular than with monomolecular films. These differences may occur in an increase of the number of possible phases and in the order of phase transitions. All that can be said concerning this at present is that the description thus far given appears to be complete.

There are two further points that should be mentioned. The analysis given of the states of films extends as far as is possible with classical thermodynamics as related to their isothermal behavior. Thermodynamics is capable of yielding much more information for non-isothermal processes. If a more explicit description is desired, it becomes necessary to construct a model and use the methods of statistical mechanics.

Second, the explanation of the adsorption phenomena is completely general and does not depend on the mechanism of adsorption. The only restrictions are that the adsorption be physical and that the effective adsorbing area should be known at all times. Actually this analysis

does not explain the adsorption of gases on the surfaces of solids from the theoretical point of view but rather shows that insoluble films are capable of the same type of general treatment regardless of the nature of the subphase; in short, two problems, the relations of films on the surfaces of liquids, and of films on the surfaces of solids, are reduced to one problem.

The question naturally arises, are the concepts presented by the writers compatible with the results of other investigators? Actually there is no conflict, as can be shown by a comparison with the theory of Brunauer, Emmett and Teller,

adsorbed films on solids should be essentially the same as those of monolayers of oil on water. This expectation is shown to be justified by the relations listed below:

1. On compression of an oil film on water the succession of phases is (1) gas, (2) liquid expanded, (3) liquid intermediate, (4) liquid condensed and (5) higher pressure condensed. The same succession is found in films on solids.

2. Except for the gaseous state no valid equations of state for films had been developed prior to the work of the writers, who have obtained the empirical equations listed below.

Compressibility | **Phase**

$$\kappa = \frac{\sigma}{kT}$$ Perfect gas

$$\kappa = -\frac{a}{\sigma + b}$$ (3) Liquid expanded

$$\kappa = -\left(\frac{a}{\sigma} + b\right)$$ (4) Intermediate

$$\kappa = \frac{1}{a\sigma}$$ Condensed phases

Equation of State

$$\pi\sigma = kT \tag{2}$$
$$p = Kv \tag{20}$$
$$\pi = c + \frac{\sigma}{a} + \frac{b}{a}\ln\sigma \tag{6}$$
$$\ln p = K + \frac{C}{2aDv^2} + \frac{b}{aDv} \tag{21}$$
$$\pi = c + \frac{1}{b}\ln(b\sigma + a) \tag{7}$$
$$\ln p = K - \frac{1}{bDv} + \frac{a}{b^2DC}\ln\frac{bc+av}{v} \tag{22}$$
$$\pi = b - a\sigma$$
$$\ln p = K - \frac{(V_M\Sigma)^2 a}{2\,RTN_0v^2} \tag{23}$$

unquestionably the most sound kinetic theory thus far proposed. However, this theory has, at present, no provision for any phase transformation, but this is not an inherent fault, since, by the application of statistical mechanics, they may be introduced. The statistical treatment of Cassie[30] could be refined to introduce phase changes into the equations for adsorption. The theory of first order phase changes for localized monomolecular films has already been developed by Fowler,[31] while Hill[32] has developed a similar theory if the film is mobile. Hill's results are in qualitative agreement with the experimental results of the writers. As soon as the writers have more data available on the effects of temperature for these first order transitions, Hill's theory can be compared with the experiment. The transitions, when the film is polymolecular, can be obtained in a similar way. Thus, since this idea can be incorporated into the theory, it is apparent that there is no conflict.

The remarkable feature revealed by the experimental work is that these equations are valid, each for the specific phase only, for either oil monolayers on water or for adsorbed films on solids.

3. The phase transformations are also the same on water and on solids: first order: gas to liquid expanded (Figs. 1 and 5); second order: liquid expanded to intermediate (Figs. 1 and 3), condensed to condensed, gas to intermediate (Figs. 2 and 7); third order: intermediate to condensed (Figs. 1 and 4).

4. The effects of temperature are in general the same on a solid subphase as on water in the low pressure region, but the sign of the entropy term is reversed at high pressures.

5. On water stable oil films are monomolecular, but on solids at high vapor pressures the film becomes in general thick and polymolecular without affecting the general phase relations. However there is one exception in that on solids the higher pressure condensed film has a higher compressibility than the lower pressure condensed film, while on water the reverse of this is true.

6. The relations of the various phases on the surface of a solid are capable of statistical treatment.

Summary

This investigation was begun with the following idea as a basis: the general phase relations of

(30) A. B. D. Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).
(31) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," University Press, Cambridge, England, 1939, pp. 429–443.
(32) T. Hill, unpublished.