148. *Resemblance between Surface Films on Solids and on Water.*

By S. J. Gregg.

As Bangham has shown, the quantities FA and FS can be calculated for the adsorbed film of a gas on a solid from the adsorption isotherm by integration of the Gibbs adsorption equation (F = surface pressure of the adsorbed film, A = area occupied per adsorbed molecule, S = " specific surface " of the adsorbent, *i.e.*, its adsorbing area per g.). Curves of FA against FS, now drawn from published isotherms, exhibit close correspondence to surface films on water : the film states gaseous (G), liquid-expanded (L_1), liquid-condensed (L_2), and the intermediate state (I) between L_1 and L_2 have their counterparts in gas–solid adsorption. From the slope of the *FA–FS* curve where it becomes linear, both the adsorbing area *S* and the monolayer capacity of the adsorbent (the number of molecules it can take up per g. in a completed monolayer) can be calculated.

Formation of layers more than one molecule thick sometimes occurs, but is not to be associated with the characteristic loops often obtained in the adsorption isotherms of vapours on gels; the *FA–FS* curves in the latter cases show that the adsorbed layer remains unimolecular throughout the region covered by the loop, and that the hysteresis orginates, not in capillary condensation, but in the transformation of state $L_1 \rightleftharpoons I \rightleftharpoons L_2$ occurring within the *monolayer.*

In van der Waals adsorption of a gas on a solid, the molecules in the adsorbed layer are frequently mobile on the surface, and consequently produce a two-dimensional pressure F analogous to the surface pressure of films on water. Two-dimensional equations of state relating F to the area A (see above) have been derived, *e.g.*, by Volmer (*Z. physikal. Chem.*, 1925, **115**, 253), Kar (*Physikal. Z.*, 1925, **26**, 615), and Bradley (*Phil. Mag.*, 1929, **8**, 202; *Chem. Reviews*, 1937, **9**, 47); Langmuir (*J. Amer. Chem. Soc.*, 1932, **54**, 2798) further envisages the possible occurrence within the film of transformations of state resembling phase changes in bulk matter, and Fowler has demonstrated by statistical mechanics that the adsorbed film should break up into two phases under suitable conditions (*Proc. Camb. Phil. Soc.*, 1936, **32**, 144).

Experimental evidence for changes of state within the adsorbed layer on solids has been obtained by Bangham and his co-workers. Using the expansion of the adsorbent, which accompanies adsorption, as a measure of the surface pressure (Bangham and Fakhoury, J., 1931, 1324) and noting that the quantity adsorbed per g. of adsorbent is inversely proportional to A, they plotted curves of FA against λF (λ is a proportionality constant) for a number of gases and vapours adsorbed on charcoal. In one experiment, water vapour and ammonia gave curves very similar to the pV–p curves of an imperfect gas, and in another experiment with water vapour the *FA–F* graph closely resembled the pV–p curve of a vapour below its critical temperature, showing a region where two-dimensional condensation occurred at constant F (Bangham, Fakhoury, and Mohamed, *Proc. Roy. Soc.*, 1932, *A*, **138**, 177). With pyridine, benzene, and the lower primary alcohols, it was found that on standing, or better, on heating the charcoal in contact with the vapour and re-cooling (" annealing ") the system, the values of F and A changed so that the *FA–F* graph took up a new, approximately linear, course, usually with a smaller slope (*loc. cit.*, p. 162); they interpreted this as a change of state from a " primary " to an " annealed " film (*ibid.*, 1934, *A*, **147**, 152), and directed attention to the similarity between the alcohol curves and the *FA–F* graphs calculable from Cassell and Salditt's data for the same substances adsorbed on liquid mercury (*Z. physikal. Chem.*, 1931, *A*, **155**, 299).

Later, Bangham (*Trans. Faraday Soc.*, 1937, **33**, 805) showed how to calculate the quantity FS from the adsorption-isotherm data alone, without recourse to expansion data, by integration of the Gibbs adsorption equation. Performing the integration graphically for Coolidge's data for water vapour adsorbed on sugar charcoal (*J. Amer. Chem. Soc.*, 1927, **49**, 713), Bangham and Razouk showed from the form of the *FA–F* graph (S being estimated by comparison with mercury adsorption) that two-dimensional condensation again occurred (*Trans. Faraday Soc.*, 1937, **33**, 1463).

The Gibbs equation has also been used by Palmer (*Proc. Roy. Soc.*, 1937, *A*, **160**, 254) to calculate F for benzene vapour adsorbed on a known area of vitreous silica, integration being performed algebraically; the resulting *FA–F* curve was similar to that for the liquid-expanded state of insoluble films on water.

It will now be shown that many other similarities appear between the states of films on water and on solids, when the data for gas–solid adsorption are set out as *FA–FS* curves, calculated by Bangham's procedure.

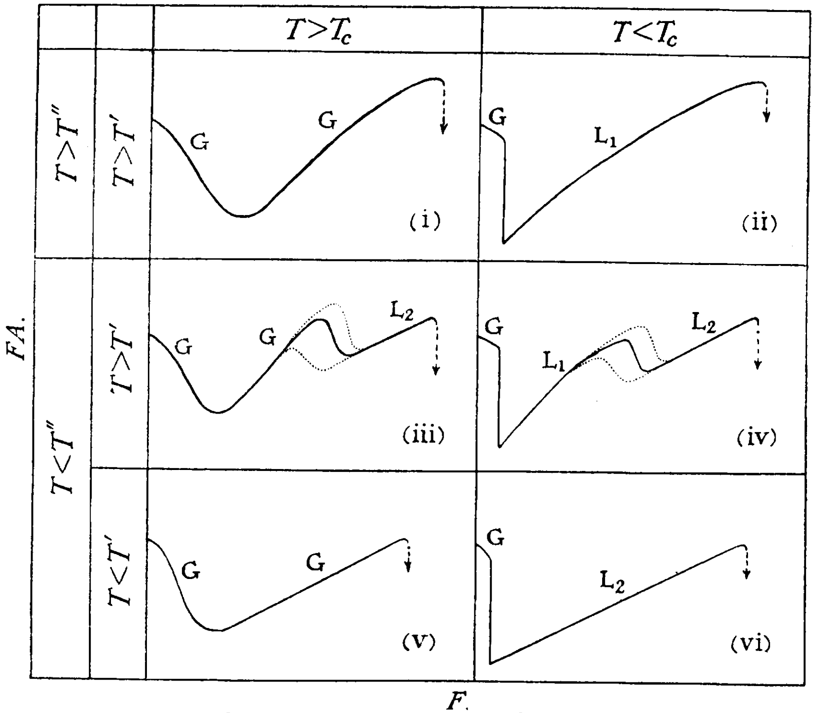
In order to facilitate this comparison, it is first necessary to summarise the *FA–F* graphs for the various states, and transformations of state, of films of insoluble substances on water. The states are those set out in the summary, the symbols being those of Harkins, Fraser, Young, and Boyd (*J. Chem. Physics*, 1940, **8**, 954; see also Harkins and Boyd, *J. Physical Chem.*, 1941, **45**, 20). The intermediate state I arises because the transition between the liquid-expanded and the liquid-condensed state, unlike that from the vaporous to the liquid-expanded, occurs over a definite range of values of F and not at one definite value. There is also a *solid* state, which could perhaps serve as an analogue of *immobile* adsorbed films on solids; it will not be considered here.

The *FA–F* curves are shown (not to scale) in Fig. 1. They can be derived from graphs given by Adam (" Physics and Chemistry of Surfaces," 1941, Chap. II), Harkins and Boyd (*loc. cit.*), or Dervichian (*J. Chem. Physics*, 1939, **7**, 931), or from the literature.

In Fig. 1, T_c is a temperature analogous to the critical temperature of liquefaction of a bulk fluid; T' and T'' also have the character of critical temperatures, but because of the experimental difficulty, or even impossibility, of working over a sufficiently wide range of temperature, it has not been possible hitherto to realise all six forms of the graph with any one substance. One cannot, therefore, say how far T_c, T', and T'' are to be regarded as constants characteristic of a given substance—*e.g.*, whether T_c would have the same value for the transition from diagram (v) to (vi) as from (i) to (ii); nor is the question of importance in the present connection, which is merely to show the possible types of curve and to indicate how they are related to their nearest neighbours. In any case, in view of the well-known sensitivity of film states to the ionic composition of the trough solution (*e.g.*, p_H and the concentration of metal ions), it is certain that T_c, T', and T'' could not be constant for a given adsorbate unless the ionic environment were constant.

The *slope*, *B*, of the *FA–F* graphs is of particular importance. Schofield and Rideal (*Proc. Roy. Soc.*, 1926, *A*, **110**, 167) pointed out that the slope of the curve where it becomes linear should be equal to the corresponding incompressible area A_0 of the adsorbed molecules, and they applied this relation to the gaseous state at high surface pressure, and to the liquid-condensed state. In the latter state the value of B for long-chain compounds is usually *ca.* 19—20 A.^{2}. The detailed molecular structure of the film in this state is still in doubt, but it is agreed that the orientation of the molecules is either the same as, or very similar to, that in a sheet of molecules in the bulk crystal, the molecules being steeply, or even vertically, inclined to the water surface (Adam, *op. cit.*, p. 51; Alexander, *Proc. Roy. Soc.*, 1942, *A*, **179**, 486; Dervichian, *loc. cit.*, p. 945); Müller (*Proc. Roy. Soc.*, 1932, *A*, **138**, 514) states that the minimum area of cross-section of the hydrocarbon chain, perpendicular to its length, is 18·3 A.^{2}, and increases with temperature up to an average value of 19·5 A.^{2}. According to Langmuir (*J. Chem. Physics*, 1933, **1**, 756) the adsorbed molecules in the L_2 state are aggregated into two-dimensional micelles. The *FA–F* curve for the gaseous state is concave to the F axis in its right-hand branch, so that the slope B, and consequently the incompressible area A_0, diminish as surface pressure increases in this region; at a given pressure the value of A_0 depends very much on the particular adsorbate; A_0 is always larger than the area characteristic of the liquid-condensed state (*e.g.*, for ethyl undecanedicarboxylate it is approx. 100 A.^{2}; Adam and Jessop, *Proc. Roy. Soc.*, 1926, *A*, **112**, 376) and it is generally agreed that in the gaseous state the molecules lie flat on the water surface (thus occupying a large area) except at high surface pressures, where they begin to tilt (Adam, *op. cit.*, p. 57).

FIG. 1.



FA–F graphs for films of insoluble substances on water, *not to scale.* In general, curves intercept the *FA* axis at a value *kT*.

G = adsorbed gaseous (or vaporous) state; L_1 = liquid-expanded state; L_2 = liquid-condensed state; I = intermediate state between L_1 and L_2. The right-hand G branch of (i) and (ii) is indistinguishable in form from an L_1, and in (v) from an L_2, branch.

Broken line represents collapse of film, *i.e.*, transformation into a multimolecular layer. (Solid-condensed state, which may intervene between L_2 and collapse, omitted.)

Left-hand and right-hand dotted lines in (iii) and (iv) show curves for lower and higher temperatures respectively than the full line between them.

T_c = critical temperature; T' = temperature above which the L_2 state cannot occur; T'' = temperature below which the L_1 state cannot occur.

Experimental examples. There are numerous experimental results illustrating individual parts of the above curves, but the examples below have been chosen so as to cover as much as possible of the particular curve in a single experiment.

In the examples for (ii), (iii), (v), and (vi) the measurements were not carried as far as the collapse point.

Curve (i) $C_{14}H_{29}\cdot CO_2C_2H_5$ at 25°; Harkins and Boyd, *loc. cit.*
(ii) Myristic acid at 14·5°; Adam and Jessop, *Proc. Roy. Soc.*, 1926, *A*, **110**, 423.
(iii) Tridecyl methyl ketone at 12·5°; *idem, ibid.*, 1926, *A*, **112**, 362.
(iv) Pentadecoic acid at 27·5°; Harkins and Boyd, *loc. cit.*
(v) Nearest example $C_{16}H_{32}(CO_2Et)_2$ at 1°, where the right-hand branch is solid, not liquid-condensed; Adam and Jessop, *loc. cit.*, p. 376.
(vi) Ethyl stearate at 14°; Adam and Jessop, *ibid.*, 1926, *A*, **110**, 423.

The slope B for the liquid-expanded state also gradually diminishes as F increases, its value throughout being greater than that for the liquid-condensed state, and less than that ordinarily obtained for the gaseous state; typical values are *ca.* 43 A.^{2} for pentadecoic acid on 0·01N-hydrochloric acid (Nutting and Harkins, *J. Amer. Chem. Soc.*, 1939, **61**, 1180) for the range $F = 0{\cdot}5$—$2{\cdot}0$ dynes/cm. and *ca.* 30 A.^{2} for the range 6—8 dynes/cm. It is clear that on the average the molecules of the film become progressively more steeply tilted as F increases, thus producing a gradually diminishing value of A_0. It is no longer possible to say, however, either for the L_1 state, or for the G state at higher pressures, that the slope of the FA–F curve at any point gives the exact value of A_0 at that point, for in deriving the relationship $B = A_0$ it is assumed that the attraction between the molecules in the film (due to a two-dimensional van der Waals's a) is independent of F, whereas in fact the gradual alteration in orientation cannot fail to change the interattraction, and that in a manner very difficult to predict. The slope should nevertheless give an approximate measure of A_0. The most widely accepted theory of the liquid-expanded state is Langmuir's theory of duplex films (*loc. cit.*), which is compatible with the idea that the molecules become progressively more steeply tilted as F increases.

The Adsorbed Film on Solids.—Gibbs's adsorption equation $\Gamma = (1/\boldsymbol{R}T)\mathrm{d}F/\mathrm{d}\log_e p$ may, as Bangham (*loc. cit.*) has shown, be integrated to

$$F = \boldsymbol{R}T\int_0^p \Gamma \mathrm{d}\log_e p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Γ is the quantity adsorbed, in moles/sq. cm.; p is the equilibrium gas pressure in the free space.

Generally we are ignorant of the specific surface per g. of adsorbent, so only x, the number of molecules adsorbed per g. of asdorbent, *i.e.*, S sq. cm., can be measured. Since $\Gamma = x/\boldsymbol{N}S$, where $\boldsymbol{N}$ is Avogadro's number, $F = \boldsymbol{R}T\int_0^p (x/\boldsymbol{N}S)\mathrm{d}\log_e p$, *i.e.*,

$$FS = \boldsymbol{k}T\int_0^p x\mathrm{d}\log_e p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $\boldsymbol{k}$ is the Boltzmann constant, $\boldsymbol{R}/\boldsymbol{N}$. The area per molecule, A, is S/x, so

$$FA = FS/x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Following Bangham's procedure, FS will first be calculated by plotting x against $\log_e p$ and taking the area under the curve from zero up to any pressure p; FA is then found from (3), and plotted against FS.

Some difficulty arises in the graphical integration of $\int x\mathrm{d}\log_e p$ when, as is frequently the case, accurate measurements of adsorption are lacking at low pressures. Since $\log p$ becomes negative and infinite when $p = 0$, at one limit of integration, graphical integration becomes very uncertain. However, it is known that at sufficiently low pressures adsorption becomes very nearly proportional to the pressure. This relationship (analogous to Henry's law for the solubility of gases in liquids) provides a very easy means of integration, for when $x = mp$,

$$\int_0^{p_1} x\mathrm{d}\log_e p = mp_1 = x_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where x_1 is the value of x when $p = p_1$. Consequently, $FS = \boldsymbol{k}T\int_0^{p_1} x\mathrm{d}\log_e p = \boldsymbol{k}Tx_1$, *i.e.*, $FS/x_1 = \boldsymbol{k}T$, or from (3), $FA = \boldsymbol{k}T$.

This relationship between the Gibbs and the Henry equation was derived by Langmuir and applied to the adsorbed film of soluble substances at the surface of aqueous solutions (*J. Amer. Chem. Soc.*, 1917, **39**, 1888); he concluded that the film when very dilute acted as an ideal, two-dimensional gas. [As Langmuir pointed out, Traube (*Annalen*, 1891, **265**, 27) had already shown that the surface layer of dilute solutions obeyed a law analogous to Boyle's.] Langmuir and Kingdon reached a similar conclusion for very dilute films of cæsium vapour adsorbed on tungsten (*Proc. Roy. Soc.*, 1925, *A*, **106**, 61).

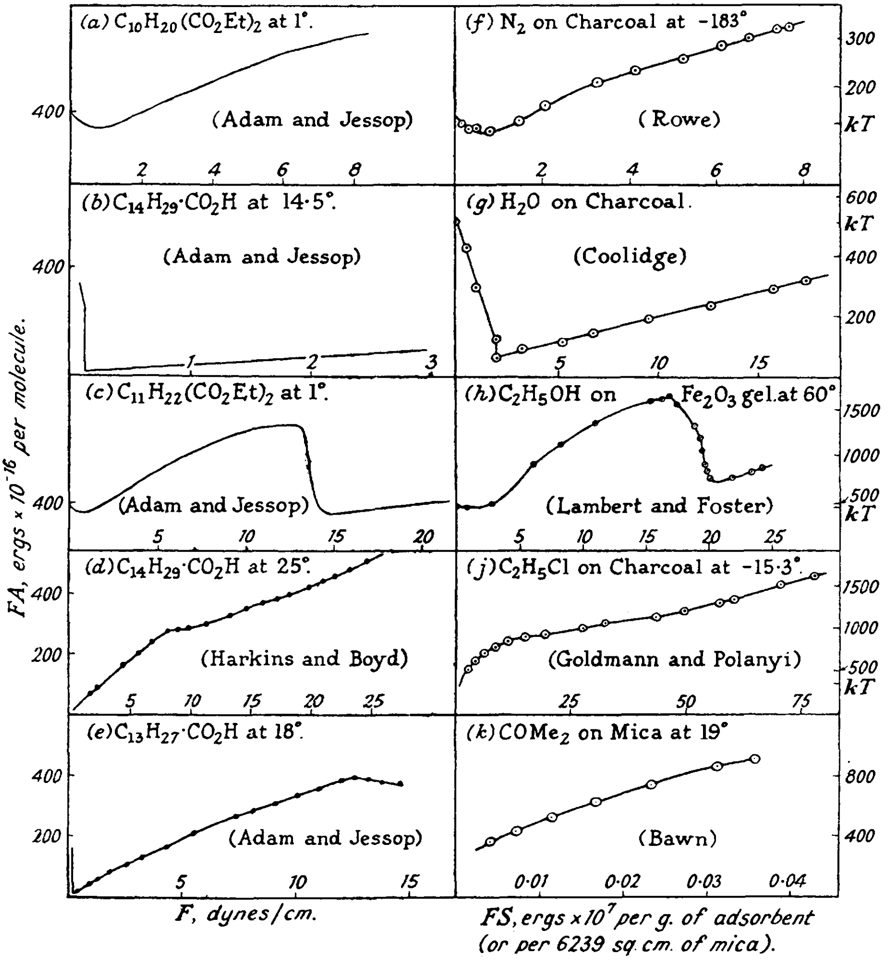
In gas–solid adsorption it may be that *exact* proportionality between x and p at low pressures obtains only if both adsorbent and adsorbate are particularly pure (Magnus and Kratz, *Z. anorg. Chem.*, 1929, **184**, 242); but ordinary cases of adsorption may be expected to approximate more or less closely to this, the film behaving *very nearly* as a two-dimensional perfect gas at low pressures. Every FA–FS graph may therefore be assumed to intersect the FA axis at or near the value $\boldsymbol{k}T$. Its detailed course for the region of low adsorptions can but rarely be mapped out, but in the range of high and medium adsorptions it is not much affected by uncertainties in the isotherm at low adsorptions, and so can still be drawn even if low-pressure data are scanty.

Numerous FA–FS graphs have been constructed from adsorption-isotherm data suitable for integration; examples and references are given in Figs. 2, 3, 4, and 5. In Fig. 2 there are given also the corresponding curves for insoluble films on water; the resemblance between the two sets of curves is striking, and leaves little doubt as to the similarity between adsorbed films on water and on solids.

One assumes that the extreme left-hand ends of curves (j) and (k) of Fig. 2 and of all the curves in Figs. 3, 4, and Fig. 5a are of the general form shown in (a) or (b) of Fig. 2, though much compressed along the FS axis. In Fig. 4b, branch YZ denotes the formation of a layer more than one molecule thick, as will be explained later.

The " imperfect gas " type of curve exemplified by Fig. 2f must always result from any adsorption isotherm which deviates slightly from Henry's law first in a " positive," then in a " negative " sense—*i.e.*, is first concave then convex to the pressure axis. Several such cases are on record, but in all of them the deviations from $x = mp$ are small and possibly do not exceed experimental error (*e.g.*, hydrogen and nitrogen on charcoal at — 183°, Rowe, *Phil. Mag.*, 1926, **1**, 1042; hydrogen on charcoal at — 78°, Barrer and Rideal, *Proc. Roy. Soc.*, 1935, *A*, **149**, 240; nitrogen on sodium chloride at 18°, Durau, *Ann. Physik*, 1928, **87**, 307). More low-pressure data are required before it can be decided whether this behaviour exists or not.

FIG. 2.



References: (*a*), (*c*) *Proc. Roy. Soc.*, 1926, *A*, **112**, 376.
(*b*) *Ibid.*, 1926, *A*, **110**, 423.
(*d*) *J. Physical Chem.*, 1941, **45**, 21.
(*e*) *Proc. Roy. Soc.*, 1926, *A*, **112**, 364.
(*f*) *Phil. Mag.*, 1926, **1**, 1042.
(*g*), (*h*), (*j*) Ref. (12), Table, p. 701.
(*k*) *J. Amer. Chem. Soc.*, 1932, **54**, 77.

The existence of a "hydrogen type" of gaseous film is more certain. The FA–FS curves for this state (which does not seem to be represented amongst films on water) rise steadily from the value $FA = \mathbf{k}T$ at $F = 0$ and soon become linear; an example is provided by Langmuir's data for carbon dioxide adsorbed on mica at — 118° (*J. Amer. Chem. Soc.*, 1918, **40**, 1361). The Langmuir adsorption equation, $x = k_1k_2p/(1 + k_2p)$, where k_1 and k_2 are constants, gives rise to a curve similar to the hydrogen type: on integration, we have $FA = -(k_1/x)\log_e(1 - x/k_1)$ and $FS = -k_1\log_e(1 - x/k_1)$, and on plotting FA against FS a curve rising steadily from its intercept with the FA axis at $\mathbf{k}T$, and slightly convex to the FS axis, is obtained. Its slope becomes nearly constant as $x/k_1 \rightarrow 1$, and for the range $x/k_1 = 0{\cdot}90$—$0{\cdot}95$ it is approx. $1{\cdot}2k_1$. [The relationship between the Gibbs and the Langmuir equation has been discussed by Innes and Rowley (*J. Physical Chem.*, 1941, **45**, 158), who derive an expression for F in terms of A and A_0, also for FA in terms of x, though not of F.]

Fig. 2*g*, for water vapour on charcoal (Coolidge, *loc. cit.*), is very similar in shape to the curve given by Bangham and Razouk (*loc. cit.*) (see p. 697). The vertical branch, denoting condensation from a G to an L_2 film, results from an isotherm having a region where p remains constant whilst x increases; this behaviour is rare and may even be confined to the water–charcoal system, for no other examples of the phenomenon can be traced.

Systems corresponding to type (iii) *or* (iv) *of Fig.* 1.

Adsorbent.	Temp.	Adsorbate.	Monolayer capacity, c.c. (N.T.P.) per g.	Ref.	Fig. No.
NaCl	−183°	NO	—	1	4*a*
Mica	35	C_6H_6	—	2	—
Glass	0	C_6H_5Me	—	3	—
Casein	—	NH_3	26 ± 2	4	—
Fe_2O_3 gel ...	40	C_6H_6	69 ± 2	5	5*a*
,, ...	60	EtOH	76 ± 5	6	2*h*
SiO_2 gel	60	H_2O	292 ± 15	7	—
,, ...	*ca.* 15	H_2O	840 ± 15	8	—
Charcoal......	30	CO_2	147 ± 5	9	—
,, ...	0	CO_2	150 ± 5	,,	3*b*
,, ...	−76	CO_2	145 ± 5	,,	—
*Charcoal I	0	CO_2	152 ± 8	10	3*a*
,,	,,	C_2H_2	123 ± 5	,,	3*d*
,,	,,	C_2H_4	98 ± 10	,,	3*c*
,,	,,	C_2H_6	90 ± 10	,,	—
*Charcoal I...	0°	N_2O	140 ± 5	10	—
,, ...	,,	SO_2	112 ± 12	,,	—
*Charcoal II	,,	N_2O	145 ± 15	,,	—
,,	,,	SO_2	120 ± 10	,,	—
*Charcoal I...	40·3	SO_2	105 ± 10	,,	—
Charcoal ...	0	EtCl	208 ± 15	11	—
,, ...	−15·3	EtCl	226 ± 15	,,	2*j*
,, ...	20·5	CS_2	305 ± 10	,,	—
† ,, ...	0	H_2O	218 ± 5	12	2*g*
,, ...	147	C_6H_6	185 ± 10	,,	—
,, Xb	0	SO_2	135 ± 3	13	—
,, Xc	,,	SO_2	136 ± 3	,,	—
,, Xa	,,	SO_2.	119 ± 3	,,	4*c*
,, XIIb	,,	EtCl	47 ± 2	,,	4*b*

* In these cases the "intermediate" region I is only just detectable. The low-pressure end of the *FA–FS* curve is somewhat doubtful (owing to paucity of low-pressure isotherm data) and it is just possible that the curves may be of the "hydrogen" type. The slope of the right-hand end, and therefore the value of the monolayer capacity, would scarcely be altered if this were so.

† This is comparable to type (vi), Fig. 1.

References. [1] Tomkins, *Trans. Faraday Soc.*, 1936, **32**, 643. [2] Bangham and Mosallam, *Proc. Roy. Soc.*, 1938, *A*, **166**, 558. [3] Carver, *J. Amer. Chem. Soc.*, 1923, **45**, 63. [4] Bancroft and Barnett, *J. Physical Chem.*, 1930, **34**, 489. [5] Lambert and Clark, *Proc. Roy. Soc.*, 1929, *A*, **122**, 505. [6] Lambert and Foster, *ibid.*, 1932, *A*, **136**, 367. [7] *Idem* (Expt. 7), *ibid.*, 1931, *A*, **134**, 246. [8] Anderson, *Z. physikal. Chem.*, 1914, **88**, 191. [9] Titoff, *ibid.*, 1910, **74**, 650. [10] Gregg, J., 1927, 1494. [11] Goldmann and Polanyi, *Z. physikal. Chem.*, 1928, **132**, 321. [12] Coolidge, *loc. cit.* [13] Gregg, to be published.

Much the commonest kind of curve appears to be that corresponding to curves (iii) and (iv) of Fig. 1 (see Figs. 2*h*, 2*j*; 3, 4, and 5*a*; also table). Owing to the lack of low-pressure data it is not usually possible to assign a given curve definitely to one or other of these classes, *i.e.*, to say whether it is G–I–L_2 or G–L_1–I–L_2. Fig. 2*h* represents a G–I–L_2 curve of an uncommon type, in that the perfect-gas behaviour appears to persist up to higher pressures than usually; the initial flat branch, however, depends on three experimental points only, and if more were available the curve might fall in line with either (iii) or (iv) of Fig. 1.

The degree of prominence of the intermediate region I differs considerably from one curve to another, and frequently the L_1 branch passes almost imperceptibly into the L_2. Similar diversity in this respect is found amongst films on water, where *FA–F* graphs are known corresponding to successive stages from the almost vertical I branch of Fig. 2*c* to the scarcely perceptible I region of Fig. 2*d*, the prominence of the I region being controlled for films on water by various factors, notably temperature and molecular structure.

Acetone on mica (Fig. 2*k*) is compared with a liquid-expanded film on water (Fig. 2*e*), but if we had enough low-pressure data it might prove to be comparable with a *gaseous* film at high surface pressure.

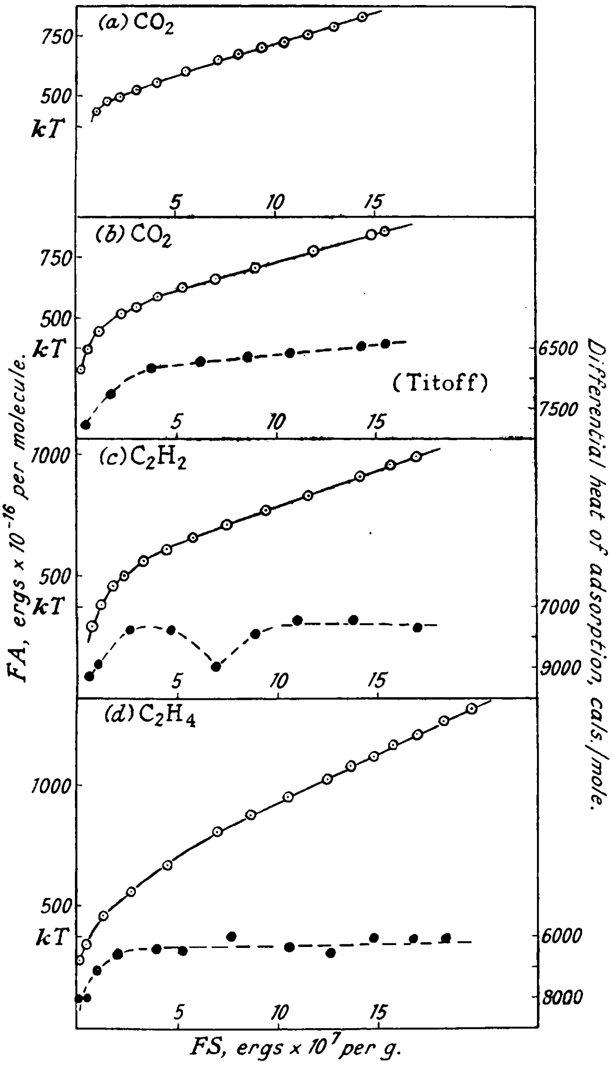
The rather sparse data for the differential heat of adsorption are consistent with the foregoing interpretation of the *FA–FS* curves. The heat of adsorption is made up of two parts : (*a*) heat of adsorption proper, due to the interaction of the adsorbed molecules with the adsorbent, and (*b*) the heat effect (a kind of two-dimensional Joule–Thomson effect) arising from the forces of attraction and repulsion between the adsorbed molecules themselves. Let the former be $\Delta H'$ cals./mole and the latter ΔJ; the measured differential heat of adsorption is then given by $\Delta H = \Delta H' + \Delta J$. Now, for those parts of the *FA –F* curve of constant slope, the orientation of the adsorbed molecules is constant, and since A is not far from A_0, the average separation of the adsorbed molecules in the layer does not alter much; ΔJ should therefore be nearly independent of x and of F. Also, for a surface of uniform activity $\Delta H'$ does not depend on the amount adsorbed either, so that ΔH should be independent of x and of F. Perhaps when the adsorbed layer is nearly full, ΔJ and therefore ΔH might increase slightly, due to the liberation of a heat of two-dimensional compression when the adsorbed molecules are pushed very close together. Where the *FA–FS* curve is non-linear, the orientation of the molecules, and hence their mutual interaction, varies with x, so that ΔJ is now a function of x and therefore of F : ΔH should now vary with F.

In Figs. 3 and 4, the curve of ΔH (measured calorimetrically) against *FS* is plotted alongside that of *FA* against *FS*, in those cases where sufficient data are available. It will be seen that the value of ΔH is fairly constant for the L_2 state, where the *FA–FS* curve is straight, and varies with *FS* for the L_1 state where the *FA–FS* curve is bent.

For a two-dimensional perfect gas, the interaction between the adsorbed molecules is zero, so ΔH should be independent of x or of F : in agreement with this, Magnus and Giebenhain have found that the differential heat of adsorption of carbon dioxide on silica gel is constant within narrow experimental limits throughout the Henry's law region (*Z. physikal. Chem.*, 1929, *A*, **143**, 265).

Calculation of the Specific Surface S *and of the Monolayer Capacity*, x_0.—Since the L_2 branch of the *FA–FS* curve is linear, its slope should, by analogy with films on water, be equal to A_0/S. Consequently, if a value can be assigned to A_0, the specific surface S can be calculated; A_0 is the incompressible area occupied on the adsorbent surface by the adsorbed molecules *when oriented in the manner proper to the* L_2 *state*, and exact assessment of it is difficult, for we do not know enough about either the orientation or the size and shape of molecules. Nevertheless, for small, nearly spherical molecules A_0 should not differ very greatly from the collisional area obtained from kinetic properties such as viscosity, or from the area calculated from the density of the bulk liquid, spherical or cubic molecules being assumed. An uncertainty of perhaps some 50% in A_0 and therefore in S is to be expected. A similar limitation on the accuracy of S necessarily attaches to all methods based on an estimate of the area occupied by the adsorbed molecules (*e.g.*, Harkins and Gans, *J. Amer. Chem. Soc.*, 1931, **53**, 2804; Paneth and Radu, *Ber.*, 1924, **57**, 1221; Brunauer and Emmett, *J. Amer. Chem. Soc.*, 1937, **59**, 1553; Brunauer, Emmett, and Teller, *ibid.*, 1938, **60**, 315).

FIG. 3.



References : (*a*), (*c*), (*d*)—Ref. (10), Table ; (*b*)—Ref. (9), Table.

Adsorption on charcoal at 0°. Systems corresponding to type (iii) or (iv) of Fig. 1.

Full lines represent *FA* against *FS*; broken lines ΔH against *FS*.

As an example we calculate the specific surface for Charcoal I from the curve for its adsorption of carbon dioxide given in Fig. 3*a*. The slope *B* of the right-hand, straight portion is $2{\cdot}46 \times 10^{-22}$ molecules^{-1} g. The collision diameter of carbon dioxide from viscosity measurements is 4·6 A. (see Kennard, " Kinetic Theory of Gases," 1938), giving collisional area = 15·8 A.^{2}. Hexagonal packing being assumed, this would occupy *ca.* $15{\cdot}8 \times 1{\cdot}10 = 17{\cdot}8$ A.^{2} on the adsorbent surface if the molecule were spherical; actually, it is elongated and in the L_2 state would, by analogy with films on water, probably be oriented with its longest axis nearly or quite vertical. This would reduce the value of A_0 to, say, 15 A.^{2}, which, combined with the value of *B*, gives S = 610 sq. m. Titoff's charcoal (Fig. 3*b*) gives 580 sq. m. These are of the same order as, but rather larger than, the figures obtained by Paneth and Radu using dye adsorption from solution : animal charcoal 119—452 sq. m., and limewood charcoal 61—268 sq. m. (*Ber.*, 1924, **57**, 1215); the discrepancy is not surprising, for, apart from probable differences in the charcoals, the dye molecules, being large, would not be able to penetrate to some portions of the surface which would be open to carbon dioxide. Bangham, combining expansion results with adsorption-isotherm data and assuming that the films on charcoal obeyed the same equation of state as on mercury, obtained twelve values clustering around 176 sq. m. for a pinewood charcoal (*Proc. Roy. Soc.*, 1934, *A*, **147**, 180).

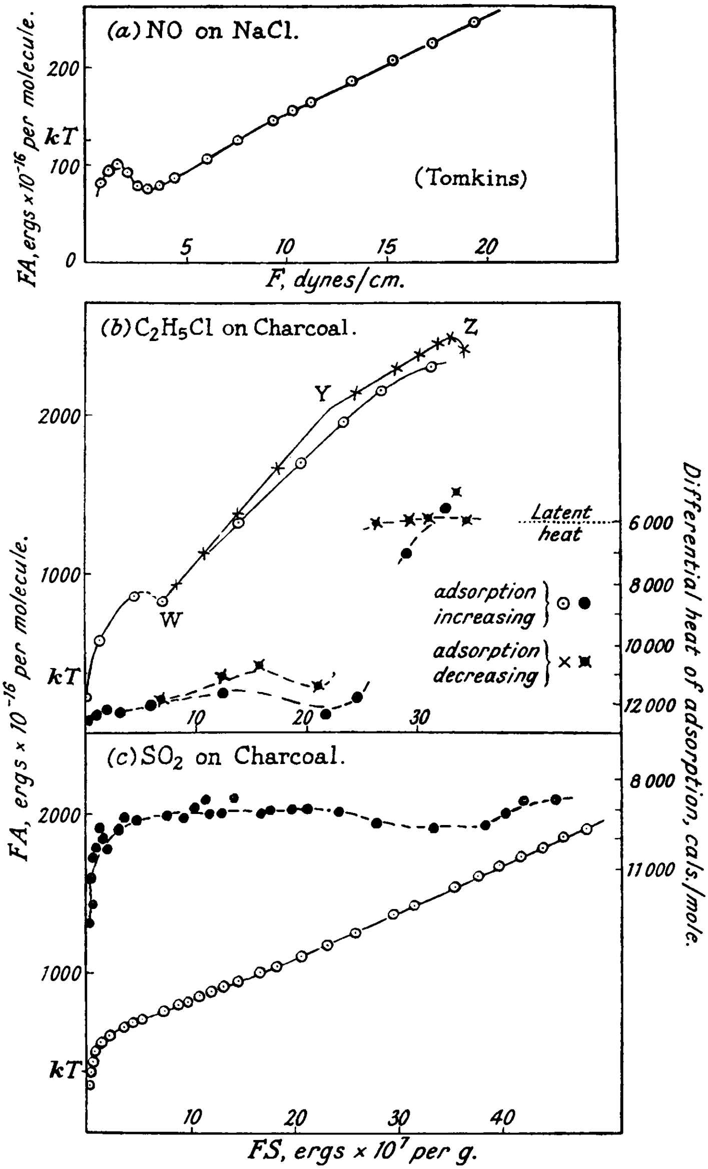
Rough estimates of the specific surface can also be based on the approximate slope of the L_1 branch of the *FA–FS* curve. Since the curve is no longer linear, the result cannot be accurate, but a useful approximation to *S* can frequently be obtained. The slope of the G branch at high pressure can be used similarly.

The correctness of the foregoing interpretation of the slope *B* can be tested by reference to a number of adsorbents of known specific surface, the value of *S* calculated by the relation A_0/S being compared with the directly measured value.

(a) *Nitric oxide on powdered sodium chloride* (Tomkins, *Trans. Faraday Soc.*, 1936, **52**, 643). The *FA–F* curve is shown in Fig. 4*a*, the values of *F* having been calculated from *FS* by using the measured value of *S*; the *FA–FS* curve required for our present purpose is, of course, of exactly the same shape. The extreme right-hand, linear branch corresponds to the L_2 state and its slope is $B = 2{\cdot}36 \times 10^{-20}$ molecules^{-1}. The collisional area of nitric oxide is 11·0 A.^{2} (Jeans, " Introduction to the Kinetic Theory of Gases," 1940, p. 183), and by arguments similar to those just used for carbon dioxide, remembering that the nitric oxide molecule is not quite so elongated, we take the value of A_0 as *ca.* 11 A. Insertion of this in $S = A_0/B$ gives $S =$ *ca.* $4{\cdot}7 \times 10^4$ sq. cm., in good agreement with Tomkins's measured value of $4{\cdot}6 \times 10^4$ sq. cm.

(b) *Benzene vapour on mica* (Bangham and Mosallam, *loc. cit.*). The *FA–FS* curve is of the (iii)/(iv) type of Fig. 1 (with a bend downwards at the right-hand end due to multilayer formation, see later). The slope of the L_2 branch is $9{\cdot}1 \times 10^{-20} \pm 1{\cdot}1 \times 10^{-20}$ molecules^{-1}, the considerable uncertainty being due to hysteresis effects which make the exact location of the *FA–FS* curve uncertain. The most reasonable value to take for A_0 in the L_2 state is that corresponding to the orientation of the molecules on edge, and this from *X*-ray data is 21·5 A.^{2} (Cox, *Proc. Roy. Soc.*, 1932, *A*, **135**, 491). Combined with the value of *B*, this gives $S = 23{,}500 \pm 3000$ sq. cm., in satisfactory agreement with the measured value of 19,000 sq. cm.

FIG. 4.



References : (*a*)—Ref. (1), Table ; (*b*), (*c*)—Ref. (13), Table.
Systems corresponding to types (iii) and (iv) of Fig. 1. In (*b*), layer thickening occurs.
Full lines represent *FA* against *FS* ; broken lines *H* against *FS*.

(c) *Acetone on mica at* 19° (Bawn, *J. Amer. Chem. Soc.*, 1932, **54**, 77). The average slope of the *FA–FS* curve over nearly the whole range, $FS = 0{\cdot}0073 \times 10^7$ to $0{\cdot}0316 \times 10^7$ erg, is $B = 3{\cdot}64 \times 10^{-19}$ molecules^{-1} ; since the *FA–FS* curve is not straight (Fig. 2*k*) and the zero extrapolation of the isotherm is rather uncertain, this value of *B* is open to considerable error. Taking A_0 as equal to the area calculated from the density of the bulk liquid, cubic molecules being assumed (since the molecules are not highly oriented in the L_1 state), *viz.*, 24·5 A.^{2}, we have $S = 6750$ sq. cm. Bawn's measured value is 6239 sq. cm. but such close agreement is fortuitous in view of the doubt as to the appropriate value of A_0, and the inexactitude inseparable from estimates based on non-linear *FA–FS* curves.

An indirect but very useful measure of the specific surface is the monolayer capacity, x_0, of the adsorbent, *i.e.*, the number of molecules which can be adsorbed in a completed monolayer; x_0 can be calculated from the slope B without any assumptions as to the value of A_0, for $x_0A_0 = S$, so $x_0 = S/A_0 = 1/B$. If the monolayer capacity is required in " practical " units such as c.c. (at N.T.P.) rather than in molecules, it is only necessary to express x in those units when drawing the curve of x against log p; $1/B$ then gives the monolayer capacity in the desired units directly.

An estimate of the monolayer capacity, like that of the specific surface, can be accurate only if based on a linear branch—more particularly the L_2 branch—of an *FA–FS* curve. If based on an L_1, or a non-linear G branch, it is only a rough approximation. The I branch is, of course, useless for the purpose. The table on p. 701 gives the monolayer capacities for the L_2 state for a number of adsorbents and various adsorbates. In many cases the zero extrapolations of the semi-log isotherm curve are uncertain, but this should not greatly affect the values of B.

The monolayer capacity for a given adsorbent will necessarily depend both on the nature of the adsorbate and on its adsorbed state,, since each of these factors will affect the value of A_0. The values of the monolayer capacity for the charcoals quoted are all of the same order, but for a given charcoal they depend on the nature of the gas; x_0 for a given charcoal should vary inversely as the incompressible area A_0 of the particular adsorbate in the L_2 orientation, if the same total area were equally accessible to all adsorbates no matter what their molecular size. This relationship between x_0 and A_0 cannot be tested rigorously, however, for equal accessibility is unlikely and the difficulty of estimating A_0 accurately still remains; but the gases adsorbed on charcoal I would not differ by more than two-fold in their incompressible areas, and the corresponding values of the monolayer capacity agree within these limits, and for gases of similar molecular structure they diminish as the number of atoms per molecule increases.

The monolayer capacity for a given gas and adsorbent should be nearly independent of temperature; if anything, A_0 might be expected to decrease slightly with rising temperature (by analogy with the van der Waals b for bulk fluids), implying a small *increase* in x_0. The values of the monolayer capacity from Titoff's data for carbon dioxide at $-$ 76°, 0°, and 30° (see Table) show the expected approximate equality, as do Gregg's for sulphur dioxide at 0° and 40·3° on Charcoal I. The small temperature variation in monolayer capacity for ethyl chloride on Polanyi and Goldmann's charcoal at $-$ 15·3° and 0° is in the correct sense.

According to Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1361), the monolayer capacity is the constant k_1 of the equation $x = k_1k_2p/(1 + k_2p)$. This equation gives rise to an *FA–FS* curve which, though resembling the " hydrogen type," has a slope which gradually increases as *FS* increases but becomes nearly constant, at $B = ca.\ 1{\cdot}2k_1$, for large values of x. This value of B gives $x_0 = 1/1{\cdot}2k_1$, which agrees tolerably well with k_1, considering that the *FA–FS* curve is never absolutely straight. The monolayer capacity is no longer calculable from the Langmuir equation if changes of state occur within the range considered.

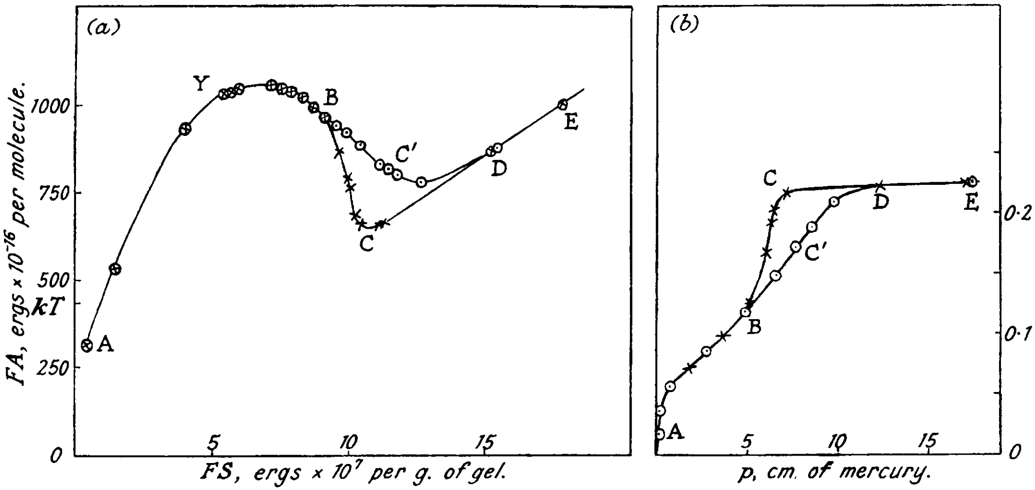
Brunauer and his co-workers (*J. Amer. Chem. Soc.*, 1940, **62**, 1723; 1938, **60**, 309) have proposed a generalised form of the Langmuir equation for determining a quantity v_m, the monolayer capacity in c.c. (at N.T.P.). Their theoretical basis is, however, quite different from that of the present paper; in particular the isotherm is regarded as *continuous*, and is represented by a single equation from zero adsorption up to many molecular thicknesses of the adsorption layer, so the possible occurrence of changes of state in the adsorbed layer is not considered. Unfortunately, most of the experimental isotherms quoted by these workers in support of their views have too few experimental points at low pressures to permit the construction of the corresponding *FA–FS* graphs, and the replotting necessary in order to compare the two methods is deferred to a later communication. Meanwhile, it may be recalled that Brunauer's equation reduces to Langmuir's form at low pressures, so the value of v_m calculated with this simplified form should show the same order of agreement with x_0 as does k_1. If, however, a change of state occurs in the film within the experimental range to which the equation (whether full or reduced) is applied, agreement between v_m and x_0 can no longer be expected : for instance, the value obtained by Brunauer *et al.* (*loc. cit.*, 1940) for v_m from Lambert and Clark's data for the adsorption of benzene on ferric oxide gel is 0·081 g./g., *i.e.*, 23 c.c. (N.T.P.) per g., as compared with our value of 69 c.c. (N.T.P.), and this is a case where a change of state ($L_1 \rightleftharpoons I \rightleftharpoons L_2$) occurs (cf. Fig. 5*a*).

Formation of Multimolecular Layers on Non-porous Adsorbents.—At sufficiently high pressures, the film of a vapour adsorbed on a non-porous solid becomes more than one molecule thick : it passes over into a multilayer. This has been shown by a number of workers who have measured the adsorption of vapours on non-porous adsorbents having a known surface area so that the thickness of the layer could be calculated. The formation of adsorbed layers in excess of unimolecular is often assumed to occur in porous adsorbents also, but direct evidence is lacking. By constructing *FA–FS* graphs from the experimental data for non-porous adsorbents (see above) and examining their characteristics in the region corresponding to the transition from monolayer to multilayer, we can obtain criteria for the detection of multilayer formation in general, which should then be applicable to porous adsorbents. Such graphs have been constructed from the data of the following experiments : the lower fatty acids on mercury (Bosworth, *Trans. Faraday Soc.*, **1932**, **28**, **903**); benzene on mica (Bangham and Mosallam, *loc. cit.*); and acetone and benzene on vitreous silica (Palmer, *loc. cit.*). In every case the graph shows a sudden change in slope at or near the point where $A = A_0$, corresponding to a completed monolayer. For example, with the vapours of valeric, propionic, and butyric acids on mercury, the *FA–FS* curve, which is very similar to the curve *ABCDE* of Fig. 5*a* for $A > ca.$ 20 A.², turns very sharply towards the *FS* axis when $A = ca.$ 20 A.², and continues to fall steeply, though (as far as can be judged from the small number of experimental points) not quite vertically, till, when the saturated vapour pressure is reached in the free space, the adsorbed layer is several molecules thick.

The *FA–FS* curve for benzene vapour on mica likewise shows a sudden turn towards the *FS* axis when *A* lies between 19 and 23 A.², where the monolayer must be just about complete (A_0 for benzene molecules oriented on edge is probably 21·5 A.², see above). The change in curvature, although not so sudden as in the mercury curves, was still sharp enough to produce a maximum in the *FA–FS* curve at a point corresponding to $A =$ 20—22 A.². The shape of the curve is very similar to the part *ABC* of Fig. 5*a*, though the significance of the branch *BC* is different in the two cases, for in Fig. 5*a* it corresponds to the I state whereas in the present case it denotes multilayer formation.

Bangham and Mosallam found that the inception of the second layer of molecules was accompanied by a sudden fall in the differential heat of adsorption calculated from the Clausius–Clapeyron equation. They say (*loc. cit.*, p. 560) " the adsorption energy is very nearly constant, its value, where the area per molecule exceeds 35 A.² being about 12,000 cals. per mole. As the area per molecule decreases from 35 to 25 A.² the energy falls to a minimum value " (about 7500 cals. per mole); " thereafter there is a slight rise to a value very near the normal heat of liquefaction." They regard it " as established that both the adsorption energy and the slope of the isotherm undergo an abrupt change at *about* the adsorption value to be expected for a unimolecular film of molecules oriented on edge " (*loc. cit.*, p. 562).

Fig. 5.



Adsorption of benzene on ferric oxide gel. [Ref. (5), Table.]

Palmer noted that his data for benzene vapour on vitreous silica also lead to a maximum in the *FA–FS* curve; the shape of the curve is again very similar to *ABC* of Fig. 5*a*. It terminates when $p = p_s$ at a point corresponding to *C* on this figure, and the area per molecule is then 6·8 A.², corresponding to a layer about 3 molecules thick. The marked change in curvature (corresponding to point *Y* in Fig. 5*a*) occurs when *A* lies somewhere between 22 and 25 A.², *i.e.*, about the correct value for a completed monolayer. The curve from Palmer's data for acetone shows a sudden change in slope (not great enough to produce a maximum in the vicinity) at an *FS* value corresponding to some 22 A.², which again cannot be far from the value for a completed monolayer (*e.g.*, A_0 for acetone from bulk liquid density is 24·5 A.²). This curve is particularly interesting in that it shows a further sudden reduction in slope when $A = ca.$ 12 A.², corresponding to approximately two complete layers. Whether the completion of the second layer produces this effect in all systems cannot be decided owing to lack of experimental data.

On the basis of the foregoing results one may suggest that the formation of an adsorbed layer exceeding one molecule in thickness is signalised by a falling off in the *FA–FS* curve, commencing at some point *Y*, say; the downward bend may be great enough to produce a maximum in the neighbourhood of *Y*, but there is probably no discontinuity in the curve at *Y*. Since the thickening process presumably commences when the first layer is nearly or quite full, the amount adsorbed at *Y* should be near or equal to the monolayer capacity x_0 calculated from the slope of the part of the curve immediately preceding *Y*, if this is near enough to linear. The shape of the curve in the region corresponding to multilayer formation is very similar to that of the I region of a monolayer curve [cf. (iii) and (iv) of Fig. 1, also Fig. 5*a*]. Various means of distinguishing these are available, however, even if *S* is unknown; thus, if the transition $L_1 \rightarrow L_2$ or $G \rightarrow L_2$ has already occurred at *lower* pressures, the falling off cannot be due to the I state but must denote multilayer formation; but if the downward bend commencing at Y is followed at *higher* pressures by the typical rising branch of the L_2 state, as in Fig. 5*a*, the bend must be ascribed to the I state and not to multilayer formation. Further, it seems likely on *a priori* grounds that the sudden fall in the differential heat of adsorption to a value near the latent heat of condensation, noted by Bangham and Mosallam, is a general effect associated with the inception of the second layer (Brunauer *et al.* make essentially this assumption in a simplified treatment of their general theory; *loc. cit.*, 1938); the transition from the L_1 or the G to the I state, on the other hand, would probably give rise to a much smaller, or even a negligible, change in the differential heat of adsorption.

Thickness of the Adsorbed Layer on Porous Adsorbents: the Theory of Capillary Condensation.—This well-known theory was first put forward by Zsigmondy (*Z. anorg. Chem.*, 1911, **71**, 356) in connection with the characteristic hysteresis loops obtained by van Bemmelen (*ibid.*, 1897, **13**, 233; 1898, **18**, 98) in the adsorption isotherm of water vapour on silica gel. Anderson (*Z. physikal. Chem.*, 1914, **88**, 212) also explained the hysteresis loops he obtained with benzene and alcohol vapour on silica gel, and Bachmann his loops with silica and ferric oxide gels (*Z. anorg. Chem.*, 1917, **100**, 41), in terms of capillary condensation. More recently, hysteresis loops have been studied experimentally by Lambert and Clark and Lambert and Foster (*loc cit.*). The isotherm for benzene on ferric oxide gel at 40° (*idem, loc. cit.*, 1932) is given in Fig. 5*b*. According to the capillary-condensation theory, branch OAB of this isotherm corresponds to an adsorbed layer, at most a few molecules thick, on the walls of the capillaries (Zsigmondy, *loc. cit.*; cf. Foster, *Trans. Faraday Soc.*, 1932, **28**, 652); at B " capillary condensation," in which the adsorbate condenses to a bulk liquid in the pores, sets in and proceeds till the pores are full of liquid (branch $BC'D$). The radius of the pore which is being filled at any pressure p is given by the Kelvin equation (*Phil. Mag.*, 1871, **42**, 448). Branch DCB, which is traced out when p is progressively reduced from its value at D, corresponds to the gradual emptying of the pores of their liquid, till at B only the wall layer remains; that branch DCB does not coincide with the capillary-filling branch $BC'D$ is ascribed to irreversible effects associated with the formation of the liquid meniscus (Foster, *loc. cit.*; Cohan, *J. Amer. Chem. Soc.*, 1938, **60**, 433), or with the advance of the meniscus along the pore wall (Zsigmondy, *loc. cit.*).

When the *FA–FS* curve is constructed from the isotherm, it proves to be of the form shown in Fig. 5*a*. This is obviously analogous to curve (iii) or (iv) of Fig. 1, and is therefore characteristic of a *monolayer*. Branch DE shows no signs of the turn downwards at the right-hand end, which, according to the author's views, would be expected if the adsorbed layer became more than one molecule thick; in fact, DE provides a clear example of a curve for the liquid-condensed (L_2) state of a monolayer. This is the more striking in that Lambert and Foster's measurements were continued till the saturated vapour pressure was nearly reached.

The values of the differential heat of adsorption, calculated by means of the Clausius–Clapeyron equation, support the view that the adsorbed layer does not become thicker than unimolecular: the x–log p curves for 40° and 50° run sensibly parallel from about a point half-way between A and B (where experimental points first become close enough to permit judgment) and along BCD and $BC'D$ respectively till D is nearly reached. The heat of adsorption is therefore practically the same (about 9500 ± 300 cals./mole) both before and after point B, and does not suddenly fall to near the latent heat (7900 cals./mole) at B, as would be expected if layer thickening—as in capillary condensation—began at this point. It must be admitted, however, that, since the heat of adsorption is so close throughout to the latent heat, this evidence is not conclusive.

It is especially significant that the hysteresis loop of the isotherm corresponds to the intermediate region I of the *FA–FS* curve; the branches OB and DE corresponding to the L_1 and the L_2 state are reversible within experimental limits, but the path between them depends on whether adsorption is decreasing or increasing. [Very similar behaviour occurs with films on water, where the I state, but not the L_1 or the L_2 state, is prone to hysteresis (Adam, *op. cit.*, p. 56).] The hysteresis is thus connected with the two-dimensional change of state $L_1 \rightleftharpoons I \rightleftharpoons L_2$ occurring within the monolayer itself, and not with the transition from a monolayer or a multilayer to bulk matter, as required by the capillary-condensation theory.

FA–FS curves of exactly the same general form as Fig. 5*a* are obtained from Anderson's isotherms for water vapour on silica gel (*loc. cit.*), and from Lambert and Foster's for ethyl alcohol vapour on ferric oxide gel (*loc. cit.*; see Fig. 2*h*). These particular isotherms have been selected solely because they have sufficient measurements at low pressures to make integration possible; and the isotherms obtained by the same authors at different temperatures or with different vapours, and some obtained by other workers, are so similar in general characteristics to Fig. 5*a* that there is no reason to doubt that the corresponding *FA–FS* curves, if they could be drawn, would have the same form as Fig. 5*b*. Isotherms of the type illustrated in Fig. 5*b*, then, signify that adsorption is confined to a monolayer, the hysteresis loop arising, not from capillary condensation, but from a transformation of state within the monolayer.

According to some versions of the capillary-condensation theory (*e.g.*, Patrick and McGavack, *J. Amer. Chem. Soc.*, 1920, **42**, 946), hysteresis is not an inevitable feature of capillary condensation, but may be an adventitious effect due, *e.g.*, to traces of adsorbed air. It is useful therefore to examine the *FA–FS* curves obtained from experiments where, though hysteresis was absent, the measurements were carried through to the saturated vapour pressure so that capillary condensation might perhaps still be expected from the theory. Such experiments are those with benzene vapour on silica gel (Lambert and Clark, *loc. cit.*) and ethyl chloride on charcoal (Polanyi and Goldmann, *loc. cit.*). In the first, the zero extrapolation of the semi-log isotherm curve is somewhat uncertain; consequently there is doubt whether the *FA–FS* curve is of the (iii)/(iv) type of Fig. 1, with the I region recessive, or of the (v)/(vi) type (the transition $G \rightarrow L_2$, or $L_1 \rightarrow L_2$, having taken place at some lower pressure), but there is no doubt as to the absence of any bend towards the *FS* axis at the right-hand end of the curve, so that thickening of the adsorbed layer beyond unimolecular seems clearly ruled out.

The second case, the *FA–FS* curve of which is shown in Fig. 2*j*, is definitely of the (iii)/(iv) type of Fig. 1, both at − 15·3° and at 0°. Again, there is no falling off at the right-hand end of the L_2 branch, so the layer never exceeds unimolecular thickness—a conclusion borne out by the fact that the minimum value quoted by Goldmann and Polanyi for the (calculated) differential heat of adsorption is still 2800 cals./mole in excess of the latent heat.

It should not be concluded from the foregoing discussion that adsorption in porous adsorbents is *invariably* confined to a unimolecular layer. Three instances will be given in which adsorption seems definitely to proceed beyond the unimolecular stage at high relative pressures.

(a) *Water vapour on silica gel* (Lambert and Foster, *loc. cit.*, 1931). During a number of experiments successively on the same sample of gel, the isotherm shifted slightly each time in the direction of increased pressure. Lambert and Foster's experiment (4) at 70° and (5) at 60° have closely spaced points at higher pressures but not at lower ones, whereas Expt. (1), at 60°, extends to low pressures but has points widely spaced at higher pressures. In order to calculate the *FA–FS* curves for Expts. (4) and (5) it has therefore been necessary to make the slightly incorrect assumptions that the semi-log isotherm curve of Expt. (5) follows the same course as that of Expt. (1), and that the semi-log curve of Expt. (4) at 10° higher is parallel to the curve for Expt. (1). (The incorrectness is due to the slight shift of the isotherm, caused by each run, already noted.) Expts. (4) and (5), both of which ceased at pressures somewhat below the saturated vapour pressure p_s, gave isotherms with hysteresis loops and yielded *FA–FS* curves very similar to Fig. 5*a*. In a later experiment, still on the same gel, the adsorption measurements were commenced at a pressure slightly below p_s and to the right of the hysteresis loop, and were continued up to $p = p_s$; at a certain point in this region (when $x = x'$, say) the isotherm turned sharply upwards, $\Delta x/\Delta p$ suddenly becoming much larger though not infinite. Owing to the absence of the rest of the isotherm, the *FA–FS* curve cannot be constructed, but it is clear that the sudden rise in the isotherm must correspond to a sharp fall (though not vertical) in the *FA–FS* curve. Thickening of the layer beyond unimolecular may be inferred. Confirmation is afforded by applying the criterion that x' should be near in value to the monolayer capacity calculated from the slope of the L_2 branch of the *FA–FS* curve. Exact agreement is not to be expected: in view of the displacements in the isotherm with their implied reduction in monolayer capacity by each experiment, x' should be smaller than the x_0 values obtained in earlier experiments, since it is derived from the last experiment. The following figures are in agreement with this:

Expt. (4) at 70°	x_0 from *FA–FS* curve = 310 ± 12 c.c.
Expt. (5) at 60°	x_0 from *FA–FS* curve = 290 ± 12 c.c.
compare last expt.	x' from rise in isotherm = 270 ± 12 c.c.

It is significant that, though layer thickening occurs in this system, the hysteresis loop is not associated with the thickening process, but still corresponds to the I state of the monolayer. Lambert and Foster point out, however, that the lack of coincidence of ascending and descending points *may* extend outside the hysteresis loop, and this would imply that the conversion of the monolayer into a thicker layer may be attended by some degree of hysteresis. Such hysteresis would not be surprising, for this conversion, like the monolayer transition $L_1 \rightarrow I \rightarrow L_2$, must be regarded as a transformation of state.

(b) *Ethyl chloride on sugar charcoal* (Gregg, to be published). Marked hysteresis effects, together with much drift (very slow reduction in pressure over long periods) without, however, any well-defined hysteresis loop, make it doubtful how far the isotherm corresponded to true equilibrium conditions. Two *FA–FS* curves are shown in Fig. 4*b*, corresponding severally to adsorption increasing (circles) and decreasing (crosses). As far as point *Y*, each is fairly definitely of the (iii)/(iv) type of Fig. 1, branch *WY* corresponding to the L_2 state. The turn towards the *FS* axis which occurs at *Y* on the " adsorption decreasing " curve (it is much less sharp on the reverse curve, most probably because of hysteresis) strongly suggests the inception of adsorption in excess of a unimolecular layer. This inference is confirmed by the large and sudden reduction in the value of the heat of adsorption which occurred at the same time (see Fig. 4*b*—solid circles and crossed circles), the heat of adsorption for the branch *YZ* being close to the latent heat. A similar result was obtained on several successive runs. This thermal behaviour is strikingly similar to that in the layer-thickening range of Bangham and Mosallam's experiment with mica (*loc. cit.*), leaving little doubt that an increase in layer thickness starts at *Y*.

The slope of the L_2 branch *WY* of the " adsorption decreasing " curve (which is probably closer to equilibrium conditions than the " increasing " curve) gives the monolayer capacity as 47 ± 2 c.c. (at N.T.P.). If the layer-thickening process commences only when the monolayer is full, this value of x_0 ought to be the same as the value of x—say x''—at which sudden reduction in the differential heat occurs. For the " adsorption decreasing " run x'' lay between 44·2 and 41·2 c.c. (N.P.T.), and although this is appreciably different from x_0, yet the difference is probably no greater than can be accounted for by difficulties due to hysteresis.

(c) *Water vapour on copper oxide* (Bray and Draper, *Proc. Nat. Acad. Sci.*, 1926, **12**, 297). The zero extrapolation of the semi-log isotherm curve is somewhat uncertain, but the *FA–FS* curve, which is similar in shape to *AYBC* of Fig. 5*a*, undoubtedly shows a maximum between points corresponding to $x = 25{\cdot}5$ and 43 mg./g. (experimental points are rather widely spaced here) and falls off fairly steeply as x increases up to 214 mg./g.

at $p = p_s$. The slope of the curve immediately before the commencement of the bend gives x_0 = approx. 38 mg./g., whence it seems clear that layer thickening occurs, giving a film some 5 or 6 molecules thick at the highest pressure reached.

Doubtless, there are many other instances besides these three of adsorption in excess of a monolayer, but the paucity of low-pressure measurements makes them difficult to discover from the extant data. At the same time, the phenomenon appears to be much less common than the capillary-condensation theory would suggest. Even when thicker layers are formed, it does not necessarily follow that the adsorbate condenses in the pores on interstices as an ordinary liquid possessing the characteristic properties, such as surface tension and density, of the liquid in bulk. Bangham and his co-workers (*Trans. Faraday Soc.*, 1937, **33**, 1463; 1938, **34**, 554) have given several reasons, experimental and theoretical, for supposing that the multilayer of a vapour adsorbed on charcoal or on mica differs considerably in surface tension from the bulk liquid; they found that several different organic vapours, even when supersaturated, frequently failed to condense on to a multilayer of the same adsorbate on mica. Consistent with this is Lambert and Foster's observation (*loc. cit.*, 1931) that at no time, in their experiments on silica gel, could water be seen to condense on to the gel even when the saturated vapour pressure was reached in the free space and liquid water could be distilled on to the mercury of the manometer.

If the possibility of condensation to an ordinary liquid is rejected, there are still two different possible mechanisms by which the adsorption process can proceed from the point where the monolayer is just complete : (i) the multilayer may build up over the whole of the adsorbing area S at the same time, so that the molecular thickness of the layer is everywhere the same, and is a function of the pressure p, or (ii) commencing with the finest pores, the whole of the cross-section of each pore of a given radius r may become full in one step as soon as p has reached a critical value characteristic of r. Mechanism (ii) would thus be similar to that envisaged by the capillary-condensation theory except that the material filling the pores would no longer be in its ordinary bulk liquid condition, and the relationship between p and r would not be given by the Kelvin equation. Although there is no direct evidence for deciding between these alternatives, yet the similarity already demonstrated between adsorption on porous adsorbents and on non-porous ones, where mechanism (ii) is necessarily excluded, argues in favour of alternative (i).

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WASHINGTON SINGER LABORATORIES,
UNIVERSITY COLLEGE, EXETER.

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