

CLXXV.—*The Translational Motion of Molecules in the Adsorbed Phase on Solids.*

By DONALD HUGH BANGHAM and NAZIM FAKHOURY.

OF recent years the conception that molecules adsorbed on solid surfaces may be in a state of translational motion parallel to the surface has been regarded with increasing favour. The supporting evidence, which has been summarised by Rideal ("Introduction to Surface Chemistry," 2nd Edition, Cambridge, 1930; see also *Ann. Reports*, 1928), though fairly direct in certain isolated instances, is nevertheless hardly sufficient to justify any conclusions of a general nature. Evidence of a new type is now advanced, and the means are indicated whereby relative measurements of the surface pressures may be made.

Evidence of Expansion Experiments.—Measurements of the expansion which wood charcoal undergoes in taking up carbon dioxide, ammonia, and sulphur dioxide (*Proc. Roy. Soc.*, 1930, *A*, **130**, 81) have led to the following empirical equation as expressing the relation between x , the percentage linear expansion, and s , the number of g. of gas adsorbed per g. of charcoal :

$$x = ks/(S - s) \dots \dots \dots (1)$$

Here k is a constant depending on the gas, and S is a limiting adsorption value which s approaches asymptotically. An additional constant was found necessary to represent the expansion caused by water vapour. To explain the results it was supposed that the expansion is some index of a two-dimensional bombardment pressure operative at sharp re-entrant angles in the surface. Schofield and Rideal (*Proc. Roy. Soc.*, 1925, *A*, **109**, 57) have shown that the adsorbed phase at the surface of certain solutions (such as those

of the fatty acids in water) behaves as a two-dimensional gas, of which the pressure F is given by

$$F(A - B) = iRT \dots \dots \dots (2)$$

Here $1/A$ is the surface concentration (in g.-mols. per sq. cm.), B is the "incompressible" cross-sectional area per g.-mol., and i (the maximum value of which is unity) is a constant determined by the mutual cohesion between the molecules. In terms of s and S , the corresponding equation for an adsorbate of molecular weight M on a solid adsorbent of specific surface Σ would be (since $A = M\Sigma/s$ and $B = M\Sigma/S$)

$$F = \left(\frac{iRTS}{M\Sigma} \right) \frac{s}{S - s} \dots \dots \dots (2a)$$

It being highly improbable that a significant change in Σ accompanies the expansion of charcoal, the expression in parenthesis should be constant for a given gas at a given temperature. The formal resemblance between equations (1) and (2a) suggests that in the range covered by our experiments the adsorbed films on charcoal may also behave as two-dimensional gases, and that the expansion is actually directly proportional to their pressure; *i.e.*,

$$x = \lambda F \dots \dots \dots (3)$$

where λ is a constant depending probably both on the charcoal and on the gas used.

If this hypothesis is correct, by plotting Mx/s against x one should obtain characteristic graphs comparable with the $FA-F$ graphs of Schofield and Rideal and others; further, if equations (2a) and (3) are both valid, it follows that

$$\frac{x \left(\frac{S}{s} - 1 \right)}{\lambda} = \frac{iRTS}{M\Sigma}$$

or

$$Mx/s = \lambda iRT/\Sigma + Mx/S \dots \dots \dots (4)$$

whence

$$d(Mx/s)/dx = M/S = B/\Sigma$$

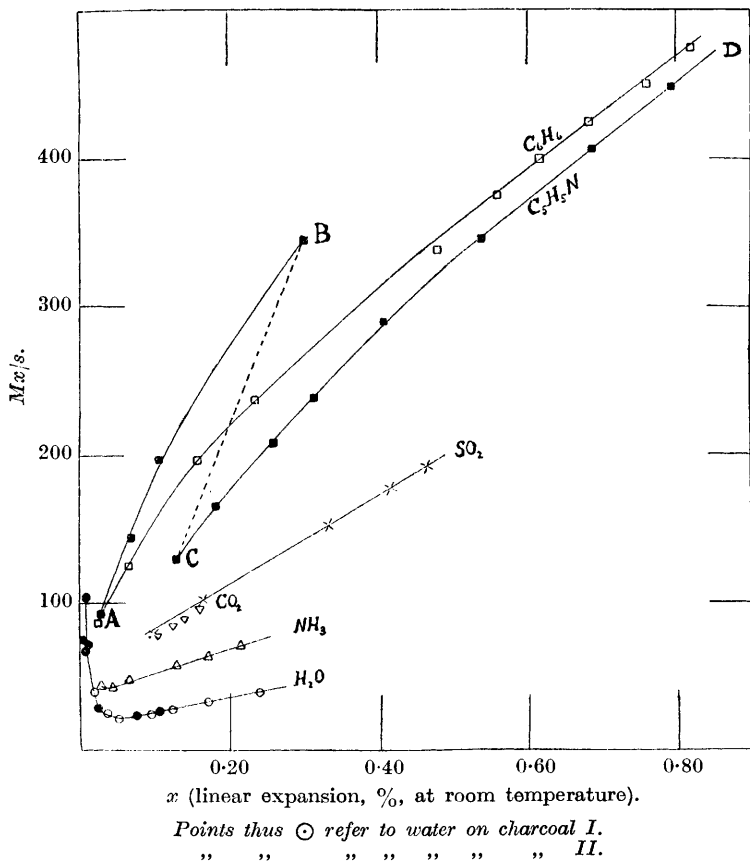
and the graphs should then be linear, cutting the ordinate axis at a point giving the value of $\lambda iRT/\Sigma$.

A typical series of such graphs is shown in Fig. 1.* Resemblance to the $PV-P$ graphs for imperfect gases is particularly striking in

* The data for benzene and pyridine refer to a piece of charcoal different, and differently treated, from that used with ammonia, carbon dioxide, and sulphur dioxide. Since, however, the two charcoals showed identical behaviour towards water (see graph in Fig. 1), the two sets of data should be at least roughly comparable. Full details of the experiments with benzene, pyridine, and other organic vapours will be given in a forthcoming paper, in which a greatly improved technique for making $x-s$ measurements will be described.

the case of water, ammonia, carbon dioxide, and sulphur dioxide. It is unfortunate that the ordinate values at $x = 0$, a knowledge of which would be invaluable in the interpretation of the data, remain subject to considerable uncertainty. Until definite evidence to the contrary is forthcoming, it must be supposed that for each adsorbate there is a characteristic limiting value Mx_0/s_0 which is proportional

FIG. 1.



to λ and inversely proportional to Σ , the area of the film; as suggested in our earlier paper, the latter may vary with the size of the adsorbed molecules.

As x increases, all the graphs in Fig. 1 become linear, or nearly so, indicating a region of obedience to equation (1). According to equation (4) the slopes of the linear portions should give the values of B/Σ , and it is satisfactory to note the steady increase of slope with

increasing molecular size. The curves for benzene and pyridine, although their close proximity affords (in view of the structural similarity of these two substances) a strong confirmation of our hypothesis, find no counterpart in the behaviour of imperfect gases. Their curvature near the axis can hardly be ascribed to the mutual attraction between molecules, but might result either from a fraction of the molecules taking up fixed positions on the surface (this fraction becoming smaller as s increases) or from a progressive change of orientation accompanying closer packing. The possibility must be borne in mind that for these substances i may be determined by other factors than mutual cohesion, and, if the second of the above suggestions is correct, may take values greater than unity.

The observations made with pyridine throw some light on the obscure phenomenon of slow "sorption," which this substance shows to a marked degree. Adsorption of a limited quantity of this substance causes a relatively large and *immediate* expansion. On standing, however, this slowly decreases. In the experiment illustrated in Fig. 1, points lying between A and B refer to observations taken in fairly rapid succession, and point C to one made after a long interval, during which the charcoal had been heated to accelerate the rate of drift. Thereafter the course of the expansion was more or less normal (curve CD), except for a very slight tendency to drift when the system was left to stand for long intervals. This behaviour appears to preclude any possibility that the expansion is due to slow diffusion of adsorbed molecules into inaccessible parts of the substrate. The drift may be accounted for on the basis of one or other of the suggestions contained in the last paragraph. Under certain conditions, benzene could be made to show a parallel behaviour, but in a normal experiment, after following for a short distance the steep portion AB of the pyridine curve, the graph for this substance bent smoothly round close and parallel to the pyridine curve CD.

Evidence of the Isotherms.—Further support for the hypothesis under consideration is forthcoming from the dead-space pressure measurements made by us in the course of the expansion experiments. It was assumed by Schofield and Rideal, following Traube and Langmuir, that the lowering of surface free energy at the interfaces studied by them was due entirely to the two-dimensional pressure. If this were true in the case of a solid adsorbent of surface energy γ , we should have (compare Rideal, *op. cit.*, Ch. II), by applying the Gibbs equation in the appropriate form,

$$d \log_e p = - \frac{M\Sigma}{RT} \cdot \frac{1}{s} \cdot d\gamma = \frac{M\Sigma}{RT} \cdot \frac{1}{s} dF \quad . \quad . \quad (5)$$

If equation (2a) is used to eliminate dF , this becomes

$$d \log_e p = \frac{iS}{s} d \left(\frac{s}{S-s} \right)$$

and on integration

$$\log_e p = i \log_e \frac{s}{S-s} + \frac{is}{S-s} + W \quad . \quad . \quad (6)$$

where W is an integration constant depending on the temperature.

Of the gases used in our preliminary experiments on the expansion of charcoal, the isotherms of water, carbon dioxide, and sulphur dioxide show tolerably good agreement with this equation when the values of S determined from the extensometric data are inserted. This is illustrated in Fig. 2, where the experimental values of s and p are shown in relation to graphs derived from equation (6), appropriate values of i and W being used in each case. The region of divergence which occurs in the case of water at low pressures (where the observations follow the broken line instead of the full curve) is to be expected in view of the marked bending of its characteristic curve (Fig. 1) at low concentration, signifying that equation (2) is here invalid. The deviation may be partly due also to the presence of ash in the charcoal, the experiments of Coolidge (*J. Amer. Chem. Soc.*, 1924, **46**, 596) having made it clear that in this region the isotherm for water on ash-free charcoal lies closer to the p -axis than when—as in our experiments—the charcoal is untreated. The low value of i for water (*viz.*, 0.10) is in full accordance with the big initial drop (see Fig. 1) in the value of Mx/s . On the other hand, the evidence discussed in the next section strongly suggests that i for carbon dioxide should be assigned a rather higher value than that used in constructing the p - s graph for this gas in Fig. 2.

Application to Published p-s Data.—In so far as equation (6) contains three undetermined constants, it is of little value as a criterion of the mobility of the adsorbed molecules unless extensometric data are available for the independent determination of S , or, alternatively, unless i is known from other measurements with the same gas at the same temperature. It further requires that the Gibbs equation, which is strictly valid only for plane surfaces, should be applicable to that of charcoal. Nevertheless, since the partial agreement obtained in our experiments makes it unlikely that large deviations should result on the latter account, a comparison with experimental isotherms is not without interest. Discussion will here be limited to the special case for which i is unity,

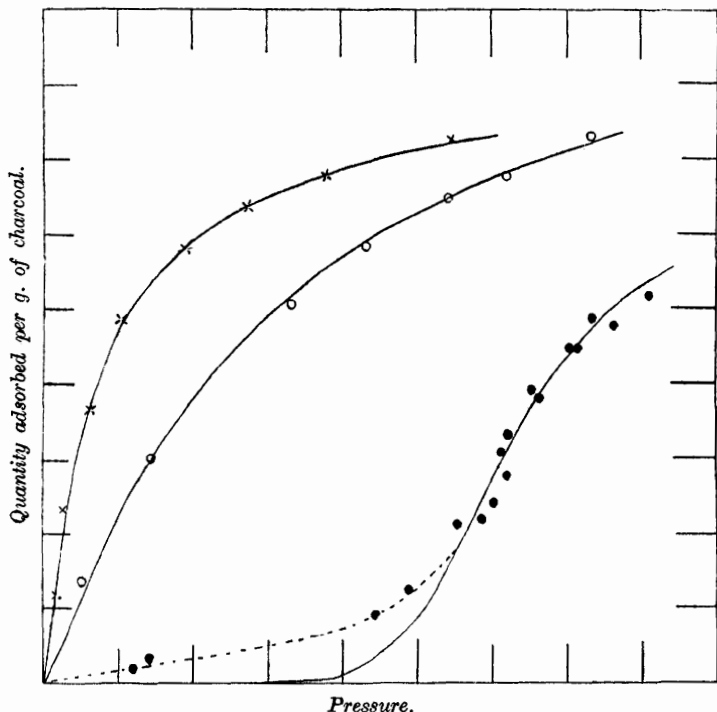
denoting the absence of significant attractive forces between the adsorbed molecules. Equation (6) then becomes

$$\log_e p = \log_e \frac{s}{S-s} + \frac{s}{S-s} + W \quad \dots (7)$$

a form previously given by Bradley (*Phil. Mag.*, 1929, 8, 202).

FIG. 2.

Adsorption isothermals of water, carbon dioxide, and sulphur dioxide at room temperature.



Water (20—21°), points thus	; {	1 abscissa scale division = 2 mm. pressure.
S = 0.158 g.; i = 0.10		1 ordinate scale division = 0.02 g. adsorbed per 1 g. of charcoal.
Carbon dioxide, points thus ○	; {	1 abscissa scale division = 100 mm. pressure.
S = 0.139 g.; i = 0.76		1 ordinate scale division = 0.01 g. adsorbed per 1 g. of charcoal.
Sulphur dioxide, points thus ×	; {	1 abscissa scale division = 20 mm. pressure.
S = 0.210 g.; i = 0.73		1 ordinate scale division = 0.02 g. adsorbed per 1 g. of charcoal.

Contrary to the usual practice, agreement is to be sought, not in the earlier, but in the middle and later stages of the adsorption, where a range of obedience to equation (2) is more likely to exist. In the following table are recorded some typical isotherm measure-

ments which give good agreement with equation (7); the range of agreement is stated in each case.

System.	Temp.	Experimental range, $s/S =$	Range of agreement with (7); $s/S =$	Observer.
Charcoal-CO ₂	0°	0—0.52	0.13—0.52	Chappuis
„ CO ₂	0	0—0.56	0.23—0.56	Titoff
„ CO ₂	30	0—0.4	0.18—0.4	Titoff
„ CO ₂	80	0—0.18	0.09—0.18	Titoff
„ CO ₂	150.5	0—0.07	0.0 —0.07	Titoff
„ NH ₃	0	0—0.56	0.13—0.56	Titoff
„ NH ₃	30	0—0.44	0.04—0.44	Titoff
„ CH ₄	0	0.08—0.35	0.08—0.35	Homfray
„ CO	— 82	0.19—0.54	0.19—0.54	Homfray
Mica-CH ₄	— 183	0.2 —0.66	0.2 —0.66	Langmuir
„ CO ₂	— 118	0.07—0.4	0.07—0.4	Langmuir
„ N ₂	— 183	0.2 —0.54	0.2 —0.54	Langmuir

References : Chappuis, *Wied. Ann.*, 1881, **12**, 161; Titoff, *Z. physikal. Chem.*, 1910, **74**, 641; Homfray, *ibid.*, p. 129; Langmuir, *J. Amer. Chem. Soc.*, 1918, **40**, 1361 (Tables VII and IX).

In this table, certain matters require comment.

(1) In the graphs for carbon dioxide given in Fig. 1 the value of i was taken as 0.76. This low value is inconsistent with the observation of Magnus that the adsorption of this gas follows Henry's law at very low pressure, and is not confirmed by the data of Chappuis, Titoff, and Langmuir quoted in the table; the latter require that i for this gas should be unity even at low temperatures. The discrepancy possibly lies in an under-estimation of the limiting sorption value S which had been calculated with the aid of equation (1) from the extensometric observations. If a slightly higher value be assigned to S , the p - s measurements plotted in Fig. 1 are fully consistent with $i = 1$, and though the agreement between the found and the calculated values of the expansion is then less perfect, the differences lie well within experimental error.

(2) It is important to note that a common value for S has been assumed for all four of Titoff's carbon dioxide isothermals, covering the range of temperatures from 0° to 150°; this virtually reduces the number of adjustable constants to one. If this restriction is not imposed, the range of agreement with the individual experiments is considerably increased. A common value for S has also been assumed for Titoff's ammonia isothermals at 0° and 30°.

(3) It is curious that while Titoff's ammonia observations agree well with equation (7), our own isothermals for this gas show substantial deviations over nearly the whole range of pressures. They agree in this and other respects with those of Richardson (*J. Amer. Chem. Soc.*, 1917, **39**, 1928).

The Kinetic Interpretation of Equation (7).—The isotherm equation

(6) has the disadvantage that its manner of derivation has provided no analysis indicating the nature of the equilibrium between the free gas and the adsorbed phase. Equation (2), from which it was derived by application of the Gibbs equation, is essentially an empirical equation of state. It is true that in the special case where the mutual attraction between adsorbed molecules can be neglected, and the molecules regarded as hard spheres, an analysis on lines identical with those of the corresponding three-dimensional problem (see, e.g., Jeans, "Dynamical Theory of Gases," Chap. VI) would give for the two-dimensional pressure F a relation, $F(A - B) = \text{constant}$, where B is twice the sum of the cross-sectional area of the molecules (compare Adam, "The Physics and Chemistry of Surfaces," Oxford, 1930, p. 125). Since, however, the analysis would necessarily neglect the mutual intersection of the "protected" areas surrounding the molecules (that is, those areas within which the centres of other molecules cannot penetrate), it could be applicable only so long as the surface concentration is fairly small. This limitation is serious, for near saturation the molecules in the surface phase must be at least as closely crowded together as in the normal liquid state. It is probable that values of B determined from data relating to nearly saturated surfaces approximate more nearly to the actual sum of the areas of the molecules than to twice that area.

In this connexion the limiting adsorption values determined from Langmuir's data for methane and carbon dioxide on mica are of interest. Here the area of the adsorbing surface was known, and although, for reasons summarised by Adam (*op. cit.*, Ch. VIII) and Rideal (*op. cit.*, Ch. V) estimates of the surface area of solid adsorbents must generally be treated with some reserve, yet it is probable that the absorbing area and the superficial area of the adsorbent were more nearly equal here than in any other experiments on gas adsorption by solids. Application of equation (7) to the data gives for the incompressible areas per molecule of methane and carbon dioxide 14 Å. and 24 Å., respectively. Of these two results, the former agrees well with the value expected, while the latter (compare Oliphant, *Phil. Mag.*, 1928, 6, 422) is some 40—50% high. It should be remarked, however, that until more is known as to the structure of the carbon dioxide molecule and its orientation at such a surface as that of mica, the area per molecule of this gas in a close-packed two-dimensional assembly must be subject to some uncertainty. At all events, the calculated areas per molecule are of the right order, and it is significant that the use of equation (7) should lead to maximum adsorption values more in harmony with known molecular magnitudes than the isotherm of Langmuir,

who was obliged to assume that only a fraction of the mica surface was active in adsorption.

It is sometimes taken for granted that Langmuir's isotherm is as consistent with the hypothesis of the mobile adsorbed phase as with that author's theory of elementary spaces (see, *e.g.*, Wilkins and Ward, *Z. physikal. Chem.*, 1929, **144**, 259). This is certainly not the case, for, although motion of the molecules parallel to the surface must be without effect on their rate of evaporation, yet it would materially affect the rate of condensation if the condensing molecules, on account of their finite size, require to strike bare patches of more than a certain limiting area.

It has been pointed out by Bradley (*loc. cit.*) that, so long as s is small, an equation of the form (7) becomes indistinguishable from Langmuir's equation expressing the kinetic equilibrium between the adsorbed and gas phases. The latter may be written

$$k_1 p(S - s) = k_2 s$$

where k_1 and k_2 are constants; and (7) becomes, on removal of the logarithms and rearrangement,

$$k_1 p(S - s)e^{-s/(S-s)} = k_2 s$$

where $k_2/k_1 = e^W$. The two equations differ only in that the left-hand side of the latter contains the term $e^{-s/(S-s)}$. As long as s is small, this term is nearly equal to unity, and its variation remains unimportant; it diminishes very rapidly, however, as s approaches S , and its variation then becomes much more important than that of $(S - s)$. Rewriting the expression in terms of the variables used in equation (2), we find it equal to $e^{-B/(A-B)}$ or, since $i = 1$, $e^{-FB/RT}$, where the numerator of the exponent is equal to the work done in forcing back the molecules present on the surface through a space equal to the "incompressible" area of a (gram-) molecule. Since the frequency of occurrence of a fluctuation of density in a medium is proportional to $e^{-\phi/RT}$, where ϕ is the maximum work obtainable by the relapse to normal or average conditions, and the integrated frequency relating to values of ϕ between $\phi = \infty$ and $\phi = \phi$ is proportional to the same expression, it is to be inferred that the rate of condensation is determined by the frequency of occurrence of (two-dimensional) density fluctuations of minimum potential energy FB . Such would be the case, statistically, if it were supposed that the condensation of a molecule is conditioned by its striking a bare patch of more than a certain minimum area. As saturation of the surface is approached, by far the greater part of the bare surface consists of patches small in comparison with the molecular cross-section, and therefore ineffective in condensation.

Summary.

A comparison of Schofield and Rideal's two-dimensional equation of state, $F(A - B) = iRT$, with the empirical equation relating the linear expansion (x) of a charcoal block with the adsorption value s (in grams) leads to the hypothesis that adsorbed films of the substances investigated behave as two-dimensional gases, of which the pressure F is directly proportional to the expansion. Graphs of Mx/s against x for water, carbon dioxide, ammonia, and sulphur dioxide are similar to the $PV-P$ graphs of imperfect gases, whilst those of benzene and pyridine are of a different type. In all cases the graphs become linear as the surface concentration rises. The hypothesis is tested by comparing the $p-s$ ($p =$ gas pressure) data with the equation

$$\log_e p = i \log_e \frac{s}{S - s} + \frac{is}{S - s} + W$$

obtained by combining the Gibbs equation with the two-dimensional equation of state, it being assumed that the change of surface energy is determined wholly by the two-dimensional pressure. This form of isotherm is well supported by experiment, but the expected deviations occur when s is small. It is shown that Langmuir's isotherm is inapplicable to a mobile adsorbed phase, because it fails to take into account the finite area of the minimum bare surface necessary for the condensation of a molecule.

FACULTY OF SCIENCE, THE EGYPTIAN UNIVERSITY
ABBASSIA, CAIRO.

[Received, March 19th, 1931.]
