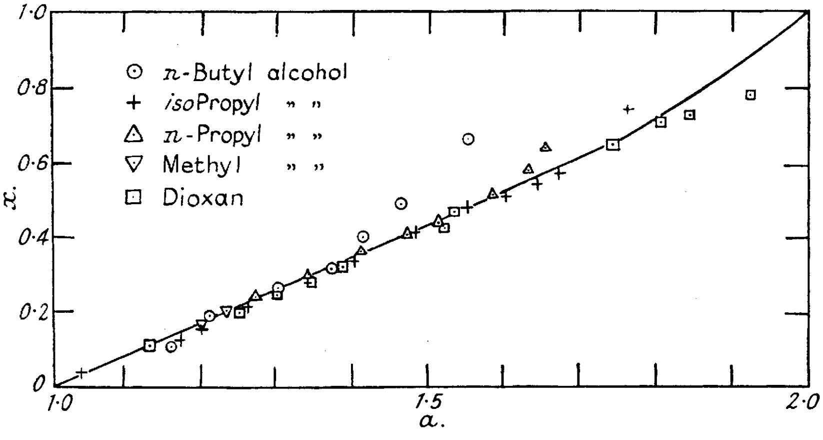
202. *The Sorption of Condensable Vapours by Porous Solids. Part IV. Linear Isothermals and the Langmuir Equation.*

By A. GRAHAM FOSTER.

The application of the theory of multimolecular adsorption to linear isothermals is discussed. It is shown that when allowance is made for multilayer adsorption, the formation of the first layer takes place strictly in accordance with Langmuir's theory. The saturation values for unimolecular adsorption calculated from the corrected data at lower pressures agree with those derived by the " point A " method of Emmett and Brunauer (*J. Amer. Chem. Soc.*, 1937, **59**, 1553) from the data at higher pressures.

IN Part III (preceding paper) the application of the Brunauer theory of multimolecular adsorption to linear isothermals was discussed. Further examples are now described, and it is shown that when allowance is made for multilayer adsorption, the true unimolecular adsorption takes place strictly in agreement with the Langmuir equation. The function represented by equation (10) of Part III is very nearly linear up to $x = 0{\cdot}6$, as shown by the full curve in Fig. 1. When plotted on a large scale, the curve is very slightly S-shaped. Actual isothermals will, of course, start from the origin $a = 0$, since when x is small equation (3) reduces to $a = cx$, but for values of $x > 0{\cdot}1$ we might reasonably expect isothermals to approximate to the simplified equations (10) and (11) when n, the number of adsorbed layers is 3 or 2 respectively, and it has already been shown that the isothermals of ethyl alcohol on silica gel B follow equation (10) very closely. Isothermals of other liquids have also been determined on this gel, *viz.*, methyl, *n*- and *iso*-propyl and *n*-butyl alcohols (Foster, *Proc. Roy. Soc.*, 1935, *A*, **150**, 77), dioxan (Broad and Foster, this vol., p. 366), hydrogen cyanide, and triethylamine (unpublished).

FIG. 1.



From the observed pressures and concentrations, a–x curves have been derived in the following manner. The linear part of the isothermal extrapolates to zero pressure at concentration z, which is taken as representing the amount required to complete the unimolecular layer (*i.e.*, $a = 1$), so that at any other concentration q, the value of a is given by q/z. If the net heat of sorption were actually zero for the second and the third layer, as supposed by Brunauer, x would of course be obtained by dividing the actual pressure p by the saturation pressure p_0. The heats of sorption have not been accurately determined in this region but are believed to be of the order 1—2 kg.-cals./mol., hence the term c_2p is no longer unity and x is not equal to the relative pressure but proportional to it for a given substance. In fact, plotting relative pressures against a does not reduce any of the observed isothermals to the theoretical a–x curve of equation (10), and arbitrary factors had to be found by trial and error for each substance. If two linear curves have a common origin it is always possible to bring them into coincidence by use of a conversion factor, but the fact that all these isothermals reduce to the same curve after conversion of the q values into a values, as described, suggests that the z values obtained by extrapolation have some real significance and do actually represent the amounts required to saturate the first layer. In the table below, the conversion factors actually used are compared with the theoretical values ($1/p_0$). The ratio of the " observed " to the " calculated " values of c is seen to vary from 1·2 to 3·4, corresponding to Q = 100 to 700 cals./mol.

	MeOH.	EtOH.	n-PrOH.	*iso*-PrOH.	n-BuOH.	Dioxan.	HCN.	NEt_3.
10^3 c (calc.)	14	25	56	27	20	63	13	22
,, (obs.)	8·6	16·7	48	23	15	29	3·8	13
Ratio	1·6	1·5	1·2	1·2	1·3	2·2	3·4	1·7

When c_1p is moderately large, the values of a given by equation (2) will not differ appreciably from those given by the relation

$$a = \{c_1p/(1 + c_1p)\}\{(1 + 2x + 3x^2 + \ldots)/(1 + x + x^2 + \ldots)\}$$

It has already been shown that when $n = 2$ or 3 the second term is, over a limited range, an almost linear function of x, so that we may write $a = \{c_1p/(1 + c_1p)\}(1 + kx)$, where k is the slope of the linear range and the first term represents the true unimolecular adsorption according to the Langmuir equation. Therefore, if we denote total and unimolecular adsorption by q and q_1, respectively, we have $q_1 = zc_1p/(1 + c_1p)$ and $q = q_1(1 + bp)$, whence the true unimolecular adsorption is given by $q_1 = q/z(1 + bp)$, a relation which enables an approximate estimate of q_1 to be made if b is known. Since, over the linear range, q has almost reached its saturation value z, this part of the isothermal will follow approximately the relation $q = z(1 + bp)$ with intercept z and slope zb, from which b can be calculated.

FIG. 2.

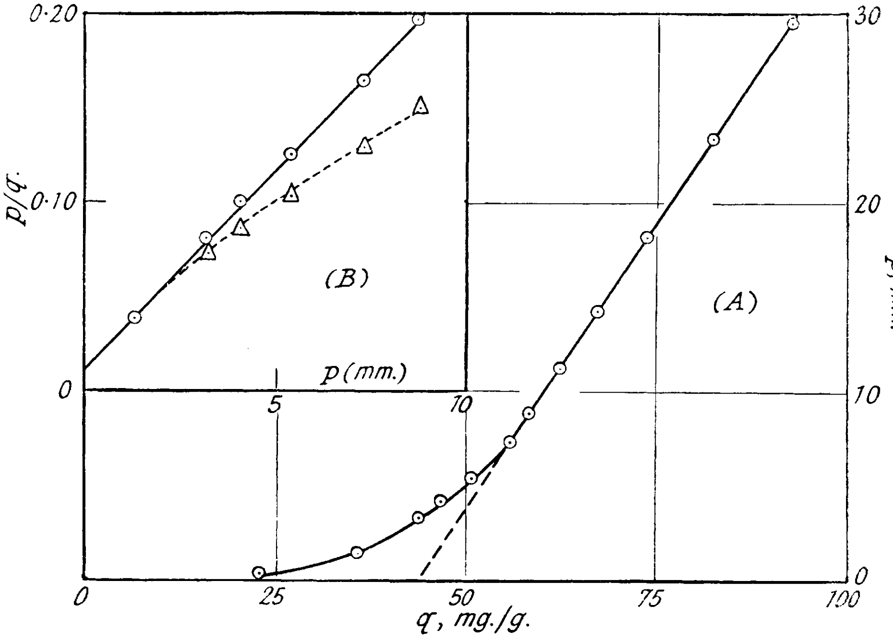


Fig. 2 (A) shows the lower part of an isothermal of hexane on ferric oxide at 20°, which is strictly linear from q = 56 to 100 mg./g., following the relation $q = 44(1 + 0{\cdot}038\,p)$. The six lowest points plotted as p/q against p are represented by the triangles of Fig. 2 (B) and clearly do not lie on a straight line, whereas the values of p/q_1 calculated from the relation $q_1 = q/44(1 + 0{\cdot}038\,p)$ give the linear plot $p/q_1 = 0{\cdot}012 + 0{\cdot}021\,p$ shown by the circles. The value of z calculated from this is 1/0·021 or 47 mg./g., agreeing well with the value of 44 obtained by extrapolation.

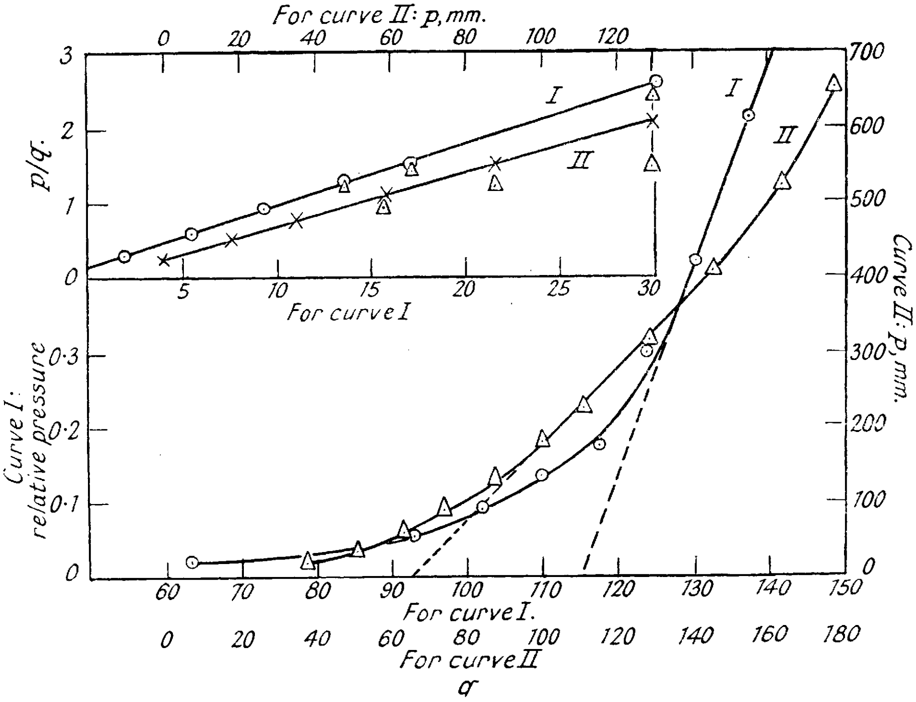
The following table summarises the data for other systems which give linear isothermals, some of the p/q–p curves being shown in Figs. 3 and 4. In order to distinguish between the saturation values for the unimolecular adsorption derived by different methods, the symbol z is used for the value calculated from the Langmuir equation, and, following Emmett and Brunauer's nomenclature (*J. Amer. Chem. Soc.*, 1937, **59**, 1553), the value obtained by extrapolation of the linear isotherm to zero pressure is designated as " point A." Reference has been made in Part III to the fact that these workers concluded that " point B," where the linear range begins, corresponded to the completion of the first layer, although there is no theoretical basis for this assumption. The values of z and points " A " and " B " are recorded in cols. 4, 5, and 6 of the table, and although in some instances the " point B " values lie somewhat closer to the z values than do the " point A " values, the general agreement is much less satisfactory. It should, however, be pointed out that the isothermals here discussed bend away from the concentration axis when the linear range ends, whereas those described by Emmett and Brunauer eventually turn in the opposite direction. It has already been shown in Part III that, as c_1 becomes smaller, the isothermal becomes concave to the p axis at lower pressures and runs back to

			Concns., mg./g.					
Vapour.	Adsorbent.	Temp.	*z.*	Point A.	Point B.	c_1 (mm.$^{-1}$).	*b* (mm.$^{-1}$).	Ref.
EtOH	SiO_2 (A)	60°	110	107	118	0·91	0·00253	(1)
H_2O	,,	60	54·4	50·8	120	0·263	0·0423	(1)
MeOH	SiO_2 (B)	25	123	126	150	2·7	0·0167	(2)
Dioxan	,,	25	200	220	225	50·0	0·0733	(3)
EtI	,,	25	317	285	420	0·477	0·0272	(4)
H_2O	Fe_2O_3	60	42·9	39	60	0·39	0·021	(5)
C_6H_6	,,	40	50	48	60	1·67	0·0295	(6)
n-C_6H_{14}	,,	20	47·6	44	60	1·27	0·0397	(4)
C_2H_5Cl	C	$-15·3$	487	471	490	0·171	0·00033	(7)
Et_2O	,,	0	385	378	388	0·65	0·000292	(7)
C_5H_{12}	,,	0	333	327	335	0·75	0·00306	(7)
MeOH	,,	20	123·5	115	128	50·62 *	0·235 *	(8)
SO_2	SiO_2	0	71·4 †	62·5 †	100 †	0·05	0·00308	(9)
EtOH	,,	30	129 ‡	130 ‡	170 ‡	77·5 *	2·61 *	(10)
CCl_4	,,	30	204 ‡	200 ‡	240 ‡	40·8 *	4·25 *	(10)

* Relative pressures. † C.c. of gas (at N.T.P.) per g. ‡ Volumes (mm.^{3}/g.).

References.—[1] Lambert and Foster, *Proc. Roy. Soc.*, 1931, *A*, **134**, 256. [2] Foster, *ibid.*, 1934, *A*, **146**, 129. [3] *Idem*, this vol., p. 368. [4] *Idem*, unpublished. [5] Lambert and Foster, *Proc. Roy. Soc.*, 1932, *A*, **136**, 363. [6] Lambert and Clark, *ibid.*, 1929, *A*, **122**, 497. [7] Goldmann and Polanyi, *Z. physikal. Chem.*, 1928, *A*, **132**, 313. [8] Bangham, Fakhoury, and Mohamed, *Proc. Roy. Soc.*, 1934, *A*, **147**, 167. [9] MacGavack and Patrick, *J. Amer. Chem. Soc.*, 1920, **42**, 946. [10] Patrick and Opdyke, *J. Physical Chem.*, 1925, **29**, 601.

FIG. 3.



I, MeOH–C. II, SO_2–SiO_2.

$a = 0$ instead of $a = 1$. In conjunction with the convexity at higher pressures, this may give rise to an apparently linear range which extrapolates back to a value of $a < 1$, thus making " point A " too low. In such systems " point B " values will necessarily agree better with the z values merely because they are higher than the " point A " values, so that the method may succeed by some compensation of errors and be justified empirically for some types of isothermal. On the other hand, it must be admitted that Brunauer (" Physical Adsorption of Gases and Vapours," Oxford, 1944, p. 288) has presented extensive evidence in support of the " point B " method, but the isothermals which he describes correspond to values of $n > 5$ whereas those discussed here correspond to $n = 2$ or 3. However, there can now be little doubt that both points A and B generally lie fairly close to the true saturation value for unimolecular adsorption.

It is noteworthy that the experimental results for the systems summarised in the table can be represented by three-constant equations from zero pressure right up to the end of the linear range; *e.g.*, taking the mean of the z and " point A " values for ethyl alcohol on silica gel A, we find

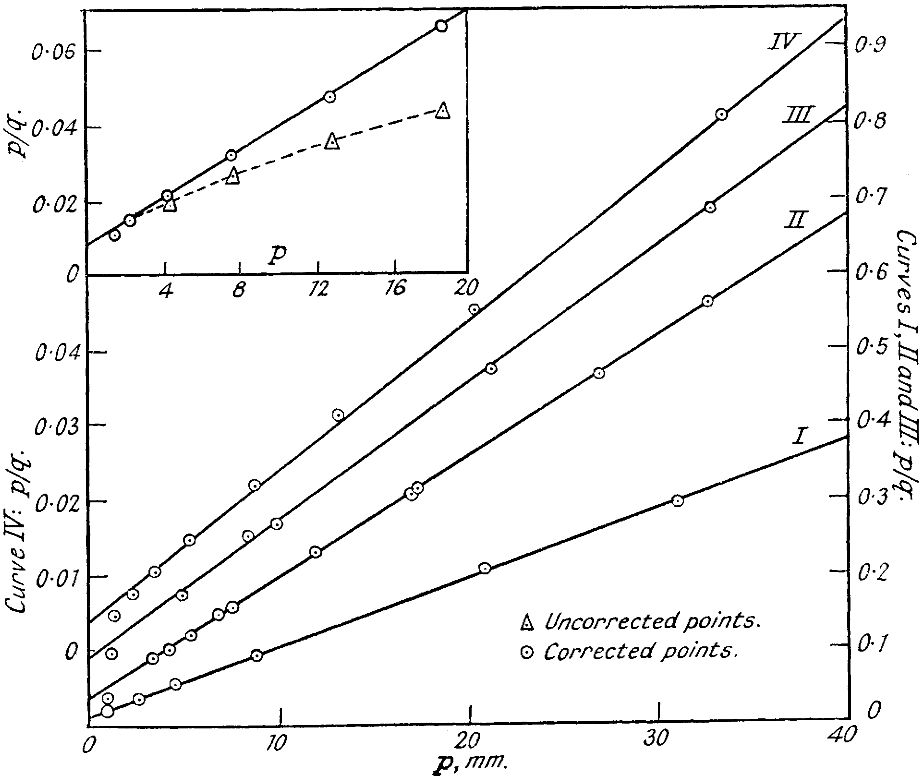
$$q = 108·5 \times 0·91p(1 + 0·00253p)/(1 + 0·91p)$$

which gives the following close agreement with the experimental values :

p (mm.)	1	5	10	50	100	150	200
q (calc.)	52	90	100	120	135	149	162
q (obs.)	52	88	100	120	135	149	158

The table is not intended to be a complete record of systems giving linear isothermals, since attention has been directed to those systems where the data at lower pressures are sufficient to permit a test of Langmuir's equation to be made. In general, the z values and the " point A " values agree within 10%, which may be regarded as satisfactory in view of the approximations involved. A more important result is that in all these systems the corrected low-pressure data agree with the Langmuir equation, indicating that this relation is of much more general validity than has been hitherto supposed. We may conclude that the formation of the first layer takes place as originally postulated by Langmuir, and that the apparent lack of agreement with his equation is due to the building up of further adsorbed layers before the completion of the first.

FIG. 4.



I, EtOH. II, C_6H_6. III, H_2O. IV, MeOH. *Inset*, EtI. (*All on silica gel.*)

ROYAL HOLLOWAY COLLEGE (UNIVERSITY OF LONDON),
ENGLEFIELD GREEN, SURREY.

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