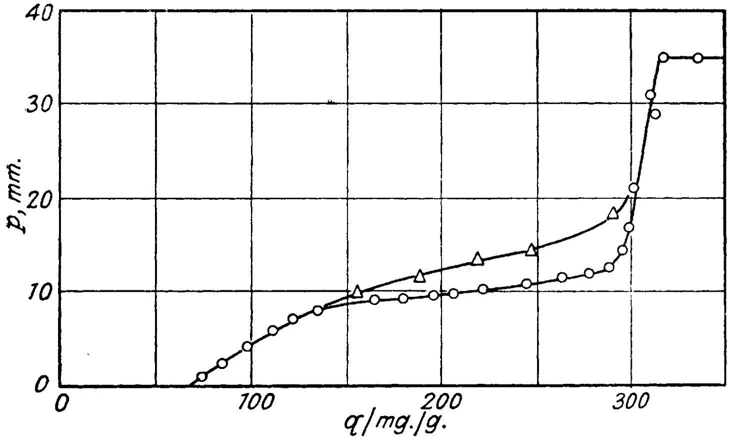
84. *The Sorption of Vapours by Ferric Oxide Gel. Part II.*

By D. W. Broad and A. G. Foster.

Sorption isothermals of the following substances on ferric oxide gel have been determined : carbon tetrachloride, chloroform, *cyclo*hexane, dioxan, ethyl iodide, *n*-hexane, morpholine, *n*-octane, di*iso*propyl ether, toluene and triethylamine. All show an intermediate linear range followed by a large hysteresis area. The results are in general agreement with the capillary theory, since the pore radius of the adsorbent calculated by means of the Kelvin equation remains reasonably constant. The application of the theory of multimolecular adsorption and its possible bearing on hysteresis phenomena is also discussed.

In Part I (*Proc. Roy. Soc.*, 1934, *A*, **147**, 128) isothermals of the alcohols from methyl to *n*-butyl were described, following earlier work by Lambert and Clark (*ibid.*, 1929, *A*, **122**, 497) with benzene. Isothermals of D_2O and H_2O on ferric oxide have recently been determined by the authors (J., 1945, 372) who also examined the sorption of a large number of vapours by silica gels (*ibid.*, p. 366). This paper describes isothermals of these substances on a new batch of ferric oxide gel, prepared according to the instructions of Lambert and Clark (*loc. cit.*). The results obtained in the earlier investigations may be summarised as follows. On silica gel B, constant volumes are adsorbed at saturation, q, the weight adsorbed, being proportional to d, the density of the liquid. The amount (z) held in the unimolecular layer corresponds to the covering of a constant surface area, since $z\sigma^2/M$ is constant, σ being the molecular diameter. Neither of these simple relations holds for silica gel A, where both q/M and $z\sigma^2/M$ are functions of σ. On ferric oxide the amounts of the various alcohols held in the unimolecular layer correspond to a constant number of molecules, but this is still consistent with a constant surface area if it is assumed that the molecules are oriented perpendicularly to the surface. The capillary radii (calculated by means of the Kelvin equation from the pressure at the point of inflexion in the desorption curves) remain constant.

Fig. 1.



In the present work, attention has been directed mainly to the following objects : (i) calculation of the capillary radius, (ii) determination of the amounts held in the unimolecular layer. The former requires an accurate determination of the course of the descending branch of the hysteresis loop in order that the point of inflexion may be accurately located. The latter is effected by a method recently described by one of us (Foster, J., 1945, 773) in which the linear middle part of the isothermal is extrapolated back to zero pressure. The descending branch of the hysteresis loop and the linear portion of the isothermals have therefore been investigated in detail, whilst the ascending branch has in many cases not been examined. The absence of extensive data at lower pressures, before the linear range begins, is due to the fact that the pressures were too low to be measured accurately on a mercury manometer. Some low-pressure measurements with the Pirani gauge have been described recently (Foster, J., 1945, 360).

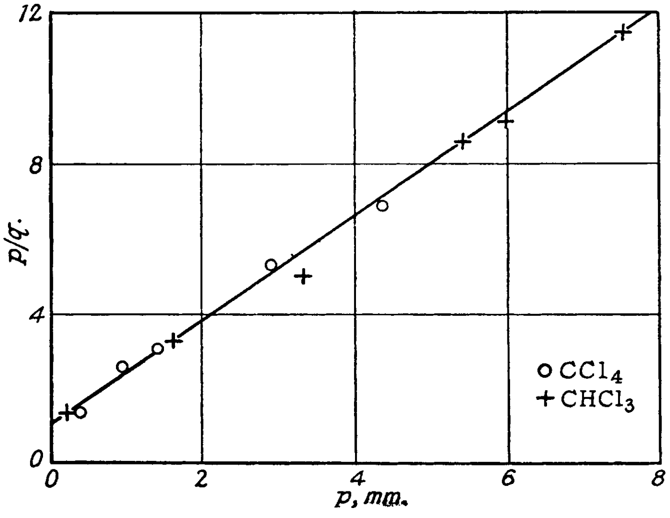
Experimental.

The experimental technique was described in Part I. The isothermals were determined at 25° except those for chloroform and hexane which were investigated at 20°. A typical isothermal, that for dioxan, is reproduced in Fig. 1, but owing to the importance of accurate comparative data for testing rival theories of adsorption, the remaining results are recorded in tabular form. In Table I, concentrations (q) are expressed in mg./g. of gel, and pressures (p) in mm. of mercury at the temperature of the experiment. The lower part of the hexane isothermal has already been described (Foster, J., 1945, 774) in illustrating the method of estimating the saturation value for unimolecular adsorption. The lowest points on the isothermals of carbon tetrachloride and chloroform give linear plots of p/q against p in agreement with the Langmuir equation. These curves, which happen to coincide, are shown in Fig. 2, and follow the relation

TABLE I.

Carbon tetrachloride.															
q ……………	400	387	376	365	354	345	334	323	313	303	292	282	272	262	253
p ……………	53·9	48·0	45·4	43·8	42·8	42·2	41·7	41·2	40·4	39·7	39·1	38·5	38·4	37·9	37·4
q ……………	244	234	225	215	206	197	181	166							
p ……………	36·6	36·6	35·5	34·2	33·9	32·1	29·4	25·9							
Chloroform.															
q ……………	409	371	335	300	266	234	204	179	158	141	127	116	108	102	97
p ……………	102	70·7	68·2	65·3	63·0	58·9	55·1	48·0	41·5	34·4	27·4	21·8	17·3	14	11·7
q ……………	93	89	54		Ascending	q	185	277							
p ……………	9·6	8·2	1·5		points	p	55	77							
*cyclo*Hexane.															
q ……………	224	204	186	169	153	138	123	111	100	90	81	73	67	57	50
p ……………	74·6	40·1	35·9	34·3	33·0	31·6	29·9	28·3	26·1	23·4	21·2	18·3	15·7	11·9	8·7
q ……………	45														
p ……………	6·6														
Ethyl alcohol.															
q ……………	232	217	201	178	155	117	102	98	77	70	66	61			
p ……………	46·7	38·6	37·5	36·3	35·6	33·9	32·3	30	24	16	8·3	2·5			
Ethyl iodide.															
q ……………	525	498	472	447	423	400	354	312	275	241	211	187	151	121	109
p ……………	92·4	65·5	62·8	60·9	59·6	57·8	55·2	52·2	48·5	43·7	37·9	31·7	20·0	9·4	5·2
q ……………	86	72			Ascending	q	237	270	305	363					
p ……………	1·3	0·3			points	p	46	52	61	68					
n-Hexane.															
q ……………	195	187	178	168	160	150	141	131	122	105	93	83	74	68	63
p ……………	89	59	48·5	45·3	45	43·7	42·5	40·8	39·3	35·9	29·5	23·3	18·1	14·1	11·1
q ……………	59	56	51	47	36	23									
p ……………	8·8	7·3	5·4	4·1	1·3	0·4									
n-Octane.															
q ……………	192	189	185	181	161	130	124	117	108	100	91	86	74	66	48
p ……………	11·5	7·2	4·3	3·8	3·6	3·3	3·2	3·1	2·9	2·8	2·6	2·4	1·8	1·4	0·5
Di*iso*propyl ether.															
q ……………	210	185	165	143	138	123	117	100	87	77	66	60	56	51	
p ……………	99·3	56·3	52·0	49·6	49·3	47·1	45·2	37·5	29·3	21·1	12·9	7·9	4·5	1·5	
Toluene.															
q ……………	227	222	211	201	191	172	154	136	120	106	94	78	71		
p ……………	11·0	10·3	9·6	9·3	9·1	8·5	8·0	7·6	7·0	6·2	5·0	3·7	3·0		
Triethylamine.															
q ……………	226	213	200	192	181	163	146	130	109	102	96	85	66	56	
p ……………	54	28·7	24	23	22·3	21·1	20	18·9	16·9	16·0	14·7	11·4	5·0	1·8	

FIG. 2.



$p/q = 0{\cdot}010 \pm 0{\cdot}014p$, according to which the saturation value is 1/0·014 or 71·5, agreeing well with the value of 72 extrapolated from the linear range.

Discussion.

Table II summarises the more important data for the systems examined, including some figures for benzene, which was re-investigated for comparative purposes. Col. 2 gives the saturation volumes and col. 3 the number of moles required to saturate the unimolecular layer, determined by extrapolation as already mentioned. The saturation volumes are not absolutely constant, but the fluctuations (which are far beyond experimental error) do not seem to depend on the diameter (σ) of the adsorbed molecule, in which respect ferric oxide gel appears to resemble the silica gel B rather than the gel A investigated by the present authors. On these silica gels it was found that z/M was a linear function of $1/\sigma^2$, but no such simple relation holds here, since col. 4 shows that the values of $z\sigma^2/M$, which should be constant for the covering of a constant surface area, vary from 0·0152 to 0·0342, nor is it possible to draw a smooth curve through the plot of z/M against $1/\sigma^2$. It will be seen that approximately twice as many molecules of dioxan as of *cyclo*hexane are held in the first layer, in spite of the similarity of size and shape. The maximum value of $z\sigma^2/M$ is 0·0342 for water, the smallest molecule, but the lowest values (0·0152—0·0179) are not associated with the largest molecules. It must, however, be remembered that the value of σ calculated from the density of the liquid is only an average value and no assumptions as to the orientation of the adsorbed molecules have been made. The work of Herington and Rideal (*Trans. Faraday Soc.*, 1944, **40**, 505) on the poisoning of metallic catalysts suggests a possible reason for some of the low adsorption values. If a hexagonal molecule, in order to be adsorbed, needs to be attached at all corners to fixed points in the lattice, the surface will never be completely covered, and even at saturation, about 35% will be bare, according to their calculations. Presumably a hexagonal molecule with a polar group like the oxygen atom in dioxan can attach itself more readily.

Table II.

Substance.	Saturation vol. (mm.^{3}/g.).	$10^5 . z/M$ (moles/g.).	$10^4 . z\sigma^2/M$.	r (A.).	$r + 2\sigma$.
Benzene	281	49	164	19·0	31·0
Carbon tetrachloride	270	48	179	19·0	31·0
Chloroform	282	62	205	20·5	32·0
*cyclo*Hexane	295	38	152	20·0	32·5
Deuterium oxide	306	275	340	19·0	26·0
Dioxan	302	74	258	19·0	31·0
Ethyl alcohol	300	125	337	20·5	31·0
Ethyl iodide	295	62	204	21·0	32·5
n-Hexane	308	52	239	18·5	32·0
Morpholine	282	77	268	19·5	31·0
n-Octane	278	35	187	20·0	34·5
Di*iso*propyl ether	290	47	230	18·0	32·0
Toluene	272	49	164	19·5	32·0
Triethylamine	300	50	238	18·0	32·0
Water	302	280	342	19·0	26·0

From the pressure–concentration data it is possible to construct " radius–volume " curves by application of the Kelvin equation as previously described (Foster, *Trans. Faraday Soc.*, 1932, **28**, 645). These r–v curves have a point of inflexion, which can be located by drawing tangents, at which dv/dr reaches a maximum similar to that of the Gauss error function. The value of r at this point corresponds to the radius of the most frequently occurring pores of the adsorbent, so that by determining the point of inflexion of the r–v curve we can define fairly sharply (± 0·5A.) an " average radius " which would be characteristic of a given adsorbent if the adsorbed layer did not vary in thickness. The r values obtained in this manner, tabulated in col. 5, show quite good agreement, but must actually be less than the true pore radius. Since the amounts held in the unimolecular layer are about half those held when hysteresis begins, it has been assumed that the adsorbed layer is two molecules thick, so that the values of $r + 2\sigma$ should represent the true radius of the capillaries and therefore be constant. As shown in col. 6, the agreement is good except for water and *n*-octane, but since the hysteresis loop of the water isothermal does not begin until 120 mg./g. have been adsorbed, and the first layer is saturated at about 40 mg./g., it would not be unreasonable to assume that the adsorbed layer is at least three molecules thick by the time condensation begins, which would make $r + 3\sigma = 29{\cdot}5$ A. A long-chain molecule like *n*-octane would probably tend to lie flat on the surface, and if a value of 5 A. is assumed for the " width " of the hydrocarbon chain, $r + 2\sigma$ is approximately 30 A.

In view of the somewhat divergent values reported by different workers for the physical constants of some of the liquids investigated, it was thought desirable to record the values actually used for calculating the capillary radii. The surface-tension data of Table III are mainly from the extensive series of measurements carried out by Hennault, Roland, and Lek (*Chem. Abs.*, 1931, **25**, 5322) and a re-calculation of the capillary radii from the alcohol isothermals described in Part I has been made, using these data instead of the earlier figures of Ramsay and Shields, which, as pointed out by Sugden (" The Parachor and Valency," London, 1930), are subject to a meniscus correction. Values marked with an asterisk were determined by us where no data could be found in the literature. Surface tensions were determined in a vacuum by the capillary-rise method.

TABLE III.

Physical constants of adsorbed liquids at 25°.

	d.	*γ.*	V. p. (mm. Hg).	*r* (A.).
Carbon tetrachloride	1·584	26·16	115	
Chloroform (20°)	1·489	27·28	160·5	
*cyclo*Hexane	0·773	24·40	96	
Dioxan	1·028	34·69	35·5	
Ethyl iodide	1·93	28·22	135	
n-Hexane (20°)	0·660	18·42	122·5	
n-Octane	0·699	21·25	14·0	
Di*iso*propyl ether	0·719	17·01 *	149·3 *	
Toluene	0·862	27·96	28·9	
Triethylamine	0·726	20·67 *	74·1 *	
Water	0·997	72·7	23·75	
Alcohols :				
Methyl	0·787	22·12	116	22·0
Ethyl	0·785	21·90	59	20·0
n-Propyl	0·799	23·30	21·2	23·5
*iso*Propyl	0·781	20·90	43·7	22·0
n-Butyl	0·806	24·16	6·75	23·5

The isothermals of benzene on ferric oxide described by Lambert and Clark (*loc. cit.*) have been interpreted in a rather different manner by Brunauer, Deming, Deming, and Teller (*J. Amer. Chem. Soc.*, 1940, **62**, 1723) who modified the earlier multilayer theory (Brunauer, Emmett, and Teller, *ibid.*, 1938, **60**, 309) in an attempt to include capillary condensation. The last adsorbed layer closes the capillary or cavity and causes a considerable decrease in the exposed surface of the adsorbed liquid, which is accompanied by considerable evolution of heat, shown by the rise in the heat of sorption just before saturation. It is therefore assumed that the constant c of the general equation [see Foster, J., 1945, p. 770, equation (1)] has a higher value for the last layer than for the intermediate layers, since the net heat of sorption is no longer zero. Brunauer *et al.* (*loc. cit.*, 1940) assume that the heat evolved is equal to the decrease in free energy and hence is determined by the product of the surface area and the surface tension (γ), but actually the differential heat effect accompanying a change of surface is determined by the total surface energy ($\gamma - T.d\gamma/dT$) and not the free surface energy (γ) (cf. Lewis and Randall, " Thermodynamics," p. 249). The predicted rise in the heat of sorption just before saturation is a well-known characteristic of layer adsorption, as pointed out by Kruyt and Moddermann (*Chem. Reviews*, 1930, **7**, 320) and illustrated by the results of Goldmann and Polanyi (*Z. physikal. Chem.*, 1928, *A*, **132**, 313). On the other hand, according to Hückel (*Trans. Faraday Soc.*, 1932, **28**, 138), the capillary theory requires the heat of sorption to remain constant during condensation in pores of uniform radius. The use of an increased value for c for the last layer can therefore hardly be regarded as an adequate mode of including capillary condensation, and must be considered merely as an arbitrary method of making the isothermals assume the desired shape.

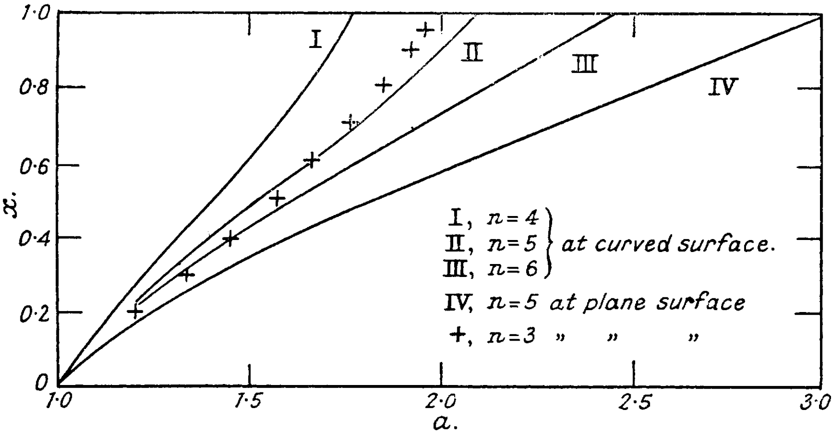
The exceedingly complex equations, to which the modified multimolecular theory finally leads, were found by Brunauer *et al.* to give reasonable agreement with the experimental curves of Lambert and Clark (*loc. cit.*) when suitable values were assigned to the various constants. The amount required to saturate the first layer was taken as 81 mg./g. compared with 48—50 mg./g. estimated by Foster (J., 1945, 775); the number of adsorbed layers was assumed to be 3, whereas the capillary theory requires 5—6, and finally, the net heat of sorption was supposed to fall to zero after the formation of the first layer and to rise to 1690 cals./mole for the last, whereas the " observed " value (calculated by means of the Clapeyron equation) remains quite constant at 780 cals. over the latter half of the sorption process. The multimolecular theory thus assumes a pore radius so small that one could not expect the Kelvin equation to hold, whereas in fact excellent agreement is observed with this equation. The layer theory also predicts a rise in the heat of sorption which is non-existent, and suffers from the additional drawback that, unlike the capillary theory, it provides, by itself, no explanation of the hysteresis phenomena. It is noteworthy that the sorption of benzene on silica gel, which was also investigated by Lambert and Clark (*loc. cit.*), does actually show the predicted rise in heat of sorption just before saturation, but there is no evidence that capillary condensation takes place on this gel, and later work by the present authors (J., 1945, 366) indicates that it contains no pores wider than 10 A.

The claim that the extended multilayer theory includes capillary condensation is thus hardly justified, and the theory should be regarded as an attempt to develop a more accurate picture of layer adsorption rather than as a new or modified capillary theory, since the only capillary effect which it considers is that which necessarily accompanies the last stage of layer adsorption in any closed space. When true condensation occurs the decrease in free surface takes place gradually as the pores fill and the associated heat effect is determined by the pore radius.

A further defect in the multilayer theory, admitted by the authors, is the assumption that the walls of the cavities are parallel, and therefore that the same area is available for the formation of the last layer as for the first. Obviously in a cylindrical pore the surface of successive layers falls off in an arithmetical progression, and if the relative diameters of the capillary and the adsorbed molecule are known, an exact correction can be applied. Suppose, for example, that five layers will just fill a cylindrical capillary, then the volumes of the first and second layers, respectively, will be in the ratio (5^2—4^2) : (4^2—3^2) or 9 : 7, and the volumes occupied by the five layers when completely filled would be in the ratio 9 : 7 : 5 : 3 : 1. The ratio of the total adsorption volume to that of the first layer will thus be reduced to 25 : 9 compared with 5 : 1 at the plane surface. In calculating the total adsorption (a) at the latter, the fraction (s_n) covered by n layers is counted n times, *e.g.*, $a = s_1 + 2s_2 + 3s_3 + 4s_4 + 5s_5$. For the cylindrical pore we must replace the factor 2 by $(9 + 7)/9$ and the factor 3 by $(9 + 7 + 5)/9$ and so on, giving the total sorption as $a = s_1 + \frac{16}{9}s_2 + \frac{21}{9}s_3 + \frac{24}{9}s_4 + \frac{25}{9}s_5$. Similar relations can be derived for systems of different relative dimensions, and when introduced into the general equations of the multilayer theory will cause the isothermals to rise more steeply than the corresponding curves for a plane surface, as shown in Fig. 3 where the curves for adsorption in pores of radii 4, 5, and 6 times the diameter of the adsorbed molecule are compared with those for 3 and 5 layers on a plane surface.

As already mentioned, little attention has been paid to the hysteresis phenomena in this work, but it has been established that on ferric oxide gel, in contrast to silica gel, there is no significant variation in the size of the hysteresis loop with the size of the adsorbed molecule. It has been pointed out (Foster, *Trans. Faraday Soc.*, 1932, **28**, 647) that over the " ascending " branch the adsorption potential at constant volume is independent of temperature, in agreement with the older " potential " theory of multilayer adsorption (Polanyi, *Verh. deut. physikal. Ges.*, 1916, **18**, 55), whereas, during desorption, the potential is determined by the Kelvin equation. It is therefore noteworthy that the attempt made by Brunauer *et al.* to apply the new multilayer theory to the benzene isothermals gave a curve which, over the hysteresis loop, followed the "ascending" and not the " descending " branch, so that the pores appear to fill up in accordance with the multimolecular theory and to empty in accordance with the capillary theory. The logical conclusion is that, during adsorption, the pores fill by layer formation, the adsorbed layer gradually extending further outward from the walls until it fills the entire pore space and the pores are blocked in the middle by the formation of the last layer. During desorption the pores empty from the top downwards, leaving an adsorbed layer about two molecules thick on the walls. This, however, would not completely account for the behaviour of systems in the hysteresis area, since one would expect to be able to re-trace the ascending curve by withdrawing vapour, provided that the adsorbent had not been completely saturated and all the pores blocked. In fact, a withdrawal from any point on the ascending branch leads to a point inside the loop and eventually to the descending branch, whence it must be inferred that the process by which the pores fill up is irreversible and therefore not a simple layer adsorption.

FIG. 3.



It has been suggested (Foster, *loc. cit.*) that the higher pressures observed during addition must be attributed to the liquid which is held in a metastable state on the walls of those pores in which the meniscus has not formed. In an assembly of uniform capillaries one would expect the pressure, during adsorption, to remain abnormally high until enough liquid had accumulated on the walls to enable the meniscus to form, then to drop abruptly to the descending curve. In any actual assembly of non-uniform pores, the narrower capillaries will fill before the wider, so that there will always be some pores blocked and some open. The pressure over the former would be determined by the Kelvin equation, and over the latter by the multimolecular theory. The liquid held on the walls at the higher pressure cannot distil into the pores over which the lower pressure prevails because the latter are either filled completely, or would, by further condensation, be filled to a larger radius, where the pressure would be higher. It must therefore remain on the walls until enough accumulates to block the pores by forming a meniscus, but meanwhile, a similar process will be repeating itself in the next larger set of pores, and until all the pores have been filled, the layer adsorption continues to mask the condensation process. Naturally, if layer adsorption takes place at a lower pressure than capillary condensation, no hysteresis should be observed. For this reason, the development of a more exact theory of multimolecular adsorption, in cylindrical pores rather than at a plane surface, would be of considerable importance in elucidating the mechanism of hysteresis. Some of the factors which determine the size of the hysteresis loop will be discussed in a later paper.

KING'S COLLEGE, STRAND, W.C.2.
ROYAL HOLLOWAY COLLEGE (UNIVERSITY OF LONDON),
ENGLEFIELD GREEN, SURREY.

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