

89. *The Sorption of Condensable Vapours by Porous Solids. Part II.** *The Validity of Gurwitsch's Rule.*

By D. N. BROAD and A. G. FOSTER.

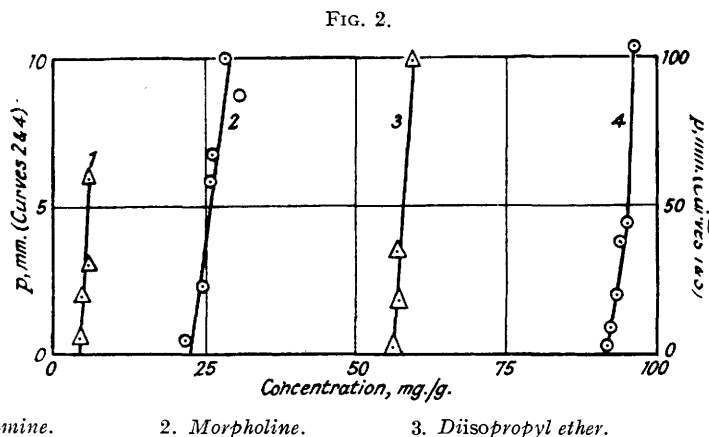
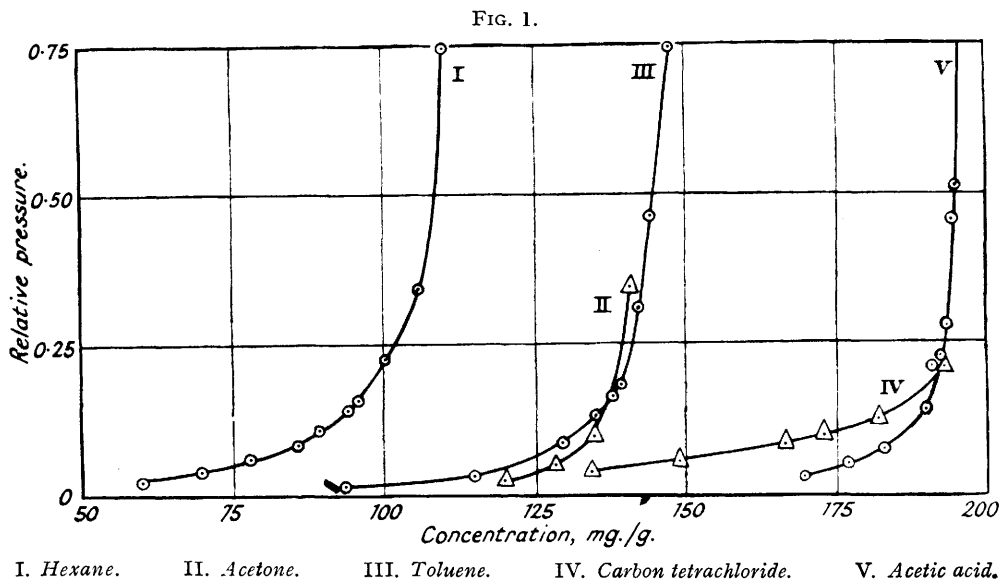
Isothermals of the following liquids have been determined on silica gel at 25°: acetic acid, acetone, diisopropyl ether, dioxan, *n*-hexane, morpholine, *n*-octane, toluene, and triethylamine. The amounts adsorbed at saturation decrease as the diameter of the adsorbed molecule increases. The observed relations can be explained by assuming that the adsorbent contains tapering capillaries. In these systems Gurwitsch's rule breaks down and is seen to be a special case of a more general relation. The number of molecules held in the unimolecular layer also decreases as the molecular diameter increases.

THE object of the present research was to examine how far the nature of the adsorption isotherm is determined by the size, shape, and polar nature of the adsorbed molecule. Isothermals of the following substances on silica gel have been described previously: benzene (Lambert and Clark, *Proc. Roy. Soc.*, 1929, *A*, **122**, 497), water (Lambert and Foster, *ibid.*, 1931, *A*, **134**, 246), methyl and ethyl alcohol (Foster, *ibid.*, 1934, *A*, **146**, 129), *n*- and *iso*-propyl and *n*-butyl alcohol (*idem, ibid.*, 1935, *A*, **150**, 77), carbon tetrachloride (*idem, Trans. Faraday Soc.*, 1936, **32**, 1559). For investigation of ethers, ketones, and carboxylic acids, the most convenient substances were found to be diisopropyl ether, acetone, and acetic acid, respectively. For comparison with benzene, toluene, *n*-hexane and *n*-octane were investigated. Other substances whose isothermals have been examined are dioxan, morpholine, triethylamine, and ethyl iodide. For comparative purposes the isothermals of water and carbon tetrachloride were redetermined. The two types of silica gel used have been described by Foster (*loc. cit.*). Only a small amount of the original "gel A" was available, so the work was continued with a gel of similar type described by Allmand and Burrage (*Proc. Roy. Soc.*, 1931, *A*, **130**, 626).

The isothermals on gel A fall quite sharply into two classes: (i) "normal" curves showing a gradual increase of pressure with concentration, which do not rise steeply until fairly high concentrations are reached; (ii) curves falling almost vertically from abnormally low saturation values to very low pressures. Fig. 1 shows the "normal" curves all reduced to the same scale by plotting relative instead of actual pressures. This group comprises acetic acid, acetone, carbon tetrachloride, *n*-hexane and toluene. The isothermals are of the same general shape as those of benzene described by Lambert and Clark (*loc. cit.*). The second group, shown in Fig. 2, consists of *n*-octane, diisopropyl ether, morpholine, and triethylamine, in order of decreasing

* Part I of this series appeared in *Trans. Faraday Soc.*, 1932, **28**, 645.

extent of adsorption. Similar curves have been observed by McBain ("The Sorption of Gases by Solids," London, 1932), who has applied the term "persorption" to cases where the formation of the unimolecular layer completely fills the pores of the adsorbent. It appears that the pores of the silica gel act as a molecular sieve and will not admit large molecules like those of triethylamine.



According to the well-known Langmuir theory, the formation of a unimolecular layer follows the relation $c = zb p / (1 + b p)$, where b is a constant and z the saturation value. This may also be written in the form $p/c = 1/zb + p/z$, showing a linear relation between p/c and p , the slope of which is $1/z$. The remarkable fact now appears that the data for both types of isothermal when plotted in this way give straight lines over the entire pressure range investigated. The actual curves are not reproduced, but the constants are recorded in Table I.

TABLE I.
Summary of data for Langmuir curves.

Substance.	$1/zb$.	$1/z$.	z (mg./g.).	z/M (millimols.).	σ^2 (A. ²).	$z\sigma^2/M$.
Acetic acid	0.00025	0.00515	194	3.23	26.0	84
Acetone	0.10	0.0070	143	2.45	31.4	77
Carbon tetrachloride	0.01138	0.00467	214	1.45	37.2	54
Diisopropyl ether	0.0001	0.0165	61	0.59	49.0	29
Dioxan	0.00002	0.0082	122	1.39	34.8	48.4
n-Hexane	0.0375	0.00875	114	1.32	45.0	59.4
Morpholine	0.0088	0.0372	27	0.30	34.8	10.5
n-Octane	0.0005	0.0104	96	0.84	53.3	45
Toluene	0.00167	0.00667	150	1.63	39.7	65
Triethylamine	0.030	0.171	6	0.06	47.6	2.9

An isothermal for water at 25° has been described by Foster (*loc. cit.*, 1936, p. 1567, Fig. 9). Dioxan gave the erratic results summarised in Fig. 3, isothermals being numbered in the order in which they were determined. The gel was not evacuated between runs 2 and 3, or between runs 4, 5, and 6; but between runs 1 and 2, and 3 and 4, it was evacuated and reactivated at the original temperature of activation, 150°. Equilibrium was established very slowly; sometimes samples of gel left immersed in liquid dioxan slowly absorbed the excess overnight and appeared quite dry the next day. After run 6 the container was transferred to the low-pressure apparatus described in the preceding paper, and the desorption continued down to $p = 0.002$ mm. by using the Pirani gauge. These low-pressure data are in agreement with the Langmuir equation, and are included in Table I. The saturation value of 122 mg./g. obtained by extrapolation of these low-pressure data is lower than those of Fig. 3. The sorption of *n*-octane was also examined in the low-pressure region (see preceding paper) and gave a saturation value (54 mg./g.) considerably lower than that calculated from the high-pressure data described here (98 mg./g.). This suggests that too much importance should not be attached to the linear plot of p/c against p unless this extends over the entire concentration range, from low pressures up to

FIG. 3.

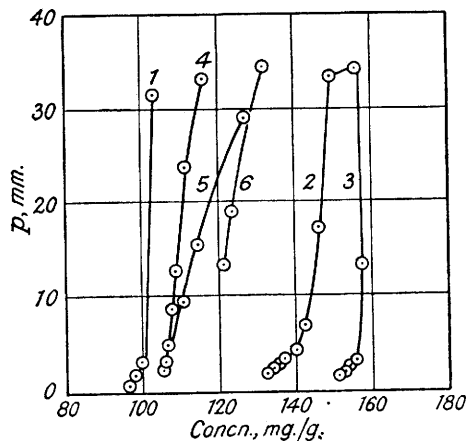
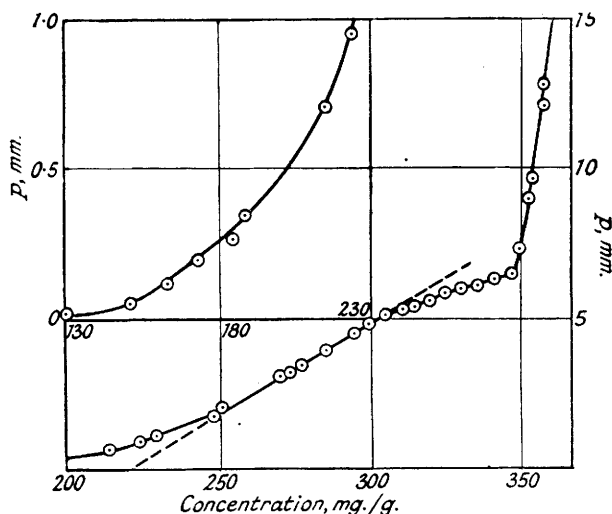


FIG. 4.



saturation. In this connection it is noteworthy that Wang (*Proc. Roy. Soc.*, 1937, A, 161, 127) has shown that, where the adsorbed molecules interact with mutual repulsion, the relation between p and c begins on one Langmuir isothermal and ends on another.

Fig. 4 shows the isothermal of dioxan on silica gel B, which was quite reproducible and showed none of the peculiarities observed with gel A. Here again the measurements were extended down to low pressures. From 0.02 to 4.0 mm., $p/c = 0.0001 + 0.0005p$, whence $z = 200$ for the saturation value of the first layer. The linear middle portion of the isothermal extrapolates back to zero pressure at 220 mg. It has already been suggested (*Proc. Roy. Soc.*, 1935, A, 150, 77) that this linear part is associated with the formation of a second adsorbed layer.

Experimental.—The procedure was similar to that previously employed (Foster, *loc. cit.*, 1934). The majority of the substances used were purified by the methods described by Weissberger and Proskauer (*"Organic Solvents,"* Oxford, 1935). Before use, all were carefully fractionated through a long Scoriah column, and the vapour pressure checked. The few vapour pressures (mm. Hg at 25°) which either did not agree with those reported by other workers or had not hitherto been recorded were: diisopropyl ether, 149.3; morpholine, 10.05; triethylamine, 74.15.

The results are summarised in Table II, where d , M , and σ have their usual significance and q is the saturation value.

DISCUSSION.

The majority of the early workers on adsorption found that the volumes of different liquids adsorbed at saturation were approximately constant for a given adsorbent. This generalisation, usually referred to by the name of its discoverer (Gurwitsch, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 805; *Z. physikal. Chem.*, 1914, 87, 323), is admirably illustrated by the extensive results of Hallstrom (Diss., Helsingfors, 1920) with a wide variety of solids and vapours, but many later workers, including McBain (*"Sorption of Gases by Solids,"* London, 1932, p. 140), have cast doubt on its general validity. It is evidently inapplicable to the results obtained in the present work with gel A (see Table II), where the saturation volumes (q/d) vary from 8 to 220 mm.³/g. From Fig. 5, where the number of moles adsorbed at saturation (q/M) is plotted against the molecular diameter, it is clear that the lowest saturation values are associated with the largest molecules. Since these molecular diameters are calculated from the well-known relation $\sigma = 1.33 \times 10^{-8} (M/d)^{1/3}$ (Moelwyn-Hughes, *"Kinetics of Reactions in Solution,"* Oxford, 1933, p. 15), q/M was then plotted against d/M (the reciprocal

TABLE II.
Summary of results for silica gel A.

Substance.	q , mg./g.	d .	q/d .	$10^4 q/M$, mols./g.	$10^3 d/M$.	σ , A.
Acetic acid	190	1.044	182	32.3	17.4	5.1
Acetone	143	0.79	181	24.5	13.6	5.6
Benzene ¹	176	0.88	195	22.5	11.25	5.9
Carbon tetrachloride ²	224	1.585	141	14.5	10.3	6.1
Diisopropyl ether	60.5	0.72	84	5.9	7.04	7.0
Dioxan ³	162	1.03	157	18.3	11.7	5.9
Ethyl alcohol ⁴	165	0.785	210	35.8	17.1	5.2
<i>n</i> -Hexane	111	0.655	170	13.2	7.52	6.7
Hydrogen cyanide ⁵	160	0.715	224	59.3	26.5	4.5
Methyl alcohol ⁴	171	0.787	217	53.8	24.6	4.6
Morpholine	26	0.994	26	3	11.4	5.9
<i>n</i> -Octane	100	0.70	143	8.4	6.14	7.3
Toluene	155	0.862	180	19.3	9.35	6.3
Triethylamine	6	0.726	8.3	0.6	7	6.9
Water	218	0.997	219	117	55.6	3.5

References : ¹ Lambert and Clark, *loc. cit.* ² Foster, *loc. cit.* ³ Maximum value, curve 3, Fig. 3. ⁴ Foster, *loc. cit.* ⁵ Foster and Batchelor (unpublished).

of the molar volume), with the result shown in Fig. 6. The best curve through the rather scattered points is seen to be a straight line $q/M = 0.25d/M - 0.0007$. Two important deductions may be drawn from this relation : (i) The volume adsorbed should reach a maximum value of 0.25 c.c./g. when the adsorbed molecule is very small, *i.e.*, the second term becomes negligible as d/M increases. (ii) When $d/M = 0.0007/0.25$ or $M/d = 357$ we should find $q = 0$, *i.e.*, no substance with a molecular volume greater than 357 should be adsorbed. This corresponds to a molecular diameter of 9.5 Å., whereas the diameter of the triethylamine molecules is 6.9 Å. and this substance is scarcely taken up by the gel.

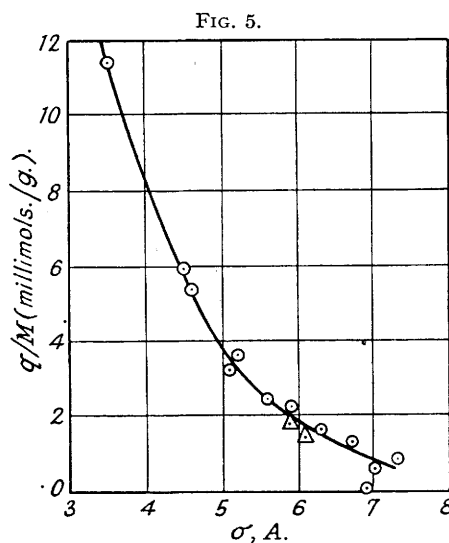
There is ample evidence therefore that gel A does indeed act as a molecular sieve, which large molecules are unable to penetrate, although the linear relation between q/M and d/M is rather surprising since one would expect to find an abrupt change in the amount adsorbed at a certain critical value of the molecular diameter. This relation can only be explained by assuming that the gel contains tapering capillaries; *e.g.*, Fig. 7 shows that the portion of the total adsorption volume cut off by an adsorbed molecule will depend on its size. We may consider the "inaccessible" volume V_i as equal to that of the cone OAB minus that of the hemisphere, *i.e.*, $V_i = \frac{1}{3}\pi a^2 h - \frac{2}{3}\pi r^3$. Now $h = r \sec \theta$ and $a = r \operatorname{cosec} \theta$, whence $V_i = \frac{1}{3}\pi r^3 (\sec \theta \operatorname{cosec}^2 \theta - 2) = Kr^3$ for a constant value of θ , so the inaccessible volume is directly proportional to the volume of the adsorbed molecule and hence to M/d . The actual volume available for adsorption is the total volume of the assembly of conical pores minus the volume of the inaccessible parts; *i.e.*, $V_s = V_0 - V_i$ or $V_s = V_0 - KM/d$, but since $V_s = q/d$, we have $q/d = V_0 - KM/d$ or $q/M = V_0 d/M - K$, which is the observed relation.

It is apparent from these considerations that the best test of Gurwitsch's rule is to plot q against d , rather than to inspect the actual values of q/d . The plot should not only be linear but should also pass through the origin. Coolidge (*J. Amer. Chem. Soc.*, 1924, **46**, 596) found variations from 424 to 490 mm.³ per g. of charcoal, but it is evident from a large-scale plot of q/M against d/M that his results are in accord with Gurwitsch's rule.

TABLE III.
Summary of results on silica gel B.

Substance.	q , mg./g.	d .	q/d .	z .	z/M .	z/q .	$10^3/\sigma^2$.
<i>n</i> -C ₄ H ₉ ·OH	290	0.81	360	184	2.49	0.63	27.8
CCl ₄	545	1.59	344	—	—	—	—
Dioxan	364	1.03	354	220	2.50	0.605	28.7
EtOH	302	0.79	385	155	3.37	0.51	37
HCN	260	0.72	363	—	—	—	—
MeOH	302	0.79	384	126	3.94	0.42	47.2
<i>n</i> -C ₃ H ₇ ·OH	290	0.80	351	174	2.90	0.60	31.9
<i>iso</i> -C ₃ H ₇ ·OH	293	0.78	362	168	2.80	0.58	31.2
NEt ₃	267	0.726	358	175	1.73	0.66	21
H ₂ O	350	0.997	351	40	2.22	0.11	81.6

The results obtained with silica gel B, summarised in Table III, show no evidence of "persorption," and



the saturation volumes remain reasonably constant, q being proportional to d (Fig. 8). It is true that the saturation volume varies from 344 to 385 mm.³ per g., but the deviations from the mean (355) cannot be correlated with the molecular diameter. The difference in behaviour of the two gels seems to be determined by the shape rather than the size of the capillaries, since the actual capillary radii calculated from the water isothermals by means of Kelvin's equation are of the same order, *viz.*, 9 Å. for gel A and 10 Å. for gel B.

The fact that part of the total pore volume is inaccessible to large molecules implies that part of the total surface is also inaccessible, and that the amounts of various substances held in the unimolecular layer should also decrease as the molecular size increases. This is illustrated by the data of col. 6 in Table I. The inaccessible surface will be proportional to r^2 and hence to the square of the molecular diameter σ , so we

FIG. 6.

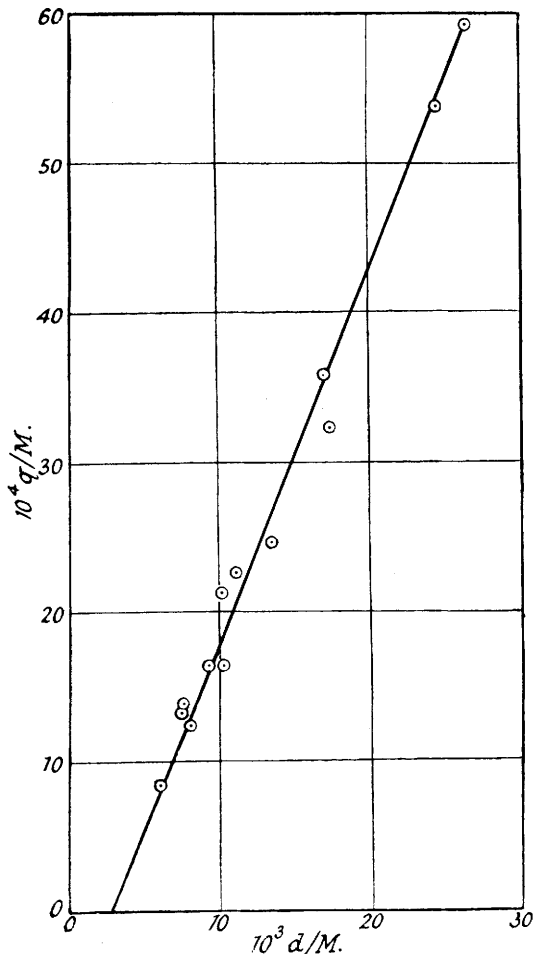


FIG. 7.

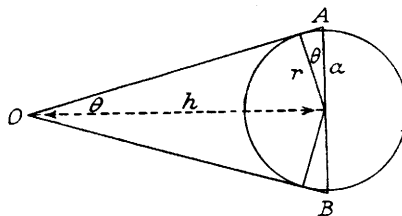
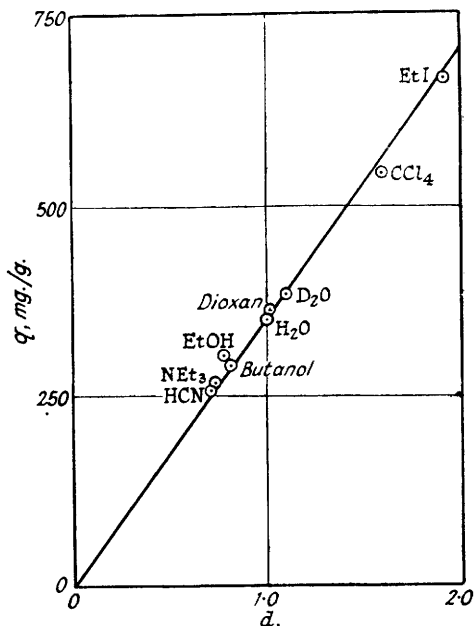


FIG. 8.



should expect to find "available surface" = total surface - "inaccessible" surface, or $N(z/M)\sigma^2 = S_0 - K\sigma^2$ or $z/M = S_0/N\sigma^2 - K/N$, *i.e.*, z/M should be a linear function of $1/\sigma^2$ as illustrated by Fig. 9, where the data of Table I are plotted in this manner. The equation of the straight line is $z/M = 0.102/\sigma^2 - 0.001$, whence $S_0/N = 0.102$ or S_0 , the total surface area per g. of gel = $0.102 \times 6.06 \times 10^{23} \text{ Å}^2 = 6.2 \times 10^6 \text{ cm}^2$. It also follows that $z/M = 0$ when $0.001\sigma^2 = 0.102$ or $\sigma^2 = 102$, *i.e.*, $\sigma = 10 \text{ Å}$. as compared with the value 9.5 Å. derived from the corresponding volume relationship.

It has been suggested (preceding paper) that the linear middle portion exhibited by certain isothermals is due to the formation of a second layer, and that by extrapolation back to zero pressure an approximate estimate of the amount held in the first layer (z) can be obtained. The z values derived in this manner are recorded in Table III, and the corresponding graph of z/M against $1/\sigma^2$ in Fig. 10. The best curve through the points is the straight line $z/M = 0.088M/\sigma^2$, thus demonstrating the absence of "persorption" on gel B. The slope of this curve is 0.088, giving a value of $5.3 \times 10^6 \text{ cm}^2$ for the surface area of 1 g. of gel.

It was suggested by Goldmann and Polanyi (*Z. physikal. Chem.*, 1928, **132**, 356) that, where a two-dimensional adsorbed layer covers a constant surface area, the product $(z/M)(M/d)^{2/3}$, which corresponds to our $(z/M)\sigma^2$, should be constant. The actual values which they recorded vary between 1.12 and 1.40,

and a plot of z/M against $1/\sigma^2$ gives the linear relation $z/M = 0.365/\sigma^2 - 0.004$, which shows that their charcoal resembles our silica gel A in its behaviour. It is noteworthy that most of the methods available for the determination of the surface area of adsorbents are based on the assumption that at some particular point on an isotherm, a unimolecular layer is completed. It is evident that with some types of adsorbent any calculation based on measurements with a single substance must necessarily be inaccurate when $(z/M)\sigma^2$ is a function of the molecular diameter.

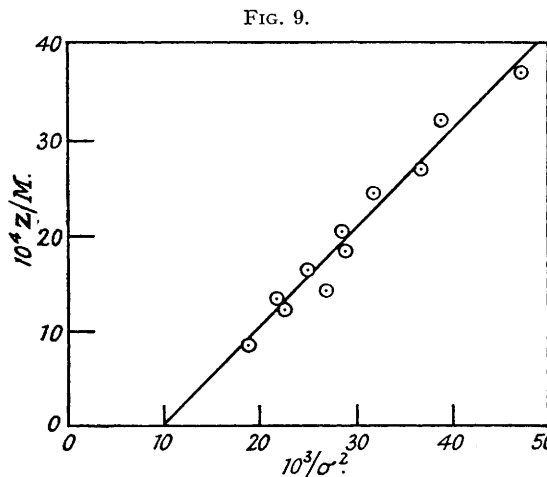


FIG. 9.

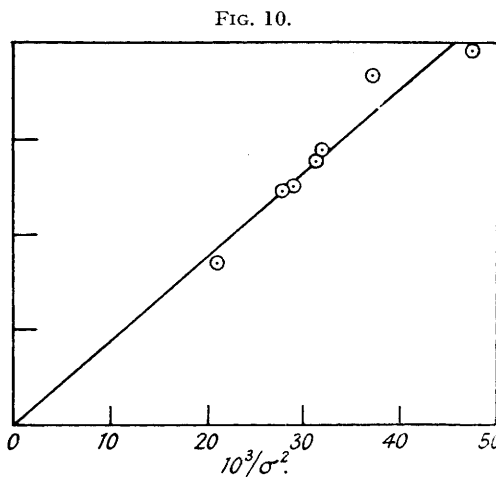


FIG. 10.

The relations derived so far may be summarised as follows. For Gel A, the saturation amount (in g./g. of gel) is given by

$$q = 0.25d - 0.0007M \quad \dots \quad (1)$$

and the amount held in the unimolecular layer by

$$z = 0.102M/\sigma^2 - 0.001M \quad \dots \quad (2)$$

These relations break down as M/d reaches 100 and σ exceeds 6 Å., whereupon q and z become identical and tend to fall below the calculated values.

For Gel B simpler relations hold, viz.,

$$q = 0.355d \quad \dots \quad (3)$$

$$z = 0.088M/\sigma^2 \quad \dots \quad (4)$$

whence it is obvious that there must be a simple relation between q and z . Since σ was calculated from M/d by the relation σ (in Å.) = $1.33(M/d)^{1/3}$ or $\sigma^3 = 2.36M/d$, we can eliminate both M and d from (3) and (4) and obtain the relation

$$z/q = 0.105\sigma \quad \dots \quad (5)$$

σ being expressed in Å., not cm. In Fig. 11, z/q is plotted against σ , and the line drawn with slope 0.105 is seen to pass evenly through the experimental points with the exception of that for water. This agreement provides further evidence that z , the amount held in the first layer, can be approximately estimated by extrapolating back the linear, middle portion of the isothermals to zero pressure. The only substance so far investigated which fails to give isothermals of this type on gel B is carbon tetrachloride (Foster, *loc. cit.*). In such cases equation (5) may possibly be of value for the indirect determination of z .

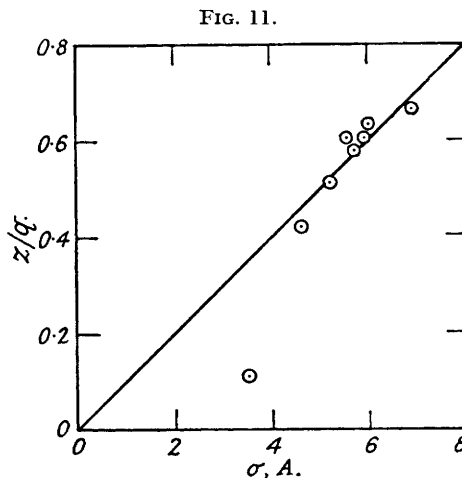


FIG. 11.

The behaviour of water is anomalous since equation (4) leads us to expect $z = 122$, compared with the observed value of 40. A similar peculiarity is found with gel A, where equation (2) gives $z = 133$ compared with a value of 50 extrapolated from the linear isotherm and 60 extrapolated from the low-pressure Langmuir plot (see preceding paper). This suggests that the water molecule may attach itself to the more active points of the gel surface, and that it is the saturation of these, not the complete surface, which gives rise to the low-pressure Langmuir isotherm. The linear, middle part (shown in Fig. 1 of the following paper) would then correspond to further sorption in the first layer on the less active sites. It is believed that hydrogen cyanide shows a similar behaviour on silica gel, and it is hoped to discuss this point in more detail when further data are available. Both substances seem to behave normally on ferric oxide gel.