

88. *Low-pressure Isothermals and Heats of Sorption.*

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A new method of calibrating the Pirani gauge for measuring the pressure of condensable vapours up to about 0.5 mm. is described. Sorption isothermals of water, ethyl alcohol, toluene, dioxan, *n*-octane, and carbon tetrachloride have been determined at 25° on silica and ferric oxide gels: all give the linear plot of  $p/c$  against  $p$  demanded by Langmuir's theory. The values calculated for the amounts held in the completed unimolecular layer show good agreement with previous estimates made from data at higher pressures.

Heats of sorption have been calculated by means of the Clapeyron equation, and compared with the values calculated by statistical theory from the constant of Langmuir's equation. The entropy changes accompanying the sorption process have also been calculated and are shown to be consistent with the view that the adsorbed molecules behave as three-dimensional oscillators. They are, however, of the same order as the changes accompanying the transition from vapour to normal liquid.

SORPTION isothermals have been determined for several vapours on silica gel (Lambert and Foster, *Proc. Roy. Soc.*, 1931, *A*, 134, 258) and on ferric oxide gel (Foster, *ibid.*, 1934, *A*, 147, 128), but although the data covered the entire range of concentration up to saturation, the initial stages of the isothermals were not adequately examined, because in most systems the major part of the sorption process took place at pressures which were too low to be measured accurately on a mercury manometer. The low-pressure measurements now described have been obtained with the Pirani gauge, by means of a technique essentially similar to that employed by Allmand and Chaplin (*ibid.*, 1930, *A*, 129, 257). Since this gauge has to be calibrated separately for each individual vapour, the choice of substances is limited by the necessity for accurate low vapour-pressure measurements. Suitable data for water, ethyl alcohol, toluene, and carbon tetrachloride are quoted in International Critical Tables, and have been obtained by dynamic methods or by the use of special types of low-pressure manometer. This paper describes isothermals of these vapours on silica and ferric oxide gels at pressures below 1 mm.

The Pirani gauge was used as recommended by Campbell (*Proc. Physical Soc.*, 1921, 33, 287), the temperature of the filament being kept constant by varying the potential across the bridge circuit. If  $V_0$  represents the balancing voltage at zero pressure, and  $V$  the voltage required at pressure  $p$ , then the following relation holds at low pressures, when the thermal conductivity of the gas is proportional to the pressure:

$$p = k(V^2 - V_0^2)/V_0^2 = f(V) \dots \dots \dots (1)$$

The usual method of calibration with vapours where the McLeod gauge cannot be employed is to take voltage readings at known low pressures, obtained by surrounding the liquid with suitable refrigerants. Although it is difficult to find many substances which can be easily purified so as to give constant *m. p.*'s between 0° and -100°, it is evident that even a single calibration will suffice if accurately determined. At higher pressures, however, the linear relation between  $p$  and the voltage function breaks down, and the calibration curve cannot be constructed without a large number of points. In many of the systems described here, the main part of the sorption isothermal lies between 0.05 and 0.5 mm. pressure, so it was essential to calibrate the gauge accurately over this range. Some of the isothermals described later follow the Langmuir equation

$$c = zbp/(1 + bp) \dots \dots \dots (2)$$

which gives an initial linear relation  $c = zbp$  when  $bp \ll 1$ , whereas  $c$  finally approaches a limiting value  $z$  when  $p$  is very large. If the equation is written in the form  $1/c = 1/z + 1/zbp$ , it is seen that  $1/c$  plotted against  $1/p$  should give a straight line over the entire pressure range. Now, the curves of  $f(V)$  against  $p$  are subject to similar limiting conditions; at low pressures  $f(V)$  is proportional to  $p$ , but at high pressures it reaches a limiting value, since the thermal conductivity of gases becomes independent of the pressure when the mean free path is small. The graphs of  $1/f(V)$  against  $1/p$  (not shown) are linear from 0.05 up to 0.5 mm., which is just the range over which the direct plot of  $f(V)$  against  $p$  is least satisfactory for calibration. When this method was first used, in 1934, it was not known that a similar reciprocal relation between thermal conductivity and pressure had been found by Dickens (*Proc. Roy. Soc.*, 1934, *A*, 143, 517). A detailed theoretical derivation has been given by Gregory (*ibid.*, 1935, *A*, 149, 35; *Phil. Mag.*, 1936, 22, 257), and the relation has also been tested experimentally for gases by Archer (*ibid.*, 1935, 19, 901). As far as is known, however, this relation has not previously been used for calibration of the Pirani gauge; its use enables a single gauge to be employed from the lowest measurable pressures right up to the manometric region, and is of particular value between 0.1 mm. and 1 mm.

## EXPERIMENTAL.

*Isothermals and Heats of Sorption.*—(1) *Water.* In the first series of experiments (1934) all taps were lubricated with Apiezon vapourless grease, but although the initial results were satisfactory, after some weeks much trouble was experienced by the liberation of permanent gas, at pressures of the order  $10^{-4}$  mm., whenever stopcocks were turned. For this reason a new apparatus was constructed in which the Pirani gauge and gel container were separated from the remainder of the apparatus by a mercury seal "cut-off." All stopcocks were then lubricated with carefully prepared Ramsay grease, which had been stored in a vacuum desiccator over charcoal; in none of the subsequent experiments was any appreciable evolution of gas from taps observed.

Three separate samples of silica gel *A* from the batch previously described (*Proc. Roy. Soc.*, 1934, *A*, 146, 129) were used, sorption and desorption points being taken. The first series is shown in Fig. 1; the best curve through the experimental points is the straight line represented by the equation  $p/c = 0.0042 + 0.0164p$  (Fig. 2*A*), which conforms to the

FIG. 1.  
Water on silica gel.

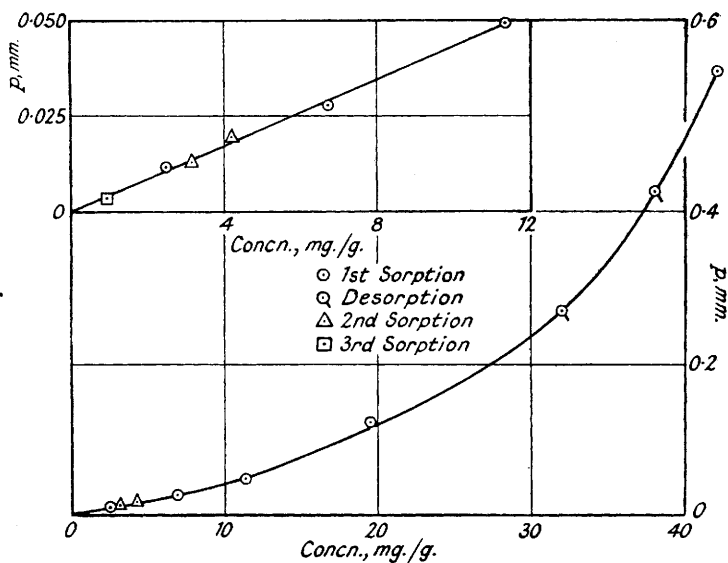
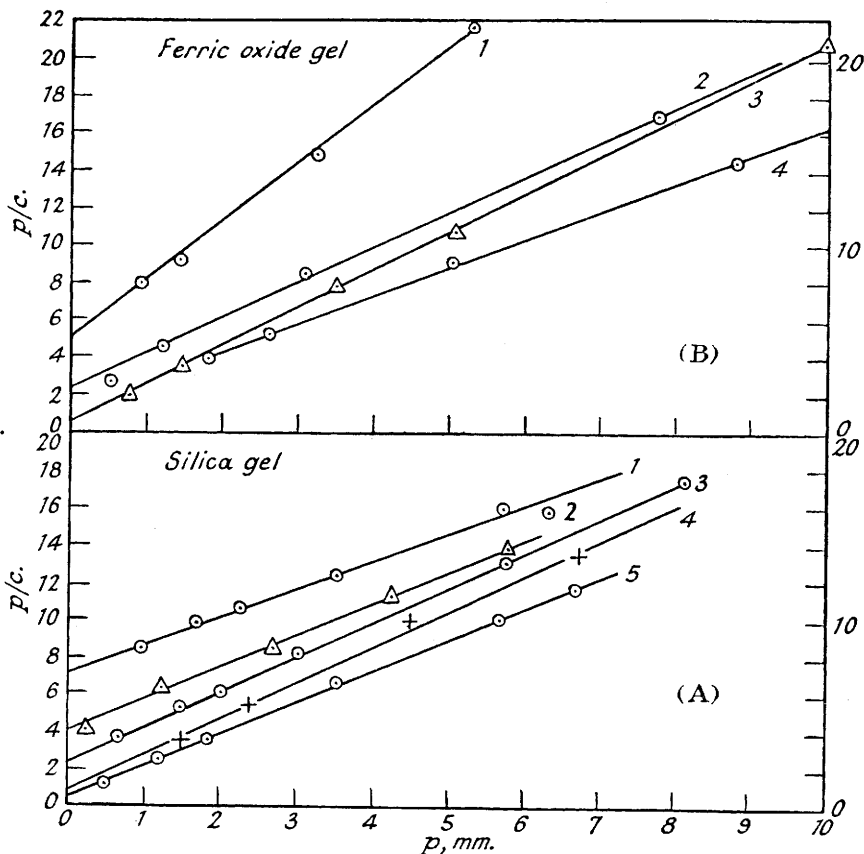


FIG. 2.



Key to Scales for Fig. 2, A and B.

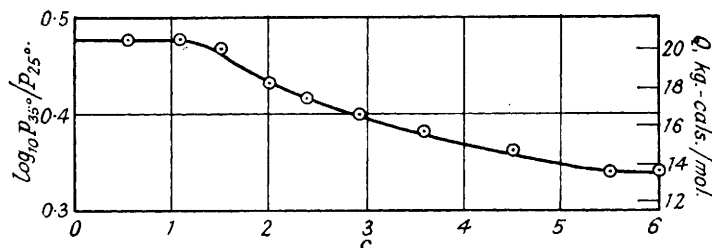
Substance.	Curve.	One scale division equals		Curve.	One scale division equals	
		$p/c$ , mm./mg.	$p$ , mm.		$p/c$ , mm./mg.	$p$ , mm.
Toluene .....	1	0.00001	0.0005	2	0.00025	0.02
Water .....	2	0.001	0.01	1	0.0005	0.05
Octane .....	3	0.0005	0.01	3	0.0001	0.01
Alcohol .....	4	0.0002	0.02	4	0.0001	0.01
Dioxan .....	5	0.00005	0.10			

Langmuir isotherm, according to which a linear plot of  $p/c$  against  $p$  should be obtained over the entire range. The excellent agreement between observed and calculated values is shown below.

Press., mm. ....	0.01	0.10	0.30	0.494
Concn., mg./g. {	Calc. ....	2.27	16.98	32.7
	Obs. ....	2.30	17.0	33.2
			40.0	40.0

The second series of experiments, carried out in 1936, gave results almost identical with the first. The Pirani gauge was run at a lower temperature to increase its sensitivity and had therefore to be recalibrated, but its behaviour did not appear to be affected by the use of Ramsay grease or by the presence of mercury vapour. The data used for calculating heats of sorption were obtained during this series by taking pressure readings at both 25° and 35°, but the only extensive readings were determined on a sample of gel which had been used for several sorption and desorption experiments, and gave non-linear isothermals with pressures falling slightly below those of Fig. 1. This is attributed to a slight change in the adsorptive capacity of the gel after repeated heat treatment and evacuation. Values of the ratio  $p_{35^\circ}/p_{25^\circ}$  at various concentrations, read off from a large-scale graph, enabled Fig. 3 to be constructed, showing  $\log p_{35^\circ}/p_{25^\circ}$  as a function of

FIG. 3.



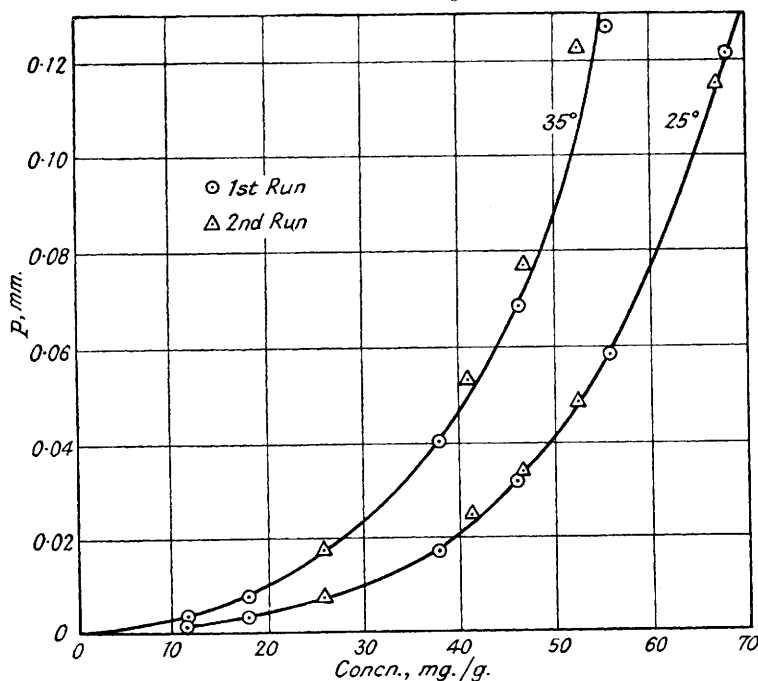
concentration. This ratio is proportional to the heat of sorption, since, according to the integrated form of Clapeyron's equation we have

$$-\Delta H_{\text{ads.}} = 4.57[T_1 T_2 / (T_1 - T_2)] \log_{10} p_1 / p_2.$$

At low concentrations  $-\Delta H$  is constant at about 20 kg.-cals./mole, but falls to 14.3 kg.-cals. at 6 mg./g. During the first series of experiments only two measurements were obtained at temperatures other than 25°. At 2.4 mg./g. a value of 15.7 kg.-cals. was found, and another reading at 3.2 mg./g. gave 14.9 kg.-cals. In another series an approximately constant value of 15.2 kg.-cals. was obtained, whence the net heat of sorption may be taken as 4.8 kg.-cals. since the heat of vaporisation is 10.4 kg.-cals.

FIG. 4.

Toluene on silica gel.

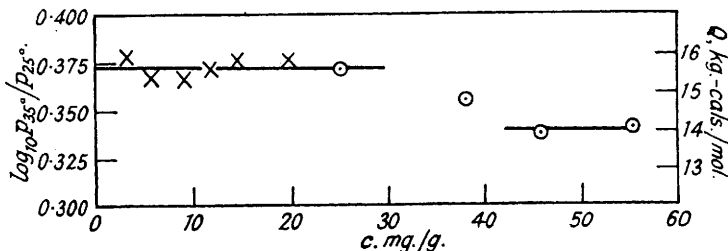


The results obtained for water on ferric oxide gel are described in the next paper but one, together with measurements on deuterium oxide. The best curve through the low-pressure points follows the line  $p/c = 0.0008 + 0.026p$ .

(2) *Toluene.* Two successive desorptions on silica gel gave the reproducible results shown in Fig. 4. The Langmuir curve corresponding to the final sorption points below 0.004 mm. is shown in Fig. 2A. The linear relation  $p/c = 0.00007 + 0.0296p$  breaks down above 25 mg./g. Fig. 5 shows the heats of sorption, which remain constant at 15.6 kg.-cals. up to

30 mg./g., but fall off to 14.0 kg.-cals., in the neighbourhood of 50 mg./g. The following table records the low-pressure data for ferric oxide, together with the corresponding heats. Although the latter remain constant up to 13 mg./g., the

FIG. 5.  
Heats of sorption of toluene on silica gel.



plot of  $p/c$  against  $p$  is not linear in this region. From 0.01 to 0.16 mm., however, we find  $p/c = 0.00055 + 0.0235p$  (Fig. 2B) and the heat of sorption averages 13.1 kg.-cals.

$c$ (mg./g.).	$10^5 p(25^\circ)$ , mm.	$10^5 p(35^\circ)$ , mm.	$\log_{10} p_{35}/p_{25}$ .	$-\Delta H$ (kg.-cals.).
2.59	24.5	50	0.310	14.73
5.18	99	222	0.351	14.77
7.76	222	499	0.352	14.77
10.36	436	980	0.352	14.45
12.93	750	1660	0.345	

Mean heat of sorption = 14.68 kg.-cals.

(3) Ethyl alcohol. The first run on silica gel had to be abandoned owing to the presence of permanent gas, which was removed by heating the charged gel to  $150^\circ$  in a vacuum. This treatment sometimes lowers the adsorptive capacity of the gel and causes a slight displacement of the isothermal towards the pressure axis (Foster, *Proc. Roy. Soc.*, 1934, A, **146**, 129). The four points obtained on the second run lay on the curve  $p/c = 0.000175 + 0.00952p$  (Fig. 2A).

With ferric oxide also, a slight shift was observed after re-evacuating the gel at  $150^\circ$ , and the second desorption run was displaced about 5 mg./g. towards the  $p$  axis. A large-scale plot of the lower points (Fig. 2B) gives  $p/c = 0.00002 + 0.021p$ . Another sample of gel was used for a sorption run, but the only reliable reading obtained was at  $c = 8.4$  mg./g., where the observed pressure was  $1.8 \times 10^{-4}$  mm. This gives  $p/c = 2.14 \times 10^{-5}$  as compared with the value  $2.36 \times 10^{-5}$  required by the above equation at this concentration. No heats of sorption were measured on this gel. Two determinations on silica gel at  $c = 66$  and  $c = 82.5$  gave the values 14.1 and 14.6 kg.-cals., respectively.

FIG. 6.  
Dioxan on silica gel B.

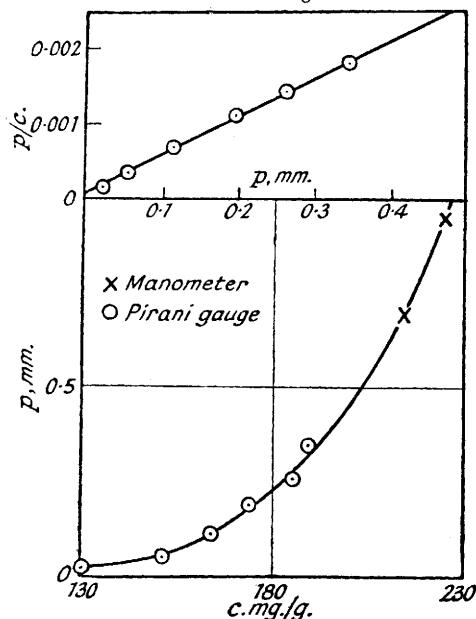
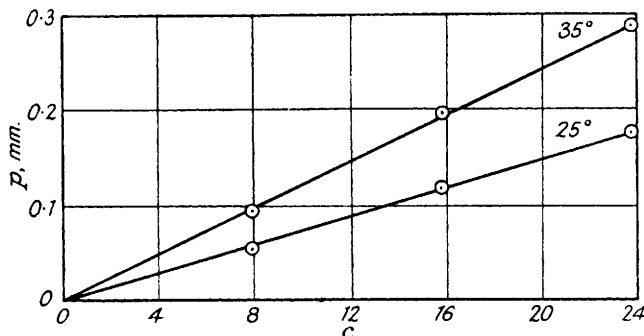


FIG. 7.

Carbon tetrachloride on silica.



(4) Dioxan. The v. p. curve of solid dioxan was determined from the m. p. ( $11.6^\circ$ ) down to  $-30^\circ$ , below which the pressure is too low for accurate measurement on a mercury manometer. The results were represented by the relation  $\log_{10} p = 10.31 - 2597/T$  which was used for calibrating the Pirani gauge, with extrapolation to  $-65^\circ$  for the lowest pressures. Fig. 2A shows the results obtained with silica gel A:  $p/c = 0.00002 + 0.0082p$  between  $p = 0.003$  and 0.8 mm. ( $c = 74-120$  mg./g.).

An experiment was also carried out with another specimen of silica gel, the "gel B," previously described by the author (*Proc. Roy. Soc.*, 1934, A, **146**, 129). Fig. 6 shows that here also a linear plot is obtained, viz.,  $p/c = 0.00012 + 0.00495p$ , and the lowest manometric points lie on the same curve as the Pirani points. The following values were obtained for the heat of sorption: at  $c = 130$ ,  $-\Delta H = 14.0$ ;  $c = 151$ ,  $-\Delta H = 13.5$ ;  $c = 163$ ,  $-\Delta H = 12.6$  kg.-cals. On ferric oxide  $p/c = 0.00013 + 0.015p$  up to 0.1 mm. (Fig. 2B).

(5) n-Octane. The vapour pressure of n-octane was determined down to the limit of the mercury manometer, and the extrapolated curve  $\log p = 8.326 - 2143.7/T$  was used for calibrating the Pirani gauge. The isothermal on silica gel followed the Langmuir curve  $p/c = 0.00012 + 0.0185p$  (Fig. 2A) up to 0.05 mm. at 50 mg./g., but a falling off was

observed at higher pressures. Two heats of sorption were determined: 13.5 kg.-cals. at  $c = 38$  and 13.7 kg.-cals. at  $c = 44$ ; mean 13.6. No heats were determined on ferric oxide gel; the Langmuir plot,  $p/c = 0.0025 + 0.0136p$ , is shown in Fig. 2B.

(6) *Carbon tetrachloride*. Silica gel adsorbs comparatively little carbon tetrachloride at very low pressures. Over the range of the Pirani gauge the isothermals are linear, but the manometric data (following paper) show excellent agreement with the equation  $p/c = 0.01138 + 0.0046p$  from  $c = 50$  to 200 mg./g., and  $p$  rising from 1 to 15 mm. Fig. 7 shows the low-pressure isothermals at 25° and 35°, from which the heat of sorption is found to be 8.98 kg.-cals. The ferric oxide results follow the relation  $p/c = 0.0059 + 0.030p$  up to 0.2 mm., after which the pressure increases linearly with concentration.

## DISCUSSION.

The vapours examined all show reasonable agreement with the Langmuir equation (2), which may also be written as

$$p/c = 1/zb + p/z \quad \dots \quad (3)$$

whence the slope of the  $p/c$ - $p$  curve is  $1/z$ , and the saturation value  $z$  is easily determined. The constant  $b$  can then be evaluated from the intercept on the  $p/c$  axis which is  $1/zb$ . If we write  $c/z = \theta$ , the fraction of the surface covered, we obtain the alternative form of Langmuir's equation

$$p = \theta/b(1 - \theta) \quad \dots \quad (4)$$

with a single constant  $b$ , which is related to the heat of sorption. According to the kinetic derivation,  $b = a\chi/RT$ , where  $\chi$  is the energy required to enable a molecule to escape from the adsorbed layer, and in the absence of any activation energy may be taken as the heat of sorption. The constant  $a$ , however, cannot be determined directly, being the ratio of the condensation and the evaporation coefficient.

The newer statistical methods (Fowler, *Proc. Camb. Phil. Soc.*, 1935, 31, 260; Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge, 1939, 426) have the advantage of giving  $b$ , which is really the mass-action constant, in terms of the partition functions, which, in theory, could be calculated from known properties of the system. In a simplified notation, Fowler's result may be written

$$b = [a(T)/g(T)]e^{\chi/RT} \quad \dots \quad (5)$$

where  $a(T)$  and  $g(T)$  are the complete partition functions for all the motions of the adsorbed and the free molecules, respectively; *i.e.*,  $g(T)$  includes the translational term  $(2\pi m)^{3/2}(kT)^{5/2}/k^3$ , which is usually written separately;  $\chi$  is the minimum energy required to enable one mole of adsorbed material to escape into the gas phase and may be taken as approximately equal to the heat of desorption;  $g(T)$  can be calculated from known properties of the molecule, but  $a(T)$  is in general too complex to be evaluated theoretically unless detailed information is available about the exact mechanism of adsorption, although Barrer (*Trans. Faraday Soc.*, 1944, 50, 374) has shown how the calculation may be performed for zeolitic solid solutions. An alternative procedure is to take the liquid rather than the gaseous adsorbate as reference state and to assume as a first approximation that  $a(T)$  is not vastly different from  $l(T)$ , the complete partition function for the liquid state. Thus we may write the well-known statistical vapour-pressure equation in the form

$$p_s = [g(T)/l(T)]e^{-\lambda/RT} \quad \dots \quad (6)$$

where  $\lambda$  is the heat of vapourisation of the liquid; (5) and (6) together give the relation

$$bp_s = [a(T)/l(T)]e^{(\chi - \lambda)/RT}$$

or  $\ln bp_s = \ln a(T)/l(T) + (\chi - \lambda)/RT$ , which reduces to

$$\ln bp_s = q/RT \quad \dots \quad (7)$$

when  $a(T)$  and  $l(T)$  are nearly equal, and  $q = \chi - \lambda$  is the so-called "net" heat of sorption. This procedure is, of course, theoretically unsound and could only be justified if it enabled us to calculate  $b$  from  $q$  (or  $\chi$  and  $\lambda$ ). Unfortunately, owing to the exponential form of the relation this constitutes too severe a test. The data of Table I do, however, suggest that the converse procedure, *viz.*, the approximate evaluation of  $\chi$  from the observed values of the Langmuir constant  $b$ , is moderately successful and provides a fairly satisfactory test of the statistical treatment of adsorption equilibria. In this table the values of  $\chi$  calculated from  $b$  by means of equation (7) are compared with the values of  $\Delta H$  derived by means of the Clapeyron equation. The differences are of the order 10% and nowhere exceed 20%. In theory, the heat of sorption should be constant if the Langmuir equation is obeyed, but in practice this has rarely been observed. A possible explanation (Brunauer, "Adsorption of Gases and Vapours," Oxford, 1944, 70) is that the change in  $q$  is compensated by a change in  $a(T)$  acting in the opposite direction.

Although further progress must necessarily await a more detailed statistical treatment of the adsorbed state, it is interesting to study these heats of sorption from another viewpoint. Barrer (*loc. cit.*) has very recently developed the statistical treatment of zeolitic solid solutions by calculating partition functions for various types of motion of the occluded molecules relative to the lattice, assuming reasonable values for vibrational frequencies and moments of inertia. From these, the entropy change accompanying the occlusion is calculated and compared with the "observed" value derived from  $\Delta H$ , whence it is concluded that the occluded molecules lose most of their translational mobility. Only three of the seven cases considered by Barrer are of interest in

TABLE I.

Vapour.	Adsorbent.	Concn. range, mg./g.	<i>b</i> , mm. <sup>-1</sup> .	<i>p</i> <sub>s</sub> , mm.	λ <sub>30</sub> , kg.-cals./mol.	<i>q</i> , kg.-cals./mol.	χ (calc.), kg.-cals./mol.	−Δ <i>H</i> (obs.), kg.-cals./mol.
CCl <sub>4</sub> .....	Fe <sub>2</sub> O <sub>3</sub>	0—20	5.08	115	7.81	3.83	11.64	9.4
Dioxan ...	SiO <sub>2</sub> (B)	130—180	41.25	35.5	9.14	4.4	13.54	12.6 at 163; 13.5 at 151; 14.0 at 130.
	Fe <sub>2</sub> O <sub>3</sub>	40—70	—	—	—	5.0	14.14	14.0 at 50.
EtOH .....	SiO <sub>2</sub> (A)	60—100	54.4	59.0	7.85	4.85	12.43	14.1 at 83; 14.6 at 66.
<i>n</i> -C <sub>8</sub> H <sub>18</sub> ...	SiO <sub>2</sub> (A)	0—50	15.5	14.0	9.8	4.6	14.4	13.6 at 40.
CH <sub>3</sub> Ph .....	Fe <sub>2</sub> O <sub>3</sub>	15—40	427	28.9	7.9	6.50	14.4	14.7 from 0 to 13; 13.1 from 20 to 30.
	SiO <sub>2</sub> (A)	0—25	423	—	—	6.35	14.25	15.6 from 0 to 25; 14.0 from 40 to 60.
H <sub>2</sub> O .....	SiO <sub>2</sub> (A)	0—40	3.9	23.75	10.46	2.82	13.26	14.3 min.; 15.2 mean.
	Fe <sub>2</sub> O <sub>3</sub>	0—40	32.5	—	—	5.38	15.84	15.7 at 11

Note.—χ is only equal to −Δ*H* when the adsorbed molecule has complete translational mobility. The exact relation is Δ*H* = −χ + (*n*/2)*RT*, where *n* is the number of vibrational degrees of freedom of the adsorbed molecule (see Barrer, *loc. cit.*, eq. 14, p. 377). If we suppose the adsorbed layer to resemble the liquid state, the molecules will retain their translational mobility, whereas if the molecules behave as three-dimensional oscillators we should have Δ*H* = −χ +  $\frac{3}{2}$ *RT*, according to which 0.9 kg.-cal. should be added to the figures of col. 9 to obtain the “observed” values of χ.

connection with the present work, *viz.*, models (i), (ii), and (iv) (*loc. cit.*, p. 376), which correspond (i) to complete translational mobility, *i.e.*, “gaseous” adsorbate; (ii) to two translational and one vibrational degree of freedom, *i.e.*, the “two-dimensional” or mobile adsorbed layer; and (iv) to loss of all translational mobility, replaced by vibrational motions in three degrees of freedom, *i.e.*, “fixed” adsorbate. The value of Δ*S*<sub>ads.</sub>, the change of entropy accompanying adsorption, depends on the units in which pressure is expressed. In this paper all entropies have been converted to *p* = 1 atm.; hence it is necessary to add *R* log<sub>e</sub> 76 = 8.6 units to Barrer’s values for *p* in cm. The following figures are then obtained for Barrer’s models (*loc. cit.*, Table II, col. 5) :

Model.	Δ <i>S</i> <sub>ads.</sub> for <i>p</i> in cm.	Δ <i>S</i> <sub>ads.</sub> for <i>p</i> in atm.	Model.	Δ <i>S</i> <sub>ads.</sub> for <i>p</i> in cm.	Δ <i>S</i> <sub>ads.</sub> for <i>p</i> in atm.
(i)	82.53	91.1	(iv)	−36.63	−28.0
(ii)	42.81	51.4			

These values are calculated for *T* = 300° K., *M* = 56, and *v* the characteristic vibrational frequency = 6 × 10<sup>21</sup> sec.<sup>-1</sup>.

The “experimental” values of Δ*S* are calculated by means of the well-known thermodynamic relations Δ*S* = (Δ*H* − Δ*G*)/*T* and −Δ*G* = *RT* ln *K<sub>p</sub>*, whence Δ*S*<sub>ads.</sub> = Δ*H*/*T* + *R* ln *K<sub>p</sub>*, where *K<sub>p</sub>*, the equilibrium constant, is defined by the relation *K<sub>p</sub>* = θ/(1 − θ)*p* and is identical with the constant *b* of Langmuir’s equation. Table II summarises the results and shows that, apart from the rather low values for carbon tetrachloride, Δ*S*<sub>ads.</sub> agrees roughly with Barrer’s model (iv), the mean value being 25.4, compared with 28 calculated.

TABLE II.

System.	−Δ <i>H</i> , kg.-cals.	−Δ <i>H</i> / <i>T</i> .	<i>R</i> log <sub>e</sub> <i>b</i> .	−Δ <i>S</i> <sub>ads.</sub> .	<i>S</i> <sub>298</sub> <sup>0</sup> .	Δ <i>S</i> <sub>vap.</sub> .
CCl <sub>4</sub> –Fe <sub>2</sub> O <sub>3</sub> .....	9.4	31.0	16.4	14.6	71	22.0
CCl <sub>4</sub> –SiO <sub>2</sub> .....	8.98	29.7	12.3	17.4	“	“
Dioxan–Fe <sub>2</sub> O <sub>3</sub> .....	14.0	46.2	22.7	23.5	47	24.1
Dioxan–SiO <sub>2</sub> .....	14.0	46.2	20.6	26.6	“	“
EtOH–SiO <sub>2</sub> .....	14.6	48.2	21.1	27.1	38	20.8
<i>n</i> -C <sub>8</sub> H <sub>18</sub> –SiO <sub>2</sub> .....	13.6	44.8	18.6	26.2	86	24.8
CH <sub>3</sub> Ph–Fe <sub>2</sub> O <sub>3</sub> .....	14.7	48.5	20.9	27.6	76	19.6
CH <sub>3</sub> Ph–SiO <sub>2</sub> .....	15.6	51.5	25.2	26.3	“	“
H <sub>2</sub> O–Fe <sub>2</sub> O <sub>3</sub> .....	15.7	51.8	20.1	31.7	44	27.6
H <sub>2</sub> O–SiO <sub>2</sub> .....	15.2	50.2	15.9	34.3	“	“
			Mean	25.4		23.2

It must be remembered that the values chosen by Barrer for *M* and *v* are arbitrary, so little importance attaches to exact agreement. A five-fold change in the assumed values of these constants alters Δ*S*<sub>ads.</sub> by an amount of the order 5—10 units, whereas model (ii) differs from model (iv) by almost 80 units. In col. 6 the standard entropies of the adsorbed substances at 25° are recorded. The figures in col. 7 represent the entropy increase in vaporising the liquid and conversion to 1 atm. pressure, calculated from Δ*H*<sub>vap.</sub> at 300° K. by means of the relation Δ*S*<sub>vap.</sub> = Δ*H*/*T* + *R* ln *p*<sub>s</sub>. The mean of these values is 23.2, just below the mean of the observed values of Δ*S*<sub>ads.</sub>.

It may therefore be concluded that the motions of the adsorbed molecules are severely restricted and approximate to those prevailing in the liquid or the solid state. It has been pointed out by Barrer (private communication) that an approximate agreement with model (iv), the three-dimensional oscillator, does not mean that the adsorbed layer is devoid of mobility. Suppose 10% of the adsorbed molecules were at any instant migrating from one sorption site to an adjacent empty site and the remaining 90% were oscillating. Such a film would spread only 10 times less rapidly than one in which all the molecules were mobile, but Δ*S* would be very nearly that for a set of three-dimensional oscillators. The concept of a “gaseous” two-dimensional film (model ii) seems to be definitely excluded. Barrer’s treatment is intended to apply to “occlusion” rather than

to "adsorption," *i.e.*, the occluded molecule is surrounded by the zeolite lattice so that interactions between adjacent adsorbed molecules do not have to be considered. This solid solution which occurs in zeolites cannot, however, differ vastly from the "persorption" which takes place on silica gel, the evidence for which is presented in the following paper. It is also apparent from Table II that ferric oxide gel gives values of  $\Delta S_{\text{ads}}$  substantially the same as those obtained on silica gel although its pore radius is considerably larger.

In discussing the significance of the  $p/c-p$  graphs, the first step is to compare the calculated saturation values with the estimates previously made for the amounts held in the unimolecular layer. From the experiments with alcohols on ferric oxide (*Proc. Roy. Soc.*, 1934, *A*, 147, 128) and silica gel (*ibid.*, 1935, *A*, 150, 77), it was assumed that this layer was already completed at the lowest pressures which could be measured on the mercury manometer, *e.g.*, 50—55 mg./g. of ethyl alcohol on ferric oxide. In this work the first run with alcohol gave 57, and the second 52 mg./g., for the saturation value. On silica gel the low-pressure data give  $z = 105$  mg./g., whereas the isothermal described by Lambert and Foster (*ibid.*, 1931, *A*, 134, 258) at 60° shows a linear portion extending from 115 to 155 mg./g., which extrapolates back to zero pressure at 107 mg./g. This agreement would appear to confirm the suggestion previously made by the author (*ibid.*, 1935, *A*, 150, 82) that the linear middle portion of these isothermals represented the formation of a second adsorbed layer. The low-pressure data for water and dioxan show similar agreement with the high-pressure data described in the following paper; *e.g.*, the water-ferric oxide isothermal extrapolates back to zero pressure at about 44 mg./g., whilst the low-pressure Langmuir curve extrapolates forward to a saturation value of 40 mg./g. On silica gel the Langmuir isotherm gives a saturation value of 50 mg./g., and the higher-pressure data extrapolate back to about the same value. Similar agreement is observed with dioxan on silica gel B, the low- and the high-pressure data giving values of 200 and 220 mg./g., respectively.

Linear isothermals have also been described by Brunauer and others (*op. cit.*, p. 286), but have been interpreted in terms of multilayer adsorption. These workers assume that the unimolecular layer is completed at the beginning of the linear portion ("point B") rather than at the point to which this linear part extrapolates back to zero pressure ("point A"). The present work, however, favours the latter view, which will be discussed in more detail in a subsequent paper describing a large number of these "linear isothermals."

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