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The thermal properties and heats of adsorption of films on vitreous silica

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As a contribution to the few existing data of sufficient accuracy for the calculation of heats of adsorption and other thermal properties of films on adsorbents simpler than charcoal, a series of measurements has been made of the adsorption of the vapours of benzene, acetone, and methyl alcohol on vitreous silica at temperatures between 70 and 25° C. Previous experience with this adsorbent (Palmer and Clark 1935; Palmer 1937) showed that it was well suited for the purpose, particularly in respect to the very rapid attainment of equilibrium. Complete isothermals at 25° for these vapours up to saturation pressures have already been investigated and recorded (Palmer 1937). The use of vapours rather than gases not only admits of experimental simplicity, but has the further advantage that the free energy of adsorption (or adsorption potential) is immediately calculable from the relative pressure at equilibrium. It is hoped that the selection of substances is representative, in that they are respectively non-polar but polarizable, polar but non-associated, polar and associated. These molecular distinctions appear prominently in the properties of the adsorption films.

EXPERIMENTAL

The preparation of the silica adsorbent, manipulation, and methods of measurement were in principle the same as those previously described, with the following modifications. The volumetric portion of the

apparatus, including the manometer bulbs b_1 and b_2 (fig. 1; cf. Palmer 1937, fig. 1) was housed in an air thermostat T_1 regulated to 42.5° , and the horizontal adsorption tube A immersed in a water thermostat T_2 that could be set at temperatures ranging from 70 to 20° . Connecting tubes were kept at 43° by means of electrically heated wrapping wire. Since there was a maximum temperature difference of only about 20° along the tube t (of 1 mm. bore) and a pressure of vapour never less than about 1 mm., no correction for thermal pressure difference was necessary (see also below, p. 194). The powdered adsorbent weighed about 15 g. and exposed about 7 sq. m. of surface; its exact specific surface was determined by the rate of solution in hydrofluoric acid, as previously described (Palmer and Clark 1935).*

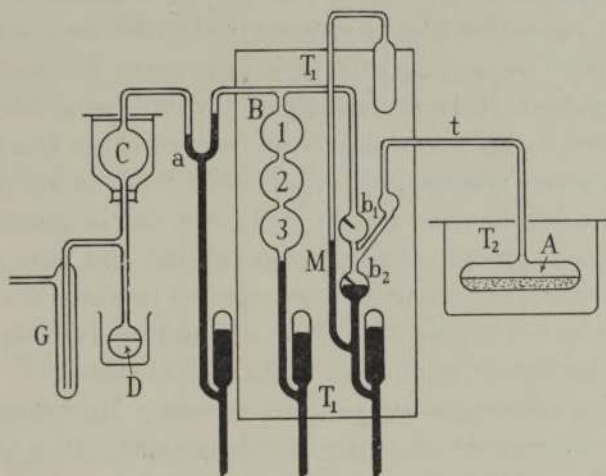


Fig. 1. Apparatus.

The vapour before expansion into the adsorption vessel A was held in the calibrated bulb system B 1, 2 and 3 (of total capacity 40 c.c.), of which one or more of the sections was brought into use depending on the final equilibrium pressure desired: the pressure was read on the manometer M with mercury set to the point b_1 . After expansion into A , the final pressure was read with mercury at b_2 , thus avoiding the disturbance of the temperature equilibrium in the connecting tube and in A , which would take place if mercury were raised again to b_1 before the equilibrium pressure was ascertained. The vessel A was then locked off by raising the mercury to b_1 , and the pressure, now that in the volumenometer, again read before the admission of a further portion of vapour.

As isothermals for different temperatures were to be used to calculate

* The author is indebted to Mrs W. G. Palmer for estimating the specific surface.

the temperature variation of the film properties and the heat of adsorption, it was clearly of crucial importance that the general surface properties, especially the area, should be invariable or that correction should be readily applicable for any changes. To ensure this two alternative methods of experimenting were adopted:

(a) *A bracketing method.* An isothermal at 70° was determined, the last and highest pressure being reached by flooding all the bulbs *B* with mercury. The temperature of the thermostat T_2 was then slowly lowered to 60° and held at that temperature for at least an hour, after which the new and slightly lower pressure was read. The bulbs were then emptied and another point of the 60° isothermal obtained from a second still lower pressure reading. The apparatus was then thoroughly evacuated and the silica heated at 100° *in vacuo* for 2 hr. to remove the last traces of adsorbate, which were collected in *G* by cooling with liquid nitrogen. The isothermal for 50° was next determined, the temperature at the end being first raised to 60° and then lowered to 40° ; two points at each of these temperatures were obtained in the above manner, with confirmation of the 50° points between. After evacuation and heating to 100° as before, the isothermal for 25° was finally determined, giving on rise to 40° at the end two points at that temperature. Sets of experiments were rejected in which the "bracketing" at 40° and 60° was not within 3%. It was found inadvisable to attempt to secure full isothermals at more than three temperatures.

(b) *A method of continuous temperature decrease.* Isothermals for 70° and 30° were first determined in separate experiments. In a third series the silica was first brought to 70° and three points taken at higher pressures to confirm the earlier measurement. The temperature was then lowered to 30° in stages of 10° , being held for at least half an hour at each stage, during which interval two points were registered as in method (a). As the temperature fell, measured amounts of vapour were removed from the system by cooling out with liquid nitrogen, so as to maintain an approximately constant range of relative pressure throughout the series. Finally, the points at 30° confirmed those already found on the full isothermal. Such methods are possible only in adsorption systems in which equilibrium is very rapidly established after change of conditions. Fig. 2 depicts the results of method (b) applied to acetone, by showing the adsorption potential ϕ plotted against the adsorption.

Before adsorption measurements were begun in any series the silica was brought to the required temperature in an atmosphere of about 100 mm. of nitrogen, which was pumped off before admission of vapour. When heated *in vacuo* the badly conducting powder only slowly reaches uniform tem-

perature, and in the absence of precautions such as the above procedure, quite misleading adsorption data may be obtained, especially at the higher temperatures. No detectable adsorption of nitrogen takes place in the temperature range of this work. In using the methods (a) and (b) the pressure of vapour must not fall below about 30 mm. if uniform temperature is to be maintained.

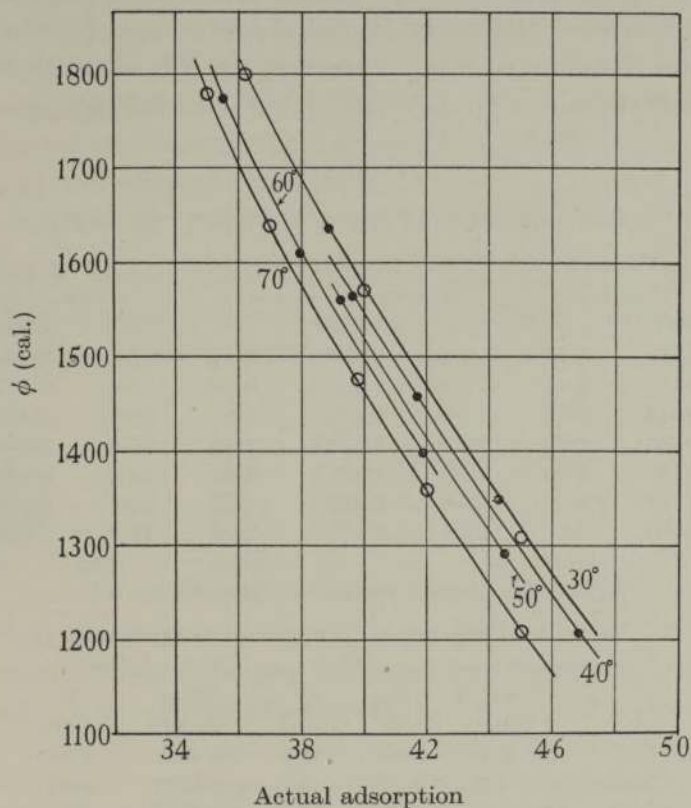


Fig. 2. Acetone.

As the apparatus did not permit the use of higher pressures at 70° than correspond to one layer, the whole work was restricted to this range of adsorption, but the nature of the results obtained leaves little doubt that they can be confidently extrapolated to larger adsorptions. A standard temperature treatment at 100–110° was adhered to in preparing and evacuating the silica; the use of higher temperatures tends to cause some drift in the surface properties. Adsorption potentials for a given adsorption are all rather higher than in the previous work wherein temperatures of about 200° were used. The effective "dead-space" was determined by blank experiments with nitrogen, the volumometer being maintained at 42°

and the adsorption tube at 70° and at 25°; no difference was detectable in the two estimates for these temperatures (which were the extremes used), thus showing that thermal effusion effects were negligible. Special experiments made to estimate the divergence of the vapour of methyl alcohol from the ideal at 42° showed that only very small corrections were involved; it had been shown previously (Palmer 1937) that even at 25° and much higher pressures the corrections for benzene and acetone were negligible.

Table I summarizes the experimental observations. In this table p is the equilibrium pressure in mm. of mercury, ϕ the adsorption potential, and a the adsorption in micromols per sq. m. $\phi = RT \log p_s/p$.

TABLE I

BENZENE. (Actual surface of silica 7.1 sq. m.)

70°: $p_s = 547.4$ mm.			50°: $p_s = 269.0$ mm.			25°: $p_s = 94.0$ mm.		
p	$\log_{10} \phi$	a	p	$\log_{10} \phi$	a	p	$\log_{10} \phi$	a
6.5	3.4835	0.29	3.1	3.4604	0.54	2.5	3.3353	1.34
15.7	3.3872	0.84	7.6	3.3630	0.96	5.6	3.2261	2.25
29.1	3.3043	1.55	15.6	3.2653	1.97	10.1	3.1243	3.18
44.7	3.2358	2.23	29.5	3.1553	2.89	16.9	3.0103	4.26
59.3	3.1837	2.66	42.6	3.0761	3.60	24.6	2.9030	5.23
68.65	3.1541	2.96	63.6	2.9698	4.65	33.6	2.7881	6.30
104.4	3.0562	3.77	94.6	2.8291	5.93	47.2	2.6140	7.99

ACETONE. (Actual surface of silica 7.1 sq. m.)

70°: $p_s = 1190$ mm.			30°: $p_s = 282.7$ mm.		
p	$\log_{10} \phi$	a	p	$\log_{10} \phi$	a
4.1	3.5900	2.05	0.2	3.6432	1.46
13.1	3.4909	2.90	1.6	3.4965	2.96
28.1	3.4094	3.60	5.5	3.3777	4.00
44.0	3.3550	4.05	12.5	3.2762	4.91
71.2	3.2865	4.57	20.75	3.1992	5.65
103.5	3.2244	5.07	27.6	3.1486	6.09
131.6	3.1796	5.65	38.6	3.0808	6.67

METHYL ALCOHOL. (Actual surface of silica 7.2 sq. m.)

70°: $p_s = 927$ mm.			50°: $p_s = 406$ mm.			25°: $p_s = 125$ mm.		
p	$\log_{10} \phi$	a	p	$\log_{10} \phi$	a	p	$\log_{10} \phi$	a
6.3	3.5352	1.21	5.1	3.4520	2.18	1.4	3.4282	2.50
18.1	3.4323	2.23	15.4	3.3256	3.51	5.1	3.2808	4.00
46.9	3.3118	3.40	31.1	3.2206	4.51	11.15	3.1592	5.18
75.2	3.2369	4.16	55.0	3.1116	5.60	20.75	3.0296	6.45
90.8	3.2028	4.52	69.5	3.0575	6.12	28.2	2.9487	7.22
138.5	3.1159	5.36	103.85	2.9453	7.23	41.5	2.8182	8.60

DISCUSSION

The following symbols will be used, in addition to those already mentioned in connexion with Table I:

θ = fraction of surface covered.

A = area per molecule (Angstroms).

(A) = fictitious area per mol. for film of more than one layer.

s = slope of $\log_{10} \phi$, a lines.

F = lateral force (dynes cm.).

α = thermal expansion of film [$\partial \log A / \partial T$].

α' = thermal expansion of bulk phase [$\partial \log V / \partial T$].

β = compressibility of film [$\partial \log A / \partial F$].

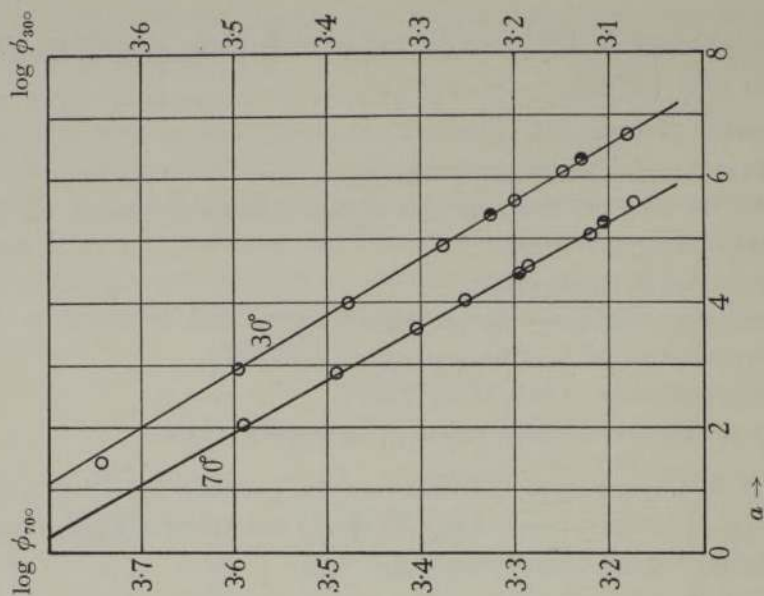
β' = compressibility of bulk phase [$\partial \log V / \partial P$].

(1) As figs. 3, 4 and 5 show, a linear relation between $\log \phi$ and a is well maintained at all temperatures. Table II shows the value of $\log \phi_0$ obtained by extrapolating the separate lines to $a = 0$.

TABLE II

	25°	30°	50°	70°
Benzene	3.476	—	3.475	3.475
Acetone	—	3.824	—	3.820
Methyl alcohol	3.690	—	3.680	3.660

ϕ_0 , which is of course independent of the evaluation of the surface area, is seen from this table to be also independent of temperature for benzene and acetone. A linear relationship between $\log \phi$ and a does not in fact extend to $a = 0$ for the powdered adsorbent (Palmer and Clark 1935, p. 377): an upward trend near $a = 0$ is already noticeable in the benzene diagram (fig. 3). A previous suggestion (Palmer 1937, p. 263) that this divergence is attributable to surface inhomogeneity and would probably not be shown by an ideal plane surface is supported by this new evidence that ϕ_0 is independent of T , which can hardly be accidental. On the other hand, for methyl alcohol the apparent change of ϕ_0 with T is well outside experimental error. This is regarded as abnormal behaviour, and is explained by association in the film (p. 200 below). Fig. 2, which shows the results of experimental method (b) applied to acetone, indicates that at least for this substance the value of $-\partial \phi / \partial T$ increases somewhat with rise of temperature, but the inevitable experimental error renders a quantitative estimate of the variation uncertain. It may be assumed that for films on silica, where no association or other chemical change occurs in the film,



● Observation of method *b* (p. 192).

FIG. 4. Acetone.

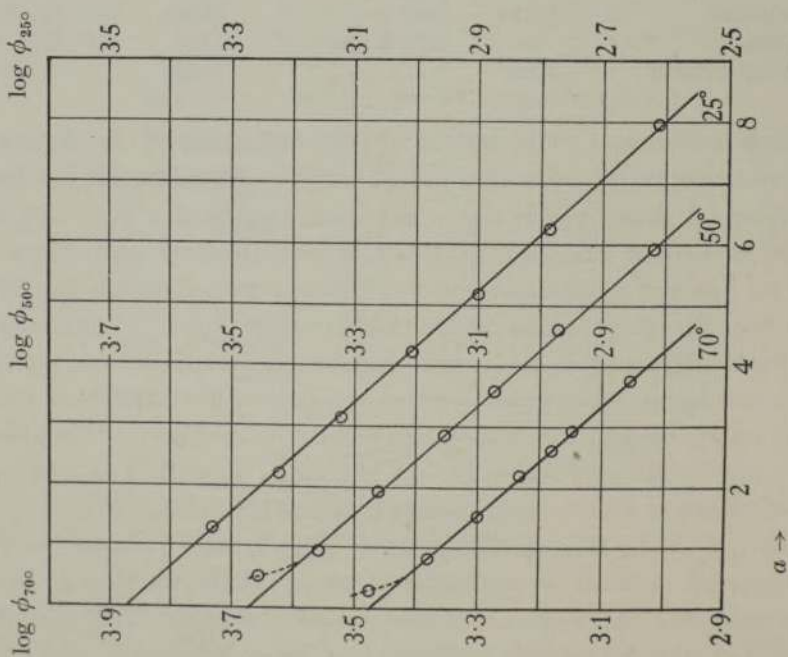


FIG. 3. Benzene.

the isothermals can be represented by straight $\log \phi$, a lines radiating fan-wise from a common origin ϕ_0 , the slope of the lines increasing with increase of temperature (i.e. $[\partial \phi / \partial T]_a$ negative).

(2) *The thermal expansion of the film.* We define the thermal expansion α_ϕ by

$$\alpha_\phi = [\partial \log s / \partial T]_\phi = -[\partial \log a / \partial T]_\phi = [\partial \log A / \partial T]_\phi.$$

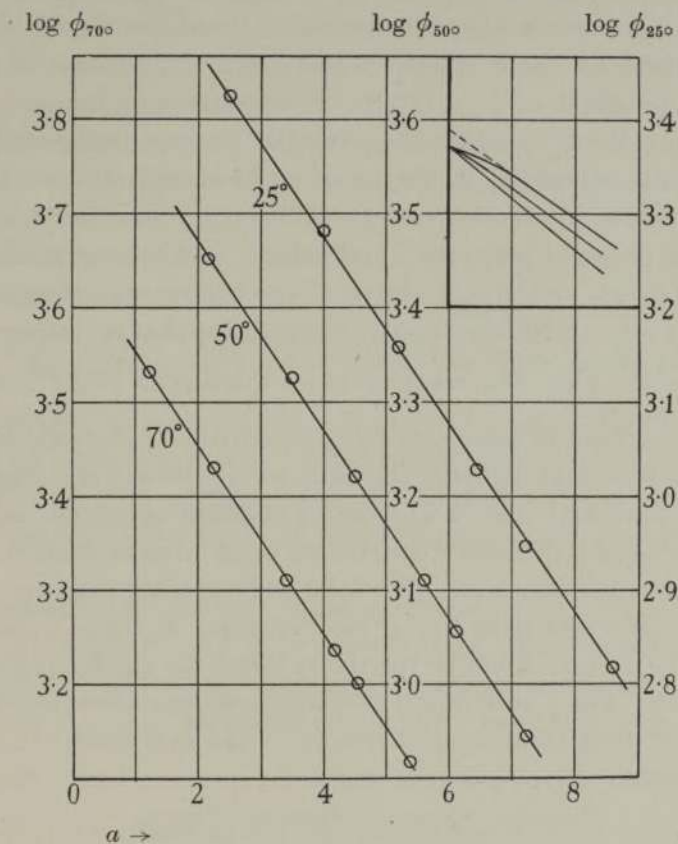


FIG. 5. Methyl alcohol.

TABLE III

	Slope of $\log \phi$ line at				Mean α	α' (liquid, at normal pressure)
	25°	30°	50°	70°		
Benzene	0.1058	—	0.1079	0.1100	0.00090	0.00117
Acetone	—	0.1115	—	0.1185	0.00152	0.00132
Methyl alcohol	0.1080	—	—	—	—	—

For benzene and acetone α is independent of a , but, as fig. 2 suggests, probably rises with increase of temperature. The values of α agree in mag-

nitide with those found by Polanyi and Goldmann (1928) and by Coolidge* in their work on charcoal adsorption of vapours, but their evidence on the dependence of α on a and T is conflicting. Thus Coolidge's data give $\alpha_{100^\circ}^{50^\circ}$ nearly independent of a for benzene and CCl_4 , and $\alpha_{60^\circ}^{0^\circ}$ independent of a for $(\text{C}_2\text{H}_5)_2\text{O}$. Neither of these authors investigated acetone; for adsorbents other than those mentioned their results fluctuate irregularly. Coolidge's data give $\alpha_{150^\circ}^{60^\circ} = 0.0013$ for benzene for a range of ϕ from 6000 to 3000 cal.

In attempting to elucidate the physical state of the film by comparison of its properties with those of liquids and compressed gases, account must be taken of the effect of orientation of permanent or induced dipoles in the surface field. We may regard the potential ϕ as consisting of three terms, $\phi = \phi_0 - E_i - E_T$, where E_i is the interaction energy due to orientation, and E_T the thermal interaction energy. If we imagine a film in equilibrium with a vapour phase at pressure p and confined on the surface by a lateral barrier which exerts on the film a force F , the barrier may be moved inward isothermally while p is simultaneously increased so that no vapour molecules leave or enter the film. The work done on the film is $\int F dA = \Delta E_i + \Delta E_T$.

Now if the adsorbate is non-polar but has isotropic polarizability ΔE_i will not depend on temperature, since the induced dipoles will maintain positions of minimum potential energy in spite of thermal agitation; with a polar substance, however, thermal disturbance must always tend to give fluctuations between positions of potential energy greater than the minimum, and ΔE_i must increase with rise of temperature. It follows that $(\partial\phi/\partial T)_a$ and therefore $\partial \log s/\partial T$ must be relatively larger for a polar than for a non-polar adsorbate. For a bulk liquid or compressed gas where no surface field imposes orientation these special effects would not exist. In agreement with these views

$$\alpha_{\text{acetone}} - \alpha_{\text{benzene}} > \alpha'_{\text{acetone}} - \alpha'_{\text{benzene}}$$

A striking example of the marked effect of dipole moment upon thermal expansion in a film is furnished by methyl alcohol where in contrast with benzene and acetone the film shows at first a large expansion that, however, decreases rapidly with increasing ϕ :

Thermal expansion of methyl alcohol films (50–70°)

ϕ (cals.)	α	
3000	0.0022	
2000	0.0013	$[\alpha' = 0.00113]$
1000	0.0010	

* Polanyi and Goldmann (1928) calculate and quote values of α obtained from the data of Coolidge, who did not himself make the calculations.

Later discussion (p. 203 below) will indicate that molecular association in this film at low values of a greatly strengthens the normal (monomeric) dipole, a behaviour reflected in the high initial value of α . Coolidge's data also give $\alpha_{50^\circ}^0 = 0.0023$ for $\phi = 3000$ for the alcohol on charcoal.

There is certainly a general agreement in the order of magnitude of α and α' but it is doubtful whether for this reason alone the film can be considered to be in the liquid state (cf. Polanyi and Goldmann 1928). While there exists no rational method of correlating F with the hydrostatic pressure P in dynes cm.², it is generally agreed that P is of the order 100–1000 atm. and must increase rapidly with a . Now data for bulk liquids show that α' decreases markedly with increase in pressure, but is little influenced by temperature, while for films of benzene or acetone the above data suggest an exactly contrary behaviour.

From the integrated expression for F previously given (Palmer 1937) it is easily seen that

$$(FA)_\phi = g[(\phi_0 - \phi)/c - \bar{\phi}] = \text{constant, independent of } T,$$

where g converts to suitable units, and $c = \log \phi_0/\phi$. If therefore points are chosen on isothermals such that $\phi = RT \log p_s/p$ has a constant value a simple Traube type of expression connects F with A at such points. Hence $-(\partial \log F/\partial T)_\phi = \partial \log A/\partial T$, and F_ϕ decreases with rise of temperature.

(3) *Compressibility (β) and value of $[d \log F/\partial T]_a$.* A comparison of $\partial \log F/\partial T$ as a function of F with $\partial \log P/\partial T$ as a function of P in the bulk phase avoids the difficulty of relating P to F ; with the same advantage we may compare β and β' as functions of these variables respectively. For a perfect gas $\partial \log P/\partial T = \frac{1}{T} \sim 0.003$, while calculation from Pv data for CO₂ under high pressure* shows that under such conditions this coefficient is much greater, but decreases with increasing pressure, being, at 25°, 0.035 for 170 atm. and 0.014 for 860 atm. Table IV gives values for an acetone film at 30°.

TABLE IV

θ	F	$\partial \log F/\partial T$
0.2	5	0.00235
0.4	18	0.00122
0.6	35	0.00077
0.8	51	0.00043

* *International Crit. Tables*, 3, 11.

The values of the coefficient tend at low θ towards that for a perfect gas and are all much less than those for compressed CO_2 , but they show, like CO_2 , a marked fall with increasing F .

For a gas under low pressure $\beta' = -1/p$, and for CO_2 between 200 and 1000 atm. $-\beta' = 0.4/p$;* for the gaseous state we may thus assume an approximately linear relation between $-\beta'$ and p^{-1} . For acetone in bulk $-\beta' = \text{const.}/p^{0.32}$ for P between 250 and 1500 atm.; for benzene the very similar relation $-\beta' = \text{const.}/p^{0.30}$ holds for P between 200 and 600 atm.† For both liquids the index to p lessens at lower pressures. When $\log \beta$ is plotted against $\log F$ for benzene films we find a slope of unity up to $A = 50$ and $F = 7$ dynes, and then a rather sudden change of slope to 0.55, which remains nearly constant to $(A) = 15$ and $F = 40$ dynes; for acetone films the result is the same, except that the change of slope occurs at 18 dynes, but this is not surprising as acetone develops a higher force than benzene. We have thus for the films $-\beta = \text{const.}/p^n$, where $n = 1$ for $\theta < 0.5$ and $n = 0.55$ for greater θ . The state of the film revealed by these data is more nearly akin to that of a compressed gas than that of a liquid.

(4) *Heats of adsorption.* (a) *Benzene and acetone.* For these adsorbates, $\log_{10} \phi = \log_{10} \phi_0 - sa = \text{const.} - sa$

$$-T(\partial\phi/\partial T)_a = T\phi a(\partial s/\partial T) \times 2.306$$

$$L_a = L + \phi - T(\partial\phi/\partial T)_a,$$

where L = the molar latent heat of evaporation of the bulk liquid at T° . $(dH/da)_a = L_a$ = the heat liberated when 1 g. mol. of vapour is adsorbed from a large volume of vapour in equilibrium with a film of indefinitely large extent and already containing a micromols. adsorbate per sq. m.

$L_a - L = \phi - T(\partial\phi/\partial T)_a$ has been termed the heat of wetting (Polanyi) or the nett heat of adsorption (Coolidge). For the three substances concerned in the present work $\partial\phi/\partial T$ is negative at all values of a , and therefore $L_a - L$ is greater than ϕ . In calculating, a mean value of $\partial\phi/\partial T$ for the temperature range has been used.

(b) *Methyl alcohol.* For this substance the slopes of the $\log \phi$, a lines are very nearly the same at all temperatures, and the principal consideration is $\partial\phi_0/\partial T$. As mentioned above the apparent ϕ_0 decreases with rise of temperature (Table II). The reason for this is suggested by earlier work (Palmer and Clark 1935; Palmer 1937, p. 256), where it is shown that in

* *International Crit. Tables*, 3, 11.

† *International Crit. Tables*, 3, 36 and 42 resp.

the first part of the adsorption of methyl and ethyl alcohols $\log \phi$ decreases more slowly than in the ultimate linear relation with a , an effect then attributed to association in the film, and one which would be expected to diminish in importance rapidly with rise of temperature. We may conclude that the true ϕ_0 is near to the value ($\log \phi_0 = 3.660$) given by extrapolating the $\log \phi$ line for 70° , and that the lines for 50 and 25° undergo increasing curvature towards this common value as a tends to zero (represented diagrammatically in the inset to fig. 5). In support of this view the heat of

TABLE V. HEATS OF ADSORPTION

ϕ	$T(\partial\phi/\partial T)$	$L_a - L$	L_a	θ
BENZENE. $L = 8050$ cal.				
2990	0	2990	11,140	0.0
2512	130	2642	10,692	0.1
2120	237	2357	10,407	0.2
1784	276	2060	10,110	0.3
1503	310	1813	9,863	0.4
1267	326	1593	9,643	0.5
1068	330	1398	9,448	0.6
898	324	1222	9,272	0.7
757	312	1069	9,119	0.8
637	296	933	8,983	0.9
537	277	814	8,864	1.0
ACETONE. $L = 7710$ cal.				
6640	0	6640	14,350	0.0
5540	465	6005	13,715	0.1
4620	775	5395	13,105	0.2
3859	949	4808	12,518	0.3
3220	1080	4300	12,010	0.4
2688	1126	3814	11,524	0.5
2240	1130	3370	11,080	0.6
1873	1099	2972	10,682	0.7
1560	1050	2610	10,320	0.8
1305	986	2291	10,000	0.9
1089	913	2002	9,712	1.0
METHYL ALCOHOL. $L = 8946$ cal.				
4570	0	4570	13,516	0.0
3470	2100	5570	14,516	0.2
2630	2190	4820	13,766	0.4
2239	1862	4101	13,047	0.5
1910	1580	3490	12,436	0.6
1622	1349	2971	11,917	0.7
1380	1150	2530	11,576	0.8
1175	977	2152	11,098	0.9
1000	832	1832	10,778	1.0

adsorption shows an initial rise, which has been shown theoretically to indicate negative interaction energy in the film. For the purposes of calculation the initial part of the $25^\circ \log \phi$ line is taken as given in form by the earlier work, and the 70° line as linear right up to $a = 0$. The values of the heat of adsorption in the neighbourhood of its maximum are thus only approximate, but there appears to be no doubt of the existence of the maximum.

The heats of adsorption are somewhat lower and more differentiated according to the type of substance than those found with vapours and charcoal: Pearce and McKinley (1928) find by direct calorimetry at low adsorptions the approximate values, benzene 17,000 cal., acetone 16,000 cal., methyl alcohol 16,800 cal.

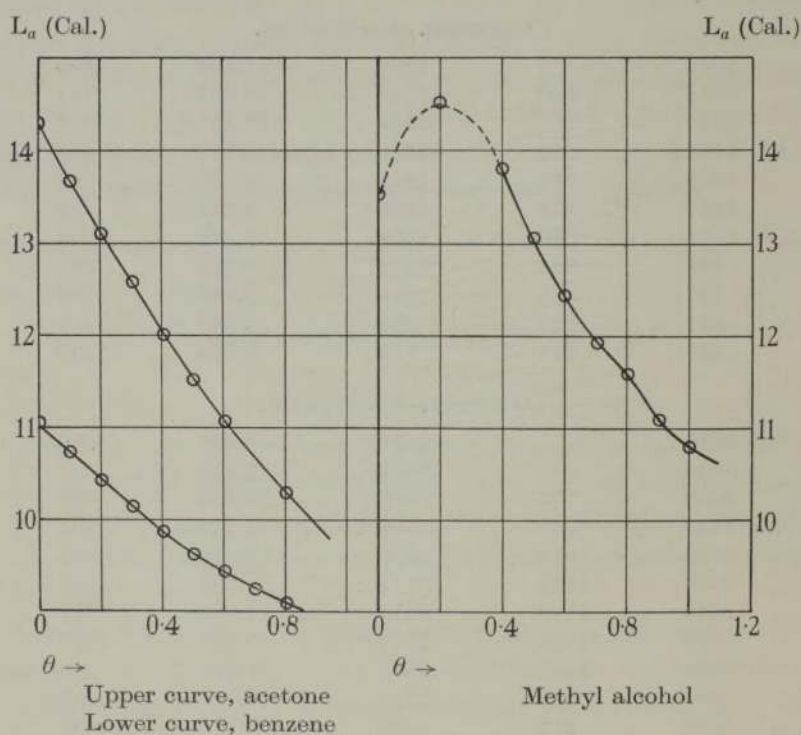


FIG. 6

It will be seen from fig. 6 that the heat for benzene and acetone decreases in nearly linear relation to θ up to $\theta \sim 0.5$: the slight divergence from a straight line is within the limits of error in determining $T \partial \phi / \partial T$. Such a relation between L and θ is in accordance with the recent calculations of J. S. Wang (1938) when the interaction energy is small (less than $kT/4$), but it may be doubted whether the vitreous silica surface presents the orderly array of sites for adsorption that Wang's calculation presumes.

In our case, where more than one layer can be built up, it seems very probable that at $\theta \sim 0.5$ a second layer begins to be formed owing to the increasing difficulty of entering the first layer against the interaction forces. Ultimately at higher pressures the first layer will gradually fill. It is significant that at $\theta \sim 0.5$ the relation of the compressibility β to F changes rather sharply (p. 200 above) and also the form of the equation of state for the film alters (Palmer 1937).

In connexion with the heat curve for methyl alcohol it is interesting to note some recent measurements of the molecular polarization of dissolved alcohols (Wolf and Herold 1934; Hennings 1935; Romanov and Eltzin 1937) where it is proved that the process of association may lead to a large increase of dipole moment, which is especially marked with methyl alcohol. As the potential ϕ is thought to depend on μ^2 (Palmer 1937, p. 265), if the moment of a dimeric complex is greater than that of a simple molecule by 50% the potential for the complex will be greater than the sum for two simple molecules, and the curvature of the $\log \phi$ line is explained. The maximum value in the polarization curves for the dissolved alcohols decreases more rapidly than in proportion to $1/kT$, which is in agreement with the rapid loss of curvature in the $\log \phi$ lines with rise of temperature.

There do not appear to be any comparable observations for methyl alcohol on other adsorbents. Neither Pearce and McKinley (1928) nor Coolidge (1924) provide data for calculation in the range of adsorption where a maximum might have been expected. Kruyt and Modderman (1930) from the experiments of Ray (1925) on adsorption of N_2O_4 — NO_2 mixtures on silica gel, where association might well be expected, find a marked maximum in the heat when calculating from isothermals at 15 and 57°, but only a steady fall when those at 57 and 80° are used. The data of Wolf and Herold indicate that the polarization falls very rapidly from the maximum on the side of higher concentration, and we may assume a correspondingly rapid fall of mean moment in the adsorption film. Wang (1938) does not consider the case of increasing moment nor of actual chemical association, but shows semi-quantitatively that a rapid decrease of moment would lead to inflexions in the heat curve, such as is actually seen in fig. 6 (methyl alcohol) at $\theta = 0.8$.

(Added 28 July 1938.) The relation of the heat of adsorption dH/da to the amount adsorbed, which in the absence of association may be expressed in the form $d^2H/da^2 = -f(1/a)$, where $f'(a)$ is positive, is in good qualitative agreement with the earlier investigations of Coolidge (1924), and especially with those of Polanyi and Goldmann (1928), on the adsorption of vapours

upon charcoal, although in the latter the complex relation between $\log \phi$ and a rendered extrapolation to $a = 0$ impossible. Bangham and Mosallam, in a recent communication (1938*b*), report that dH/da for benzene and methyl alcohol on surfaces of mica differs little from the normal latent heat when the adsorption has reached greater amounts than correspond approximately to one molecular layer, a result corroborated in Table V above. They also find 12,000 cal./mol. and 13,400 cal./mol. respectively for the initial heats of adsorption of benzene and methyl alcohol, with which our estimates of 11,140 cal./mol. and 13,520 cal./mol. are in excellent agreement, in spite of the different nature of the surfaces, but they claim that these values are maintained nearly constant throughout the formation of the first layer, and then fall abruptly. In the case of benzene their isothermals exhibit even in the first layer most marked discontinuities in slope, on the significance of which they lay some stress. Now it appears to the writer that the evidence so presented is conflicting, as the discontinuities must imply some kind of interaction between the adsorbed molecules, since heterogeneity of surface is not likely to lead to breaks except in the unlikely case of micro-surfaces associated with very widely separated "levels" of adsorption energy, and such interaction is incompatible with a constant heat of adsorption.

In an earlier paper (1938*a*) Bangham and Mosallam show that the benzene and methyl alcohol isothermals conform at low pressures to a simple Langmuir formula, and associate this with the constant heat of adsorption. However, an inspection of the literature reveals that, from an experimental standpoint, a decreasing heat of adsorption is by no means incompatible with a simple Langmuir formula (i.e. with only two constants). Thus Zeise (1928) showed that Titoff's data (1910) for adsorption of CO_2 , NH_3 and N_2 on charcoal (outgassed at 550°) over a wide range of temperature fit simple Langmuir expressions with exactness over the whole range of pressure used by Titoff; from this we may conclude that only unimolecular layers are concerned. McBain and Britton (1930) have fully confirmed the agreement for nitrogen with pressures rising to 60 atm. Titoff's own direct calorimetric measurements, however, showed (1910) that the heats of adsorption of these gases decreased steadily as follows throughout the range of pressure used: CO_2 , 8100–6400 cal./mol.; NH_3 , 11,000–7000 cal./mol. and N_2 , 8000–4000 cal./mol. These changes are all fully confirmed by indirect calculation from Titoff's isothermals (Kruyt and Modderman 1930). Magnus and Kälberer (1927), using charcoal outgassed at 600° , found the heat for CO_2 to fall steadily from 12,500 cal./mol. at very small pressures and adsorptions to 6720 cal./mol. at higher pressures. It seems clear from these and other

similar experimental facts that the Langmuir formula is not actually restricted either to a plane surface or to cases of constant heat of adsorption, which as a matter of fact appear to be rare. The constant c_2 in the formula $a = c_1 c_2 p / (1 + c_2 p)$ depends on the ratio $\alpha / e^{-L_a/RT}$, where α is the "accommodation coefficient" for the condensation process, and the constancy of c_2 means that α must vary rapidly with a (and θ) to compensate the change in L_a .

(Note added in proof.) In a note in their paper (1938*b*) Bangham and Mosallam refer to the work of Palmer and Clark (1935), and no doubt by an oversight in which specific surface was confused with actual working surface are led to an erroneous statement about the area of our silica powder. We used ca. 15 g. of powder of specific surface ca. 5000 cm.², giving a total working surface of ca. $15 \times 5000 = 75,000$ cm.², which is almost exactly four times the area of the mica used by Bangham and Mosallam, and not one-quarter of their surface as stated in the note.

SUMMARY

1. Isothermals have been obtained at temperatures between 70 and 25° for adsorption of the vapours of benzene, acetone and methyl alcohol on known surfaces of vitreous silica, by methods giving a check on the constancy of the surface condition.

2. The values of the coefficients of thermal expansion, compressibility and the temperature variation of the lateral force have been calculated and discussed in relation to parallel properties of the bulk phase.

3. The heats of adsorption have been calculated from the temperature variation of the adsorption potential. Their relations to the fraction of surface covered are in agreement with theoretical predictions for films with interaction energy.

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The rates of transformation in ethyl alcohol of ammonium and ethylammonium cyanates to the corresponding ureas

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In aqueous and aqueous ethyl alcoholic solutions ammonium and alkylammonium cyanates seem to be converted to the corresponding ureas by a reversible bimolecular mechanism associated primarily with univalent ammonium (or alkylammonium) and cyanate ions. Thus, if C_A and C_B are the concentrations of the ionic reactants A and B , based on the conception of complete dissociation, and the reverse reaction is negligible, the velocity v of the forward reaction is represented by the equation, $v = k_0 C_A C_B F$, where k_0 is the velocity constant, and F is a reaction kinetic factor which is at least qualitatively represented by $f_A f_B / f_X$, as defined by Brönsted (1922). f_A , f_B and f_X represent, respectively, the activity coefficients of the reactants and a critical complex X , which, in our case, is a neutral molecule of which the activity coefficient may be taken to be unity. For example, when the logarithm of k_C , the so-called velocity constant determined experimentally at various concentrations from the equation $v = k_C C_A C_B$ ($k_C = k_0 F$), is plotted against the square root of the average ionic strength (here, simply the average concentration) of the interval to which it refers, a curve is obtained which at low concentrations approximates to the linear relationship required by the Debye-Hückel theory. Miller (1934, 1935) showed this for methylammonium cyanate in water and in 98.1 % aqueous