

*XLIV.—The Adsorption of Benzene Vapour on the Plane Surfaces of Glass, Fused Quartz, and Platinum. The Isosteric Heat of Adsorption of Benzene on Platinum.*

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It has been previously shown that water vapour is strongly adsorbed on various surfaces at pressures above 95% of saturation (McHaffie and Lenher, J., 1925, **127**, 1559; Lenher, J., 1926, 1785).

The method of measuring the adsorption of benzene on the several surfaces is that described in the above two papers. It consists in obtaining measurements of the change of pressure with temperature

of a vapour at constant volume, using the inside surface of the constant-volume vessel as the adsorbing surface. The following modification was, however, made in the apparatus: the bulb containing the benzene was placed outside the thermostat and a mercury-sealed vacuum-tight tap was used to close it from the apparatus instead of a mercury trap as before.

In all experiments, the adsorption vessel was baked out in a high vacuum immediately before each determination. A furnace consisting of a copper tube wound with nichrome wire and asbestos sheeting was slipped over the adsorption chamber and fixed in position so that the entire tube from the top to the tip of the pointer could be uniformly heated. The furnace was slowly brought to the maximum temperature, which was maintained for 2—3 hours while the vessel was constantly evacuated to  $1 \times 10^{-6}$  cm. The experiment was then begun as soon as the tube had cooled to room temperature.

The benzene used was Kahlbaum's "thiophene-frei" brand. After a thorough drying over phosphorus pentoxide, the benzene was tested for thiophen and gave a negative result. The benzene was distilled after being frozen out twice, the fraction passing over from  $80.15$ — $80.20^\circ$  (standard thermometer) being used. Determinations of the vapour pressure of this benzene gave results agreeing well with those of Dejardin (*Ann. Physique*, 1919, **11**, 253). The saturation pressures determined experimentally agreed excellently with values of the pressure calculated from Dejardin's equation for the vapour pressure of benzene at temperature  $t$ ,  $\log p = 0.87476 + 0.020670(t - 20) - 755 \times 10^{-7}(t - 20)^2 + 16.5 \times 10^{-8}(t - 20)^3$ .

The mercury-sealed tap between the bulb of benzene and the adsorption apparatus, and the tap between the vacuum pumps and the adsorption apparatus in the thermostat, were lubricated with metaphosphoric acid prepared by the method of Chapman and Gee (*J.*, 1911, **99**, 1726). In the experiments with a silica vessel, the glass-silica ground joint was lubricated with phosphoric acid before sealing with mercury. The glass, quartz, and platinum adsorption tubes were those used in the earlier parts of this research.

#### *The Adsorption of Benzene Vapour on a Glass and on a Fused Quartz Surface.*

Before each experiment, the glass tube was baked out at  $250^\circ$  for 3 hours in high vacuum. Every experiment was done in its entirety at least twice, once from the side of increasing temperature and once from the side of decreasing temperature, to test the complete reversibility of the adsorption equilibrium. This applies also to the experiments with silica and platinum.

In calculating the number of molecules adsorbed per sq. cm. of



The results show that the equilibrium film which will just exert the saturated vapour pressure of benzene remains of practically constant thickness over the temperature range. The first reading in each series gives the data for this equilibrium film at the saturation pressure. The very low values for the decrease in free energy of the benzene on undergoing adsorption show how little affinity there is between benzene vapour and a glass surface. The data show that adsorption of benzene is measurable only over a temperature range of  $0.8^\circ$  from the saturation temperature, and that the equilibrium pressures of the loosely-held benzene films are practically the saturated vapour pressures. For comparison of these data with other adsorption work, one should consider the figures for the number of molecules adsorbed per sq. cm., for the apparently high values of  $\theta$  are apt to be misleading, the large results being due to the size of the benzene molecule itself and not to a relatively great adsorption.

The quartz vessel was baked out at  $500^\circ$  for 2 hours in a high vacuum before each experiment. The amount of adsorption was found by use of the equations  $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3.395 \times 10^{18}$ , and  $\theta = (p/T - p_1/T_1) \times 1.252 \times 10^4$ . The data of five experiments measuring the adsorption of benzene vapour on a pure silica surface are given in Table II.

TABLE II.  
Benzene-Silica.

No. 1.					No. 3.				
<i>T</i> K.	<i>p</i> .	$N/\text{cm.}^2$ $\times 10^{-14}$ .	$\theta$ .	$-\Delta F$ .	<i>T</i> K.	<i>p</i> .	$N/\text{cm.}^2$ $\times 10^{-14}$ .	$\theta$ .	$-\Delta F$ .
292.0°	71.46	93.48	32.5	0.0	295.3°	83.25	68.21	23.8	0.0
292.2	71.73	64.73	22.5	3.6	295.4	83.61	28.76	10.0	2.7
292.5	72.14	25.16	8.7	8.4	295.6	83.80	14.38	5.0	6.4
292.8	72.37	7.19	2.5	14.9	295.8	84.00			
293.0	72.46				296.0	84.04			
294.0	72.75				298.0	84.94			
296.0	73.23								
No. 2.					No. 4.				
294.0	78.67	71.90	25.0	0.0	297.8	93.62	64.73	22.5	0.0
294.2	78.95	43.14	15.0	2.8	298.0	93.98	28.76	10.0	4.2
294.4	79.20	21.57	7.5	6.4	298.5	94.38			
294.6	79.44				299.0	94.55			
294.8	79.51				300.0	94.98			
295.0	79.56				301.0	95.30			
297.0	80.11								
No. 5.									
					301.6	111.44	61.11	21.2	0.0
					301.7	111.73	32.35	11.2	0.8
					302.0	111.92	21.57	7.5	8.1
					304.0	112.84			
					306.0	113.52			

These experiments show that the amount of adsorption decreases as the pressure and temperature are increased. This means that the temperature coefficient of desorption is greater than the pressure coefficient of adsorption. The magnitude of the adsorption of benzene on quartz is seen to be almost identical with the measured values for the adsorption on glass (Table I). This is to be expected, for the unsaturated surface forces from glass and from pure silica must be essentially the same as regards their strength in attracting and adsorbing such an indifferent vapour as that of benzene.

The test applied previously of allowing the apparatus to stand at constant temperature (such that adsorption is taking place) for 24 hours or longer, to determine if the equilibrium set up was a stable one, was applied repeatedly in the above experiments. In one experiment (Table II, No. 5), the apparatus was allowed to stand at constant temperature for 4 days; the pressure read at the end of this period was within 0.02 mm. of the initial reading. The equilibrium set up is therefore stable, and over a period of many hours there is no tendency for benzene to penetrate into the bulk of the solid.

*The Adsorption of Benzene Vapour on Platinum.*

The platinum adsorption tube was made by Messrs. Johnson, Matthey and Co. from burnished seamless platinum tubing. The rounded top end of the tube (see McHaffie and Lenher, *loc. cit.*, p. 1561) was closed by hammering the tube while hot. Before the constricted bottom end was added, the inside of the tube was given a high polish with rouge and chamois. When the narrow bottom end was put on, the tube was filled with rosin to protect the polished surface. After the smaller connecting tube had been worked on to the main adsorption vessel and the rosin had been removed, the inside surface was given a light polish and was carefully cleaned chemically before use.

The equations giving the adsorption are  $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3.359 \times 10^{18}$  and  $\theta = (p/T - p_1/T_1) \times 1.169 \times 10^4$ . The tube was baked out at 300° for 2 hours in a high vacuum before each experiment. Table III gives a few of the results of 12 experiments measuring the adsorption of benzene vapour on platinum. It is noteworthy that the adsorption is much greater on platinum than on the surface of silica or glass.

It would have been interesting to continue the experiments at temperatures above 32°, but as the apparatus used was limited to measurements of less than 130 mm., determinations of adsorption at higher temperatures and pressures have been postponed. The results in Table III show that from 295°K. to 300°K. the amount of benzene vapour adsorbed on a platinum surface at the saturation

TABLE III.  
Benzene-Platinum.

No. 1.					No. 7.				
<i>T</i> K.	<i>p</i> .	$N/cm.^2$ $\times 10^{-14}$ .	$\theta$ .	$-\Delta F$ .	<i>T</i> K.	<i>p</i> .	$N/cm.^2$ $\times 10^{-14}$ .	$\theta$ .	$-\Delta F$ .
295.4°	83.84	346.0	120.5	0.0	299.2°	100.02	453.4	157.8	0.0
295.6	84.50	275.4	95.9	1.5	299.4	100.78	379.6	132.1	1.6
295.8	84.96	231.7	80.7	3.9	299.6	101.66	285.5	99.4	1.9
296.0	85.60	164.6	57.3	4.8	299.8	102.42	211.6	73.6	2.0
296.5	86.28	104.2	36.2	14.0	300.0	102.98	151.1	52.6	4.2
297.0	86.88	53.74	18.7	23.5	300.5	103.92	60.47	21.0	12.1
298.0	87.47				301.0	104.35	26.87	9.3	23.3
299.0	87.91				302.0	104.90			
301.0	88.75				303.0	105.44			
					304.0	105.86			
No. 3.					No. 8.				
295.6	84.60	366.0	127.4	0.0	299.9	103.06	456.7	159.0	0.0
295.8	85.20	305.6	106.4	2.3	300.0	103.46	403.7	143.8	1.5
296.0	85.96	225.1	78.3	2.4	300.2	104.24	335.9	116.9	2.7
296.3	86.79	137.7	49.0	4.3	300.5	105.19	241.8	84.1	5.8
296.5	87.23	97.40	33.9	7.6	301.0	106.52	110.9	38.5	11.0
297.0	87.90	36.95	12.8	13.2	302.0	107.62	30.23	10.5	31.8
297.5	88.23	30.23	10.5	28.8	303.0	108.17			
298.0	88.46				304.0	108.60			
301.0	89.46				305.0	109.10			
303.0	90.17								
No. 5.					No. 9.				
296.4	87.93	382.9	133.3	0.0	301.3	109.95	399.6	139.1	0.0
296.5	88.19	349.3	121.6	1.1	301.5	110.82	315.7	109.9	0.9
296.7	88.79	309.0	107.5	2.8	301.8	111.77	221.6	77.1	3.7
297.0	89.70	201.7	70.1	4.6	302.0	112.37	161.3	56.1	5.8
297.5	90.55	124.3	43.2	12.8	302.5	113.34	77.25	26.8	13.4
298.0	91.25	60.47	21.0	21.8	303.0	113.74	50.38	17.5	25.3
299.0	91.93	20.15	7.0	44.8	304.0	114.42			
300.0	92.35				305.0	114.96			
301.0	92.69				306.0	115.46			
303.0	93.45								
No. 12.					No. 12.				
304.0	123.85	268.7	93.5	0.0	305.5	126.72	20.16	7.0	35.8
304.1	124.21	235.1	81.8	1.5	306.5	127.30			
304.3	124.85	171.3	59.6	3.2	308.0	127.99			
304.5	125.22	151.1	52.6	7.6	310.0	128.92			
305.0	126.08	68.73	23.3	12.9					

pressure increases with increasing temperature and pressure; and that from 300°K. to 305°K., and perhaps above 305°K., the adsorption falls off rapidly with rising temperature and pressure.

The strikingly large adsorption of benzene on platinum is of great interest, for it is from 5 to 7 times greater than that on glass or silica, and it is slightly greater at certain temperatures than the adsorption of water on silica or platinum.

*The Isosteric Heat of Adsorption of Benzene Vapour on Platinum.*

The isosteric molar latent heats of adsorption may be calculated from the equation  $L = RT^2 d \log p_\theta / dT$  from the measurements of

pressure, temperature, and amount adsorbed given in Table III, where  $L_\theta$  is the isosteric molar latent heat of adsorption at constant pressure,  $p_\theta$ , and constant amount adsorbed,  $\theta$  (see Lenher, *loc. cit.*, p. 1790; Coolidge, *J. Amer. Chem. Soc.*, 1926, 48, 1795). Values of  $L_\theta$  for several isotherms at different amounts adsorbed are given in Table IV.

TABLE IV.  
 $L_\theta$  (cals. per mol.).

$\theta$ .	297° K.	297.5° K.	298.5° K.	299° K.	299.5° K.	300° K.	301° K.	302° K.
20	—	8440	7790	8070	8790	—	—	—
40	8890	9330	—	8050	8040	—	8140	8190
60	9050	—	8430	—	—	8300	—	—
80	8890	—	8280	—	—	8240	—	8200
100	8450	—	8210	—	—	8000	—	8180
120	8640	—	8110	—	—	—	—	—

The latent heat of condensation of benzene at constant pressure from saturated vapour to liquid varies from 8083 cal. per g.-mol. at 296°K. to 7968 cal. per g.-mol. at 304°K. The isosteric heats of adsorption given above are, within the limits of the accuracy of integration, little different from the latent heats of condensation at the same temperatures. This is in agreement with the results of Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, 42, 1146), who measured the "net" heats of adsorption of many organic liquids on charcoal and found that  $L_\theta$  was of about the same magnitude as the heat of condensation to liquid. Lamb and Coolidge concluded, from considerations of the heats of adsorption, volume relations in the adsorbed films of different substances, and the area of the adsorbing surface, that the vapours were deposited in a liquid film which was usually many molecules thick. The heats of adsorption of benzene given above, together with the measurements of the vapour pressure of benzene approaching the saturation pressure, are strong evidence that the forces or other causes which bring about adsorption act through a thick multimolecular film.

#### Discussion.

An explanation was previously outlined (Lenher, *loc. cit.*, p. 1788) which accounted for this pre-condensation adsorption at a solid-vapour interface, and traced the probable course of adsorption on a solid surface over a pressure range from high vacuum to saturated vapour pressure. With very low pressures of the vapour over a perfectly clean surface, the first effect will be the building up of a unimolecular layer of the type which Langmuir has studied on metallic and glass surfaces. The range of pressure over which this primary film is built up is probably quite small, as the great attrac-

tive forces acting from a bare surface must rapidly hold vapour molecules within their range. Carver (*J. Amer. Chem. Soc.*, 1923, 45, 63) found that at 0° a pressure of 0.2176 mm. of toluene vapour caused only 12% of a glass surface to be covered with toluene molecules; in this case, the unimolecular film is still being built up at 3% of the saturation pressure. When a certain definite value of the equilibrium pressure of the adsorbing substance is reached the unimolecular layer will be compact and complete. With further increase of amount, adsorbed films of varying thickness are deposited, perhaps at first with little, if any, change of pressure. A somewhat similar phenomenon has been observed in measurements made recently in this laboratory on the adsorption of various alcohols from aqueous solutions of very low concentrations on active charcoal (Garner, Faraday Society Discussion, October 1, 1926; Knight, unpublished research). We know in the present case that the formation of the multimolecular liquid film does not begin until more than 95% of the saturation pressure is reached. Trouton (*Rep. Brit. Assoc.*, 1907, 453; 1911, 328) has observed these two types of adsorption and he estimates the transition pressure to be about 50% saturation in the case of water vapour being adsorbed on a glass surface.

It is of interest to compare the actual thicknesses of the adsorbed films at corresponding pressures, ( $p_\theta/p_w$ ) ( $p_w$  is the saturated vapour pressure), as suggested by Williams, in order to follow the variations in the effective range of the attractive force from the surface. The corresponding pressure  $p_\theta/p_w = 1$ , or saturation, gives the most instructive results. The thicknesses of the saturated equilibrium films of water and benzene on the three surfaces at the highest and lowest temperatures of investigation are summarised in Table V.

TABLE V.

<i>Water Vapour.</i>	<i>Benzene Vapour.</i>
On glass at 25° ..... $5.3 \times 10^{-5}$ cm.	On glass at 25° ..... $1.1 \times 10^{-6}$ cm.
On platinum at 20.5° $6.4 \times 10^{-7}$ „	On platinum at 22.4° $7.0 \times 10^{-6}$ „
On platinum at 29.5° $1.1 \times 10^{-6}$ „	On platinum at 26.9° $9.3 \times 10^{-6}$ „
On silica at 17.8° ... $4.5 \times 10^{-7}$ „	On platinum at 31° $5.5 \times 10^{-6}$ „
On silica at 28.4° ... $1.4 \times 10^{-6}$ „	On silica at 19° ..... $1.9 \times 10^{-6}$ „
	On silica at 28.7° ... $1.2 \times 10^{-6}$ „

Assuming that all the adsorption measured takes place on a plane surface, we see that at high vapour pressures, in cases where there is no possible chemical attraction of the primary or secondary valence type, films of the order of 50 to 100 molecular layers are deposited. Apparently even when a liquid is present in bulk at a solid-liquid interface the surface forces from the solid exert a force through many layers of the liquid.



The calculation of the amount of benzene adsorbed on a solid surface rests on the assumption that the Boyle-Charles law,  $pv = nRT$ , applies to benzene vapour close to the saturation point at ordinary temperatures, and it has been suggested that the foregoing conclusions may be vitiated by the slight deviations of this law from absolute accuracy in the particular circumstances. In the present experiments, the temperature range of the measurements may be divided into two parts for consideration: (1) that region in which the pressure of benzene vapour increases linearly with temperature, and in which the validity of the assumption of the Boyle-Charles law can be tested; and (2) the region in which *apparently* the law is not obeyed, and where the observed deviation from the ideal law is attributed to the adsorption or desorption of vapour from the walls of the containing vessel. That the law holds in the region where there is no measurable adsorption of this type (at temperatures more than  $1^\circ$  above the saturation temperature in the case of benzene) is shown by the following consideration: The Boyle-Charles law states that at constant volume and constant amount of vapour  $p/T$  should remain constant; this is verified for benzene vapour, because the value of  $p/T$  calculated from the experimental data remains constant within  $\pm 0.0001$ , the actual values of  $p/T$  in different experiments ranging from 0.2600 to 0.4000. A variation of 0.0001 in the value of  $p/T$  from that required by the law would make an error of  $2.34 \times 10^{14}$  in the number of molecules adsorbed per sq. cm. ( $N/\text{cm.}^2$ ), and an error of 0.81 in the value of  $\theta$ , the number of molecular layers adsorbed. As this possible error is of the same order as the accuracy of measurement, the assumption of the ideal-gas law is justified in this calculation.

In the temperature region from saturation to  $1^\circ$  above saturation, the abnormal increase in pressure above that demanded by the ideal-gas law for the increase of pressure with temperature of a vapour at constant volume is attributed directly to the desorption of vapour molecules from the walls of the vessel. There seems to be no other cause to which this unusual pressure increase may be properly ascribed. Benzene vapour is not an associated vapour which would dissociate on heating slightly (in this case, heating  $1^\circ$ ) to give the additional number of molecules to exert the measured increase in pressure. A careful consideration of the possible physical causes of this abnormal pressure rise near the saturation temperature indicates that there are no grounds for doubting the application of the Boyle-Charles law to benzene vapour over the region from saturation to the region where it has been shown that this law is obeyed. From the nature of the problem no more direct test of the applicability of the law to this limited region can be

made, for all measurements will be vitiated by the adsorption effect observed in this research.

The replacement of the law by a more correct equation of state, e.g.,  $p(v - b) = nRT$ , would not materially affect the conclusions set forth. The equation on which the adsorption calculations are based is  $n - n_1 = (p/T - p_1/T_1)v/R$  (see McHaffie and Lenher, *loc. cit.*, p. 1565); using the other equation of state, this becomes  $n - n_1 = (p/T - p_1/T_1)(v - b)/R$ , where  $b$  is the volume occupied by the benzene molecules themselves. For the adsorption vessels used,  $v$  varies from 5.317 c.c. to 13.307 c.c.; in the experiments, the values of  $b$  vary from  $1.3 \times 10^{-5}$  to  $2.7 \times 10^{-5}$  c.c. Thus it is clear that the ratio  $v/(v - b)$  may be taken to be equal to unity for the present purpose, and it is obvious that the application of a correction to the Boyle-Charles law is unnecessary in the present case of a vapour near saturation at ordinary temperatures.

#### *Summary.*

The adsorption of benzene vapour at pressures above 90% of the saturated equilibrium pressure has been measured on the surfaces of glass, fused quartz, and platinum. An unusually great adsorption on the platinum surface was observed. The free energy changes accompanying the adsorption were calculated.

The isosteric heat of adsorption at constant pressure of benzene vapour on platinum has been calculated from the adsorption isotherms; within the accuracy of calculation, it is found to be of the same magnitude as the latent heat of condensation to liquid.

The adsorption of vapours on solid surfaces over a wide range of pressure is briefly discussed.

A table is given showing the thickness of films exerting the saturated equilibrium pressure.

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