CCLXVI.—*The Adsorption of Vapours on an Amalgamated Platinum Surface.*

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THE following experiments are a continuation of those of McHaffie and Lenher (J., 1925, **127**, 1559) and of Lenher (J., 1926, 1785; 1927, 272), who studied the adsorption of water and of benzene vapours on glass, silica, and platinum surfaces at temperatures near the saturation temperature. Assuming the surface to be perfectly plane, they deduced that this adsorption was multimolecular. This hypothesis, however, has been criticised by Fraser, Patrick, and Smith (*J. Physical Chem.*, 1927, **31**, 897) on the ground that the walls of the adsorption vessels employed were not plane, as they had been etched by acid cleaning. This was supported by the observation that the effect was not present in the case of toluene vapour on a freshly-blown glass surface which had not been exposed to moisture. The work here recorded was commenced in the belief that amalgamation of the platinum vessel would produce a perfectly plane surface without the possibility of capillaries in which the adsorbing gas could condense.

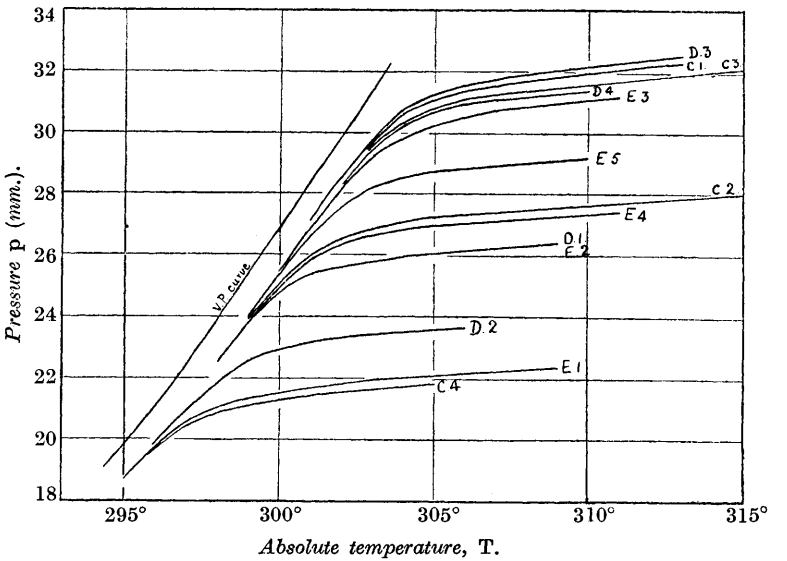
EXPERIMENTAL.

The Adsorption of Water Vapour on an Amalgamated Platinum Surface.—The apparatus employed was exactly the type used by McHaffie and Lenher (*loc. cit.*). The platinum vessel, together with a short length of glass tubing, was removed from the U-tube. It was filled with freshly prepared sodium amalgam, the end closed, and the bulb allowed to stand over-night. The amalgam was then removed, and the inside of the vessel washed repeatedly with clean dry mercury. The last traces of the sodium were finally removed by repeated washing with water. The vessel was then replaced in position, care being taken not to heat the platinum vessel and thereby drive off the mercury from its surface. Blowing was

performed through a long tube packed with phosphoric oxide and glass wool so as to prevent the admission of grease. Experiments were then carried out in the manner described by McHaffie and Lenher.

The amalgamated surface was perfectly reproducible, but in no case could a normal vapour-pressure curve be obtained in the amalgamated vessel. The same curve was always reached at the lower temperatures, *viz.*, about 1·3 mm. below the normal vapour pressure. This value was remarkably constant over the temperature range investigated. After thorough cleaning and reamalgamation of the surface, the same curve was always obtained. In each case

FIG. 1.



the vessel was very thoroughly washed for some time after the washings had lost all trace of alkaline reaction. In one case, after a series of readings had been taken, the bulb was disconnected, and again washed about 50 times with water, but exactly the same effect was observed. A selection of the results obtained is given in Table I; T is the absolute temperature, and p the pressure (mm. of mercury at 0°) read at the corresponding temperature. The volume of the platinum bulb was 5·317 c.c. and its internal surface area 15·36 sq. cm.

In Fig. 1, the values of T are plotted as abscissæ against the corresponding pressures p as ordinates. The vapour-pressure curve for water is also given, plotted from the data of Scheel and Heuse

TABLE I.

T.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	T.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.
	Expt. No. D.3.				Expt. No. E.3.		
313°	32·51	—	—	311	31·20	—	—
310	32·20	—	—	307	30·76	—	—
308	31·90	9·5	0·8	305	30·23	39·3	3·3
306	31·55	23·8	2·0	304	29·79	77·3	6·5
305	31·22	50·0	4·2	303	29·25	127·3	10·7
304	30·71	94·0	7·9	302	28·30	220·1	18·5
303	29·80	184·4	15·5	301	27·00	353·4	29·7
302	28·57	309·4	26·0	300	26·67	496·2	41·7
	Expt. No. E.2.				Expt. No. E.5.		
309	26·40	—	—	310	29·19	—	—
306	26·15	—	—	307	28·92	—	—
304	25·97	—	—	305	28·72	—	—
303	25·82	9·5	0·8	304	28·56	9·5	0·8
302	25·65	20·2	1·7	303	28·20	36·9	3·1
301	25·39	40·5	3·4	302	27·58	97·6	8·2
300	24·75	100·0	8·4	301	26·67	188·0	15·8
299	23·70	186·8	15·7	300	25·40	322·5	27·1
298	22·50	335·6	28·2	299	24·00	477·2	40·1
	Expt. No. C.2.				Expt. No. C.4.		
313	27·85	—	—	305	21·83	—	—
310	27·61	—	—	303	21·63	—	—
307	27·38	—	—	301	21·42	—	—
305	27·20	—	—	300	21·31	16·7	1·4
303	26·87	20·2	1·7	299	21·10	33·3	2·8
302	26·50	50·0	4·2	298	20·83	55·9	4·7
301	26·00	96·4	8·1	297	20·46	90·4	7·6
300	25·09	188·0	15·8	296	19·75	173·7	14·6
299	23·94	308·2	25·9	295	18·70	268·9	22·6
298	22·50	453·4	38·1	294	17·60	386·7	32·5
				Expt. No. D.2.			
306	23·67	—	—	300	22·91	29·7	2·5
305	23·58	—	—	299	22·60	53·5	4·5
304	23·50	—	—	298	21·87	114·2	9·6
303	23·41	—	—	297	20·97	221·3	18·6
302	23·31	—	—	296	19·87	339·1	28·5
301	23·18	6·7	0·56				

(*Ann. Physik*, 1910, **31**, 715). The series letters C, D, and E refer to different amalgamated surfaces. Between each series the surface was cleaned with nitric acid, washed, and reamalgamated as described above. This treatment did not alter the nature of the platinum surface itself, for the same adsorption curves were obtained before and after treatment.

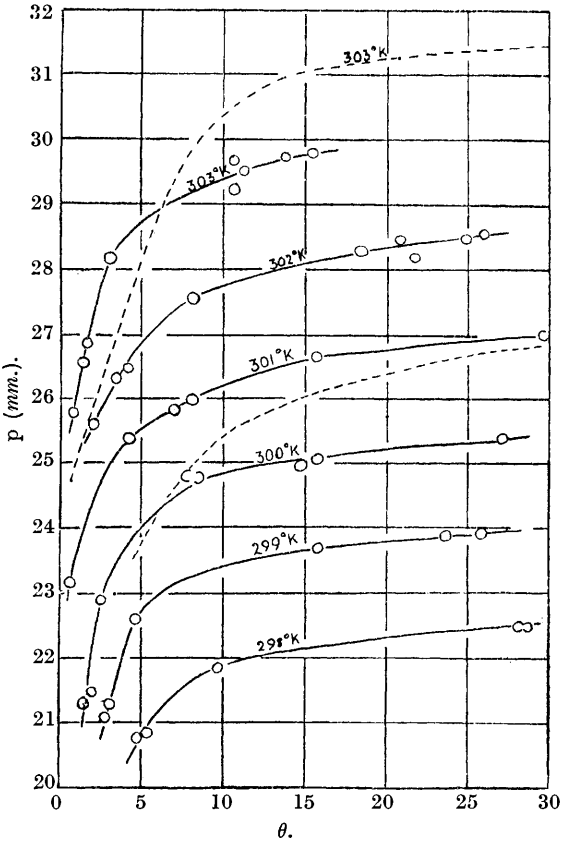
As in the case of McHaffie and Lenher's experiments, the number of molecules adsorbed per sq. cm. (N/cm.^{2}) is given by

$$N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3{\cdot}359 \times 10^{18},$$

where p is the pressure at some point on the linear portion of the

experimental curve at the temperature T, and p_1 and T_1 are the corresponding values for the point under consideration. The constant $3{\cdot}359 \times 10^{18}$ is calculated from the dimensions of the platinum vessel. Similarly, the number of molecular layers adsorbed is given by $\theta = (p/T - p_1/T_1) \times 2824$.

FIG. 2.



In Fig. 2, the thickness θ of the adsorbed film is plotted against p, the equilibrium pressure of the film at constant temperature. Small pressure differences become greatly magnified when plotted in this way, and the fact that the results at any one temperature of all three series lie on the same smooth curve attests to the constant nature of the surface. For comparison, two of the isotherms found by McHaffie and Lenher for a platinum surface are also included as broken lines.

The Adsorption of Benzene Vapour on an Amalgamated Platinum Surface.—The adsorption vessel was amalgamated in exactly the same manner as for the previous series of experiments, but in some cases the surface was washed only with dry mercury, whilst in the others it was also washed repeatedly with water. Both surfaces gave the same type of curve, but that washed with water gave the more consistent results. A few of the results obtained with such water-washed surfaces are in Table II.

TABLE II.

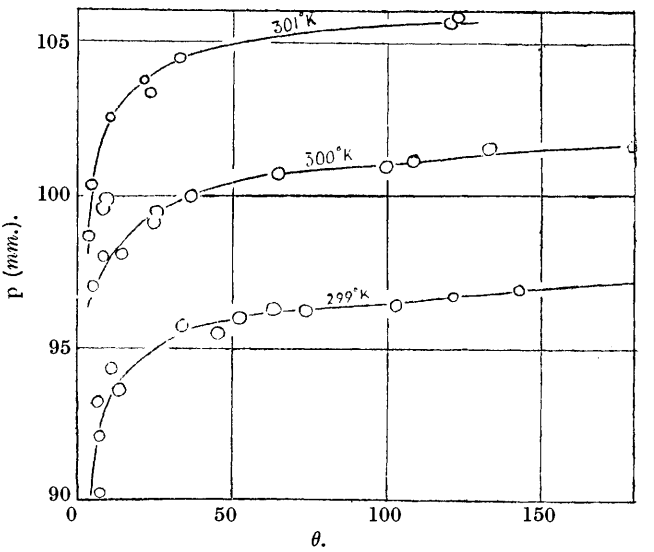
T.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	T.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.
	Expt. No. L.1.				Expt. No. L. 2.		
307·0°	110·90	—	—	307·0°	107·49	—	—
306·0	110·53	—	—	306·0	107·15	—	—
305·0	110·16	—	—	305·0	106·84	—	—
304·0	109·79	—	—	304·0	106·41	—	—
303·5	109·62	—	—	303·0	105·95	10·0	3·5
303·0	109·34	13·5	4·7	302·5	105·72	16·6	5·8
302·6	109·05	27·0	9·4	302·0	105·45	26·7	9·3
302·2	108·68	53·7	18·7	301·8	105·29	37·0	12·9
302·0	108·40	77·2	26·9	301·6	105·15	47·1	16·4
301·8	108·10	100·7	35·1	301·4	105·00	53·7	18·7
301·6	107·53	157·9	55·0	301·2	104·79	70·6	24·6
301·4	106·93	215·2	75·0	301·0	104·51	94·1	32·8
301·2	106·43	265·2	92·4	300·8	104·12	130·9	45·6
301·0	105·63	345·8	120·5	300·6	103·62	177·9	62·0
300·8	104·87	423·0	147·4	300·4	102·97	250·0	87·1
300·6	104·04	507·1	176·7	300·2	102·25	315·7	110·0
300·0	101·64	750·2	261·4	300·0	101·57	382·9	133·4
299·7	100·25	896·6	312·4	299·8	100·79	463·5	161·5
				299·6	99·91	553·9	193·0
				299·2	98·08	745·3	259·7
				299·0	97·27	858·1	299·0
	Expt. No. M.7.				Expt. No. M.9.		
304·0	91·79	—	—	306·0	103·54	—	—
303·0	91·47	—	—	305·0	103·24	—	—
302·0	91·17	—	—	304·0	102·92	—	—
301·0	90·85	—	—	303·0	102·60	—	—
300·0	90·52	3·4	1·2	302·0	102·18	—	—
299·0	90·10	16·6	5·8	301·2	101·71	27·0	9·4
298·4	89·82	27·0	9·4	301·0	101·58	33·6	11·7
298·2	89·66	40·2	14·0	300·8	101·41	43·6	15·2
298·0	89·54	47·1	16·4	300·6	101·23	57·1	19·9
297·8	89·27	70·6	24·6	300·4	100·98	77·2	26·9
297·6	88·98	97·3	33·9	300·2	100·71	100·7	35·1
297·4	88·65	127·7	44·5	300·0	100·40	127·7	44·5
297·2	88·21	167·9	58·5	299·8	99·90	174·5	60·8
297·0	87·71	221·6	77·2	299·6	99·31	235·1	81·9
296·8	87·22	268·6	93·6	299·4	98·63	302·2	105·3
296·6	86·65	325·7	113·5	299·2	97·66	393·9	140·4
296·4	86·03	389·5	135·7	299·0	96·85	486·8	169·6
296·2	85·34	460·1	160·3				
296·0	84·64	533·8	186·0				

TABLE II (*contd.*).

T.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	T.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.
	Expt. No. L.9.				Expt. No. J.3.		
306·0	100·47	—	—	304·0	95·37	—	—
305·0	100·13	—	—	303·0	95·00	—	—
304·0	99·80	—	—	302·0	94·62	—	—
303·0	99·46	—	—	301·0	94·24	—	—
302·0	99·13	—	—	300·0	93·84	—	—
301·5	98·92	—	—	299·8	93·76	—	—
301·0	98·69	10·0	3·5	299·6	93·68	—	—
300·6	98·52	16·6	5·8	299·4	93·60	—	—
300·4	98·44	20·1	7·0	299·2	93·48	6·6	2·3
300·2	98·29	27·0	9·4	299·0	93·33	16·6	5·8
300·0	98·11	40·2	14·0	298·8	93·16	27·0	9·4
299·8	97·88	57·1	19·9	298·6	92·89	50·2	17·5
299·6	97·60	80·6	28·1	298·4	92·60	77·2	26·9
299·4	97·23	117·4	40·9	298·2	92·29	104·2	36·3
299·2	96·79	157·8	55·0	298·0	91·82	151·0	52·6
299·0	96·26	211·5	73·7	297·8	91·30	201·5	70·2
298·8	95·73	265·2	92·4	297·6	90·70	262·0	91·3
298·6	95·03	335·5	116·9	297·4	90·08	325·7	113·5
298·4	94·31	409·5	142·7	297·2	89·45	389·5	135·7
298·2	93·71	470·1	163·8	297·0	88·73	463·5	161·5

The number of molecules adsorbed per sq. cm. is given by the same formula as before, and θ is given by $\theta = (p/T - p_1/T_1) \times 1{\cdot}169 \times 10^4$ (Lenher, J., 1927, 276).

FIG. 3.



The adsorption isotherms for a few temperatures are plotted in Fig. 3. In this case, again, the remarkable effect was observed

that the vapour pressure obtained was about 1·6 mm. below the normal value. This was confirmed by introducing benzene till it formed a definite meniscus above the mercury, and then determining the vapour-pressure curve. This followed exactly the curve traced by the lower portions of the other pressure–temperature curves.

Summary.

1. The adsorption of water vapour and of benzene vapour on an amalgamated platinum surface at pressures near the saturation values has been studied.

2. Such a surface is quite permanent in both vapours, but not in the laboratory atmosphere.

3. Both cases show definite effects of the type found by McHaffie and Lenher, and thus support their view that under such conditions multimolecular adsorbed films are produced, in spite of the fact that the surface, being virtually a liquid mercury surface, is presumably incapable of containing capillary cavities of the type postulated by Fraser, Patrick, and Smith.

4. In the amalgamated vessel the vapour pressure of the liquids was always low—to the extent of 1·3 mm. in the case of water and 1·6 mm. with benzene. This was constant throughout the temperature range investigated.

In conclusion, the author desires to express his great indebtedness to the Department of Scientific and Industrial Research for a grant during the tenure of which this research was carried out, and especially to Professor F. G. Donnan, F.R.S., at whose suggestion this work was undertaken, for his kindly advice and criticism during its progress.

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