CCXXXVI.—*The Adsorption of Water Vapour on a Plane Fused Quartz Surface. The Isosteric Heats of Adsorption of Water on Silica and on Platinum.*

By SAM LENHER

IN a recent communication by McHaffie and Lenher (J., 1925, **127**, 1559), the authors described an experimental method for measuring the adsorption of vapours on solid surfaces at pressures near the saturation pressure. The method consisted in measurements of the change of pressure with temperature of a vapour at constant volume, the internal surface of the constant-volume vessel being used as the adsorbing surface. This method has been employed in the present experiments.

The tube of quartz of which the inside was used as the adsorption surface was obtained from the Thermal Syndicate. It was made from clear Madagascar quartz, and the pointer was of milky quartz of the same chemical composition. The tube was blown into its shape. The composition of the quartz was 99·8% silica, the remaining 0·2% being chiefly alumina. The tube was fitted into the glass apparatus with a vacuum-tight ground glass joint, mercury sealed. The determination of the zero reading of the tip of the pointer on scale H (see diagram, *loc. cit.*, p. 1561) showed that a correction factor was necessary to convert the observed zero reading to an actual null point of pressure measurements, because the height of the mercury meniscus in the quartz tube in high vacuum (1×10^{-6} cm.) was 0·12 mm., whilst with vapour in the tube the height was 1·30 mm. The difference of these figures, 1·18 mm., is the correction which was subtracted from each reading of the manometer on scale H. Actual determinations of the vapour pressure of water showed that the correction factor remained constant over the temperature range.

Before the quartz adsorption tube was fitted into position in the apparatus it was carefully cleaned with organic solvents, hot freshly-prepared chromic acid, and concentrated nitric acid. After being repeatedly washed with distilled water, the tube was dried and set in place. It was fastened into its vacuum-tight glass seat with two rubber bands stretched over hooks on the glass and quartz. The joint was sealed with a mercury jacket. The measured internal surface of the quartz tube to the tip of the pointer was 38·81 sq. cm., the volume being 14·376 c.c.

Experiments with different amounts of water in the adsorption vessel show how the adsorption varies with pressure and temperature. The actual amount of adsorption is expressed as the number of molecules adsorbed per sq. cm. (N/cm.^{2}), and as molecular layers thick (θ), and is obtained by applying the equations $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3{\cdot}395 \times 10^{18}$ and $\theta = (p/T - p_1/T_1) \times 3023{\cdot}5$, where p and T refer to the mass of vapour calculated from the linear part of the experimental curve (where the mass in the vapour phase is constant), and p_1 and T_1 refer to the mass of vapour when adsorption takes place.

The decrease of free energy, $-\Delta F$, of water between the liquid state and that in an adsorbed film is calculated from the usual equation, $-\Delta F = RT \log (p/p_1)$, where p is the pressure of water vapour in equilibrium with liquid water at T°, and p_1 is the equilibrium pressure of the adsorbed film at T°. Selections from the results of 13 experiments (see Fig. 1) are in Table I. The pressures are given in mm. of mercury at 0°.

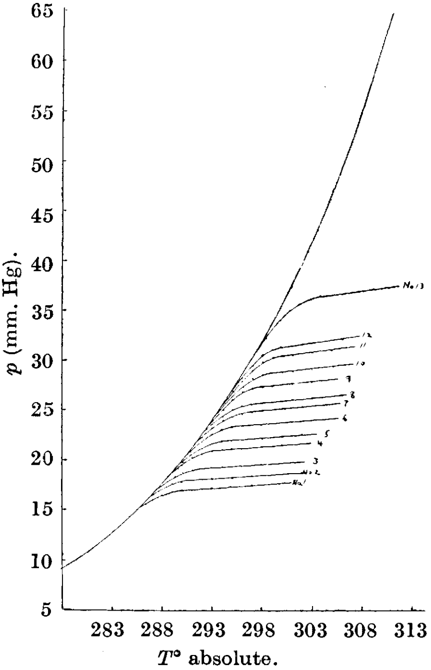
TABLE I.

T° abs.	p mm.	N/cm.^{2} $\times 10^{14}$.	θ.	$-\Delta F$.	T° abs.	p mm.	N/cm.^{2} $\times 10^{14}$.	θ.	$-\Delta F$
		No. 1.					No. 4.		
290·8	15·18	187·0	15·7	0·0	294·0	18·66	244·5	20·5	0·0
291·0	15·33	172·6	14·5	5·3	294·6	19·14	190·5	16·0	6·2
292·0	16·00	93·48	7·8	20·3	295·0	19·58	140·2	11·7	7·5
293·0	16·56	32·35	2·7	33·0	295·5	19·87	107·8	9·0	16·3
294·0	16·88				296·0	20·24	64·71	5·4	23·6
295·0	16·98				297·0	20·65	25·17	2·4	47·3
298·0	17·33				298·0	20·86	7·19	0·6	77·0
					299·0	21·01			
					303·0	21·40			
					307·0	21·69			
		No. 9.					No. 13.		
297·8	23·48	413·4	34·7	0·0	302·4	30·74	578·8	48·6	0·0
298·0	23·69	388·3	32·6	1·6	303·0	31·50	485·3	40·8	6·2
299·0	24·81	266·0	22·3	9·4	304·0	33·22	298·4	25·1	8·6
300·0	25·98	133·0	11·1	16·6	305·0	34·40	169·0	14·2	20·5
301·0	26·79	46·62	3·9	33·9	306·0	35·47	57·51	4·8	37·7
302·0	27·21	7·19	0·6	59·5	307·0	35·86	25·16	2·1	65·4
303·0	27·38				308·0	36·07	14·38	1·2	96·0
306·0	27·82				309·0	36·32			
308·0	27·96				311·0	36·66			
					313·0	36·98			

The results in Table I show that the amount adsorbed increases with increasing pressure and temperature, whilst the amount adsorbed at constant pressure decreases with increasing temperature, as one would expect. Since adsorption increases when the pressure and temperature are raised simultaneously, it must be concluded that the pressure coefficient of adsorption is greater than the temperature coefficient of de-adsorption. Each of the curves in Fig. 1 was traced in its entirety at least twice to test the complete reversibility of the equilibrium set up. No decrease of pressure with time could be detected over a period of several days, showing that no water penetrated into the bulk of the silica.

It should be emphasised in considering these results that the method used cannot yield an indisputable measure of the total amount of vapour adsorbed on a surface. Certainly one can measure accurately the additional amount of vapour adsorbed on a surface when the pressure of the vapour is approaching saturation. But, whilst we have no direct evidence here that a more stable film of adsorbed water remains on the surface, other experiments on adsorption have shown that under the thick film studied here there remains a primary film which is too firmly held to be detected at the temperatures possible in this field. So, whilst it cannot be said that the total adsorption of a vapour on a solid surface has been measured, one may say that the thickness of the adsorbed film deposited on a surface when the vapour approaches a state of saturation has been measured. The total amount adsorbed can only be determined by heating the surface, freshly freed from its thick film, to a high temperature in a high vacuum and measuring the quantity of vapour given off. The results of these high-temperature experiments along with the present results will give a true measure of the total amount of vapour which can be adsorbed on a given surface.

FIG. 1.

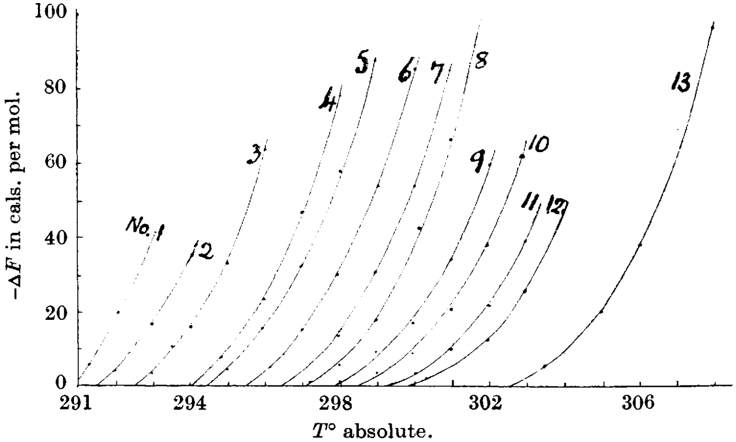


A comparison of the decreases in free energy accompanying the adsorption at various temperatures may be made from the curves shown in Fig. 2.

This study of adsorption was undertaken with the view of obtaining further information as to the cause of the thick film of water which is known to be held on a glass surface. This is usually ascribed to alkali or to fine capillaries in the surface of the glass (see, *e.g.*, Faraday, *Phil. Trans.*, 1830, **48**, 110). Warburg and Ihmori (*Ann. Physik*, 1886, **27**, 481) came to a conclusion very similar to that of Faraday and claimed to have shown that the alkali in ordinary glass is the sole cause of the thick water film. They did not detect any measurable film of water deposited on silica surfaces, or alkali-free surfaces, by their gravimetric method. The pressures of water vapour in their experiments were about 95% of the saturation values.

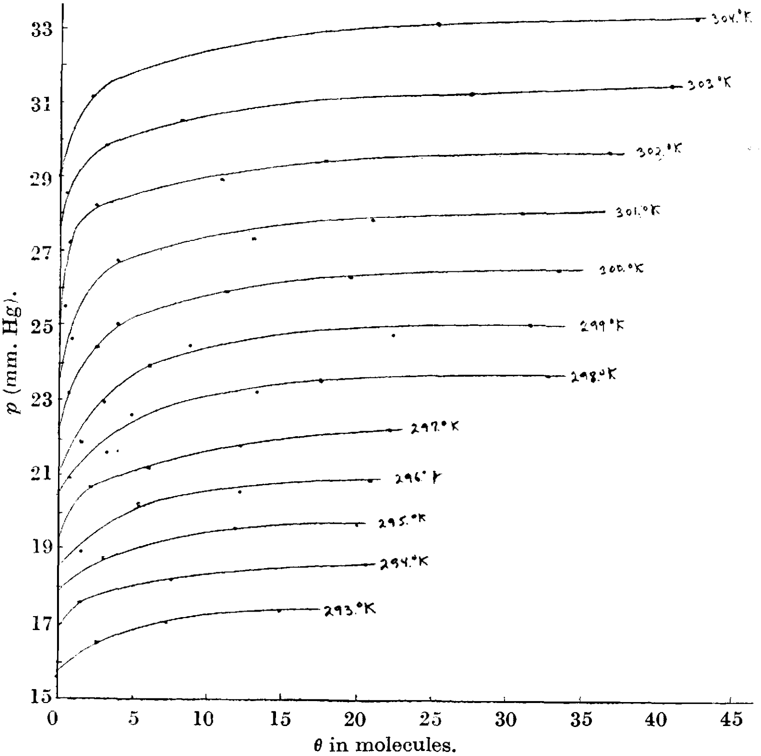
The author's results and conclusions clearly do not agree with those of Warburg and Ihmori. A consideration of the results in Table I shows that the adsorption does not become of relatively great magnitude until the saturation pressure is nearly reached. If Warburg and Ihmori had worked at pressures slightly nearer the saturation value they would have obtained results in agreement with this research instead of reporting no adsorption whatever.

FIG. 2.



In the previous paper of McHaffie and Lenher (*loc. cit.*) it was stated that in the case of the adsorption of water on platinum the observed adsorption began at a finite pressure. A curve in which thickness of film in molecules (θ) was plotted against pressure showed that on only one isotherm (298° K) was an approximation of this pressure permissible. This interesting point has been followed up in the present research, and from Fig. 3 it will be seen that for every temperature from 293° K to 304° K there *appears* to be a definite pressure below which adsorption of this type does not occur. An explanation of this phenomenon may probably be found in the following considerations. If we start with a perfectly clean surface and very low values of the pressure, the first effect will be the building up of a primary unimolecular "gas" layer as the pressure of the vapour increases. At a certain value of the pressure the unimolecular gas layer begins to "liquefy" and θ increases without increase of p. When this process is completed, θ increases with renewed increase of p, and we now have the formation of the film of multimolecular thickness observed in the measurements of the type described in this paper. The building up of this thick film corresponds to a curve $\theta = f_2(p)$ which *appears* to cut the pressure axis at a finite value of p, whereas in reality this curve stops at the "liquefaction" pressure, and is connected with the curve $\theta = f_1(p)$ corresponding to the formation of the primary unimolecular (gas) layer by the portion corresponding to the change of state of the primary film. It may be remarked that an explanation of this sort appears to be in agreement with recent results obtained by Adam (*Proc. Roy. Soc.*, 1926, *A*, **110**, 423) and by Iredale in this laboratory (*Phil. Mag.*, 1923, **45**, 1088; 1924, **48**, 177; 1925, **49**, 603).

Fig. 3.



The Isosteric Heats of Adsorption of Water on Silica and on Platinum.

The isosteric molar latent heats of adsorption at constant pressure may be calculated from the equation $H_\theta - H_v = L_\theta = RT^2 d \log p_\theta/dT$, where H_θ is the molar heat content of an adsorbed film θ layers thick, H_v is the molar heat content of the vapour, p_θ is the equilibrium pressure at T° for θ molecular layers adsorbed, and L_θ is the isosteric molar latent heat of adsorption at constant pressure p_θ and constant θ.

The use of this equation is an application of the Clausius-Clapeyron equation, $L_\omega = RT^2 d \log p_\omega/dT$ for the molar latent heat of evaporation of a liquid at constant pressure p_ω.

The quantity $-\Delta H$ or $L_\omega - L_\theta$ gives the decrease in molar heat content of a substance on undergoing a monothermic change at temperature T° from the liquid state to the state of an adsorbed film defined by θ. The experiments of this research have shown that at saturation, $p_\theta/p_\omega = 1$, there is an adsorption layer of finite thickness which exerts the equilibrium pressure $p_\theta = p_\omega$. Williams (*Trans. Faraday Soc.*, 1916, **10**, 167) has shown that at $p_\theta = p_\omega$ adsorption must be finite or infinite. Masson and Richards (*Proc. Roy. Soc.*, 1907, *A*, **78**, 412), working with water vapour on cotton wool, concluded that θ was infinite at saturation. The results of Titov (*Z. physikal. Chem.*, 1910, **74**, 641) with gases on charcoal give a finite maximum of adsorption at saturation. The present results taken in conjunction with those of Titov would indicate that there is a finite adsorbed quantity which will exert a saturated equilibrium pressure. It is clear that at saturation $-\Delta H$ will be zero.

Values for the isosteric molar latent heat of adsorption are obtained by using values of p_θ at different temperatures in the integrated form of the general equation for L_θ. Figures for L_θ for several isotherms measuring the adsorption of water on silica at values of θ from 5 to 30 are given in Table II. These calculated heats of adsorption are based on pressures read from the smoothed curves of Fig. 3 and are accurate to about 5—7%. The figures given in Table II for L_θ are the mean values of several integrations at the same value of θ over different temperature intervals.

From the data for the adsorption of water on platinum given by McHaffie and Lenher (*loc. cit.*), the isosteric heats of adsorption of water on platinum have been obtained. These figures are shown in Table III. These results are less accurate than those for water on silica, the maximum error being possibly 10% for $\theta = 15$ and $\theta = 20$.

Owing to the errors which are unavoidable in such calculations (unless the original data be of an extremely high degree of accuracy),

TABLE II.

	L_θ (cals. per mol.).				
θ.	295° K.	296° K.	297° K.	299° K.	303° K.
5	9,600	8,700	9,730	9,700	9,850
10	9,900	9,800	10,150	10,190	10,100
15	9,950	9,640	10,450	10,155	10,310
20	9,850	10,220	10,470	10,160	10,250
25	—	—	—	10,130	10,480
30	—	—	—	10,100	10,610

TABLE III.

	L_θ (cals. per mol.).				
θ.	298° K.	299° K.	300° K.	301° K.	302° K.
5	9,100	9,175	9,640	9,780	9,845
10	10,530	10,165	10,200	10,430	11,100
15	11,200	10,340	10,145	10,490	11,190
20	10,870	10,415	10,105	10,285	10,760

it would be unwise to lay too much stress on the accuracy of these results or their variation with temperature and number of molecular layers. The heat of condensation at constant pressure of saturated water vapour to liquid water in bulk varies from 10,510 cals. per g.-mol. at 295° K to 10,420 cals. per g.-mol. at 303° K. We may say, therefore, that the calculated isosteric heats of adsorption corresponding to the formation of multimolecular films on silica and platinum are of the same order of magnitude as the corresponding heats of condensation to liquid water in bulk.

An examination of the heats of adsorption given in the literature (Chappius, *Wied. Annalen*, 1883, **19**, 21; Titov, *loc. cit.*) indicates that the isosteric heat of adsorption is usually greater than the heat of condensation to liquid. Most of the heats of adsorption previously given have been in experiments with charcoal as the adsorbent. The adsorption films on charcoal are very firmly held to the surface as their equilibrium pressures may be very low or almost unmeasurable, and elevated temperatures are required to remove the film. The high equilibrium pressures of the films studied in the present work show how loosely held the water molecules must be on the silica surface. Heats of adsorption where there is a possibility of chemical union, as in the experiments of Beebe and Taylor (*J. Amer. Chem. Soc.*, 1924, **46**, 43) with hydrogen on nickel, are necessarily much greater than the heat of condensation of the gas. In a recent investigation of adsorption equilibria in binary gaseous mixtures by the coherer method, Palmer (*Proc. Roy. Soc.*, 1925, *A*, **110**, 133) has found the heat of adsorption of nitrogen on platinum to be 180 cals. per g.-mol. The heat of condensation of liquid nitrogen is 1300 cals. per g.-mol. Palmer's measurements show that nitrogen is only very weakly adsorbed on platinum, and that the heat of adsorption of oxygen, hydrogen, and other more strongly adsorbed gases is much greater than the heat of condensation, as one would expect.

As the temperature range of the present experiments is not sufficient to remove the firmly held unimolecular layer of water which persists on the surface, the values of L_θ do not apply to this region of adsorption. It is highly probable from the great stability of the primary film that the heat of adsorption for this first layer is much greater than the latent heat of condensation.

Summary.

(1) The adsorption of water vapour at pressures near the saturation values at temperatures between 290·8° K and 313° K on a plane surface of quartz has been measured.

(2) From the data yielded by 13 such measurements it has been shown that adsorption of this type appears to start at a finite pressure. An explanation of this phenomenon has been advanced.

(3) The free energy changes accompanying the adsorption of water vapour on quartz have been calculated.

(4) It has been shown that the silica content of glass surfaces, as well as the alkali content, plays an important rôle in the formation of the water film on glass.

(5) The isosteric heats of adsorption at constant pressure for water vapour on quartz and on platinum at different temperatures and for different amounts adsorbed have been calculated.

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