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LIII. *On the Thickness of the Liquid Film formed by Condensation at the Surface of a Solid.* By Dr. G. J. PARKS\*.

IT was known more than half a century ago † that when a solid is placed in a gas or vapour there is a condensation of the latter on the surface of the solid, and in particular that glass has the power of condensing water-vapour at temperatures above the dew-point.

Arago ‡ proposed to measure the amount of condensation by the optical method of interference, and quite recently Lord Kelvin § has suggested a method depending upon electrical conductivity.

In almost every department of physical research glass bulbs or tubes are used, and the presence of moisture on the surface of the glass is a continual source of trouble. Prof. J. Trowbridge || has lately called attention to this matter in connexion with spectrum analysis.

There can be little doubt also that many of the standard results for the specific heats of finely divided or porous solids are incorrect, for if a solid is perfectly dry, heat will be evolved on wetting it ¶ when it is placed in the calorimeter, and if it is not dry then the specific heat obtained is not the true specific heat of the solid; in either case the specific heat obtained will be too high. Thus, from the most recent determination of the specific heat of pure precipitated silica, well dried and sealed in a bulb, the value appears to be  $\cdot 1808$  \*\*, but the values previously obtained for amorphous silica are much higher than this.

The present brief inquiry, which is not intended to be by any means exhaustive of the subject, arose out of another investigation, not yet completed, in which the author has attempted to determine by direct experiment the surface-pressure of water and other liquids in contact with glass.

It was found that everything depended on keeping the surface of the glass perfectly free from moisture until the moment of the experiment; and the author was thus led to consider the quantity of moisture concerned in surface-pressure, in the Pouillet effect, and in surface-action generally.

\* Communicated by the Physical Society: read February 27, 1903.

† Jamin et Bertrand, *Phil. Mag.* [4] vi. p. 157 (1853); *Comptes Rendus*, June 1853, p. 994.

‡ See *Phil. Mag.* [4] vi. p. 157 (1853).

§ Lord Kelvin, *Phil. Mag.* [6] iv. p. 181 (1902).

|| Trowbridge, *Phil. Mag.* [6] iv. p. 156 (1902).

¶ Parks, *Phil. Mag.* [6] iv. pp. 240, 251 (1902).

\*\* Bellati e Finazzi, *Atti del R. Istituto Veneto*, Tomo lxi. Parte Seconda, p. 507 (1902).

In the first experiment some cotton silicate, similar to that used in the author's previous investigation\*, was packed tightly into a test-tube and the mouth of the tube was drawn out to a fine neck, but not sealed.

The weight of the silicate was 3.37 grammes, the average diameter of the cylindrical filaments was .00175 cm., the sp. gr. was 2.7, and the estimated area of surface was 847 sq. cm. per gm.

Hence the superficial area of the silicate was  $3.37 \times 847 = 2854$  sq. cm., and allowing for the area of surface of the test-tube, the whole area of glass surface amounted to about 2900 sq. cm.

The tube was placed in an open beaker, and this was covered with a large inverted beaker standing over some water in a shallow tray and kept in a closed glass cupboard at nearly constant temperature.

The vapour which filled the chamber slowly diffused into the test-tube through the narrow aperture, and became condensed on the surface of the glass. The experiment continued for 16 days, the tube being weighed at intervals. The outside of the tube was wiped with a clean cloth before each weighing, so that the observed increase of weight was entirely due to condensation by surface-action. The temperature never varied much from 15° C. The following table shows the results of the various weighings and the estimated thickness of the film of moisture. The initial weight of the tube and silicate when dry was 9.3402 grammes.

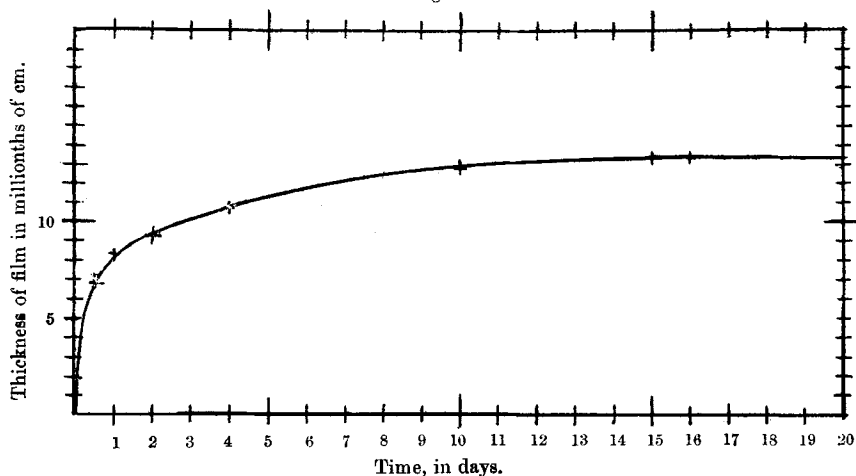
Time.	Weight of tube and silicate.	Increase of Weight.	Estimated thickness of film (cm.).
12 hours .....	9.3602	.0200	$6.9 \times 10^{-6}$
1 day .....	9.3644	.0242	$8.3 \times 10^{-6}$
2 days .....	9.3672	.0270	$9.3 \times 10^{-6}$
4 „ .....	9.3710	.0308	$10.6 \times 10^{-6}$
10 „ .....	9.3774	.0372	$12.8 \times 10^{-6}$
15 „ .....	9.3790	.0388	$13.4 \times 10^{-6}$
16 „ .....	9.3790	.0388	$13.4 \times 10^{-6}$

In another experiment the silicate was placed loosely in the tube and the mouth of the tube was allowed to remain at its ordinary width, about 1.5 cm. The experiment was made much more quickly than the first one, but the final result was the same.

\* Phil. Mag. [6] iv. p. 246 (1902).

Temperature during experiment about 12° C.  
Weight of silicate 1·10 gm.  
Total area of surface of silicate and tube about 1000 sq. cm.  
Initial weight of tube and silicate 7·9517 gm.  
Weight after 4 days 7·9650 gm.  
" " 6 " 7·9650 "  
Increase of weight 0·133 "  
Estimated thickness of film  $13\cdot3 \times 10^{-6}$  cm.

Fig. 1.



The cotton silicate thus covered with a film of moisture showed no alteration in appearance even when examined under the highest power of the microscope, but when the silicate was placed in water no heat was evolved, though when the same substance was thoroughly dried and placed in water the heat evolved amounted to 0·011 calorie per sq. cm. Hence it may be inferred that the Pouillet effect for water in contact with glass at 12° C. is confined to a film of moisture the thickness of which is about  $13\cdot3 \times 10^{-6}$  cm.

It will be interesting to compare with this result the results obtained by other experimenters with different substances and under widely different conditions. The earliest measurement of surface condensation of which the author has been able to find an account, is that of Magnus \*, who, from experiments on the expansion of sulphurous acid gas, found that the amount of gas condensed on the surface of smooth glass

\* Magnus, Phil. Mag. [4] vi. p. 336 (1853).

rods was  $\cdot 0008$  cub. mm. per. sq. mm., that is  $80 \times 10^{-6}$  cub. cm. per sq. cm. of surface.

It is not improbable that in these experiments the sulphur dioxide was condensed by chemical combination with a film of water previously existing on the surface of the glass, but it may be noticed that the result obtained is of the same order of magnitude as all the other results quoted in this paper.

Martini \* found that some precipitated silica exposed to aqueous vapour increased in weight by 80 per cent. without any alteration in appearance; on putting this moist silica into water no heat was evolved, though the heat evolved on wetting the dry silica amounted to 19 calories per gramme. Martini does not state the area of surface exposed by the powder, but the author has shown † that when dry silica is wetted, the amount of heat evolved is about  $\cdot 00105$  calorie per sq. cm.; and hence we may take the area of surface of the powder used by Martini as about 18,000 sq. cm. per gm., and the extreme thickness of the aqueous film would therefore

$$\text{be } \frac{\cdot 8}{18000} = 44 \times 10^{-6} \text{ cm.}$$

It should be remarked here that when a powder is exposed for a long time in an open tray it is likely to receive some moisture by the ordinary process of condensation at temperatures below the dew-point, and thus the more exposed portions of the powder may receive excess of moisture.

Bellati and Finazzi ‡ have recently made an excellent series of experiments showing the relation between the amount of moisture absorbed by silica and the heat evolved on putting the powder into water. The area of surface exposed by the silica is not stated, but the authors consider with good reason that if the powder were perfectly dry the heat evolved on wetting it would amount to 26 calories per gm., and hence we may assume the surface exposed by the powder to amount to about 25,000 sq. cm. per gm.

In the following table the figures of the first two columns have been selected from the original paper referred to, and the other three columns have been introduced by the author for the purposes of the present inquiry. An example will be sufficient to explain the table and the diagram (p. 522). When the dry silica has absorbed, say, 2.38 per cent. of moisture it

\* Martini, *Atti del R. Istituto Veneto*, Tomo lix. Parte Seconda, p. 624 (1900).

† *Phil. Mag.* [6] iv. p. 247 (1902).

‡ Bellati e Finazzi, *Atti del R. Istituto Veneto*, Tomo lxi. Parte Seconda, p. 514 (1902).

is put into water and the heat evolved is found to be 18.29 calories per gm.

But if the silica had been perfectly dry the heat evolved would have been 26 calories, hence the heat due to 2.38 per cent. of moisture must have been  $26 - 18.29 = 7.71$  calories per gm.

The thickness of the film of moisture is about

$$\frac{0.238}{25000} = 0.95 \times 10^{-6},$$

and the corresponding amount of heat per sq. cm. is

$$\frac{7.71}{25000} = 3.08 \times 10^{-4} \text{ calories.}$$

The results show that when the water film is only one millionth of a centimetre in thickness, the heat evolved is about one third of the whole amount, when the thickness of film is two millionths the heat evolved is about one half of the whole, and on further increasing the thickness of the film the amount of heat evolved slowly approaches a maximum which it reaches when the thickness is about  $31.6 \times 10^{-6}$ , the heat evolved being then .00105 cal. per sq. cm.

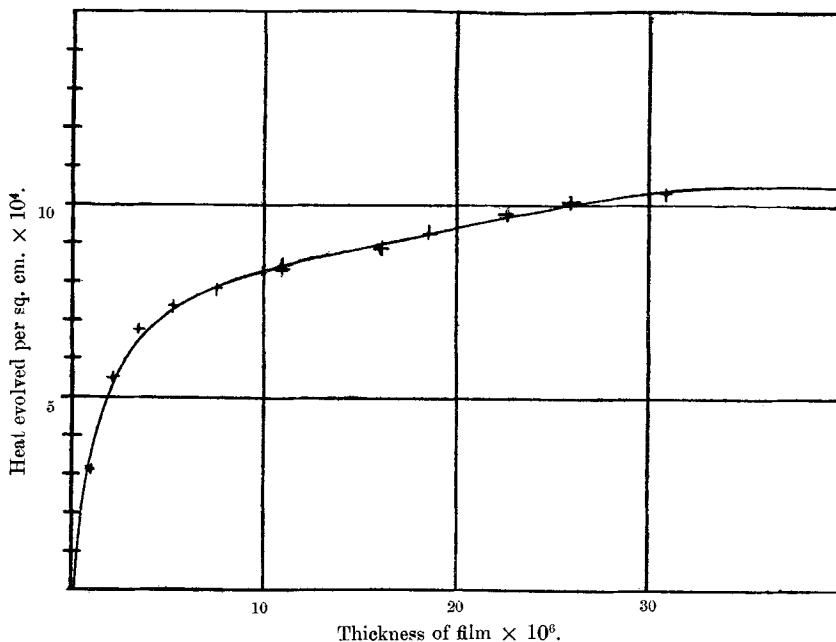
Parts of moisture absorbed by 100 parts of dry silica. (a)	Heat evolved per gramme of silica. (q)	Reduction of the heat evolved by previous absorption of moisture. (26-q)	Thickness of water film $\frac{10^6 \cdot a}{25000}$	Heat evolved per sq. cm. by a film of this thickness $\frac{26-q}{25000}$
2.38	18.29	7.71	$0.95 \times 10^{-6}$	$3.08 \times 10^{-4}$
5.35	12.23	13.77	$2.14 \times 10^{-6}$	$5.51 \times 10^{-4}$
8.59	9.17	16.83	$3.44 \times 10^{-6}$	$6.73 \times 10^{-4}$
12.92	7.61	18.39	$5.17 \times 10^{-6}$	$7.36 \times 10^{-4}$
18.83	6.50	19.50	$7.53 \times 10^{-6}$	$7.80 \times 10^{-4}$
27.36	5.25	20.75	$10.94 \times 10^{-6}$	$8.30 \times 10^{-4}$
39.95	3.70	22.30	$15.98 \times 10^{-6}$	$8.92 \times 10^{-4}$
46.35	2.94	23.06	$18.54 \times 10^{-6}$	$9.22 \times 10^{-4}$
56.48	1.66	24.34	$22.59 \times 10^{-6}$	$9.74 \times 10^{-4}$
64.78	.90	25.10	$25.91 \times 10^{-6}$	$10.04 \times 10^{-4}$
76.94	.19	25.81	$30.78 \times 10^{-6}$	$10.32 \times 10^{-4}$

Dr. C. Barus\* gives some valuable data on the size of the water particles produced by condensation on a solid nucleus. In the experiments described it seems that the condensation must in the first place be caused by the surface action of the

\* Barus, Phil. Mag. [6] iv. pp. 24 to 29 and pp. 262 to 269 (1902).

nucleus, though as the exhaustion of the chamber proceeds the average size of the water particles increases by ordinary condensation at temperatures below the dew-point. If we

Fig. 2.



subtract the average diameter of the nuclei from the average diameter of the drops, and halve the remainder, this will give the thickness of the film of water.

In the following table the first two columns have been taken from the original paper of Dr. Barus, and the last column has been inserted by the present writer. The results for the first six exhaustions only have been selected.

Dr. Barus remarks that "the use of Kelvin's vapour-tension equation breaks down quantitatively for the present purposes in practice." The reason for this will be clear when it is remembered that Kelvin's vapour-tension equation is only intended to apply to a condition of equilibrium existing between a liquid and its vapour; but in condensation upon solid surfaces another element must be taken account of, viz., a force of the nature of an attraction between the solid and the liquid or vapour, which causes a pressure,

Diameter of nucleus  $260 \times 10^{-6}$  cm.

Number of exhaustions.	Diameter of water particle.	Thickness of film.
1 .....	$280 \times 10^{-6}$	$10 \times 10^{-6}$
2 .....	$310 \times 10^{-6}$	$25 \times 10^{-6}$
3 .....	$330 \times 10^{-6}$	$35 \times 10^{-6}$
4 .....	$360 \times 10^{-6}$	$50 \times 10^{-6}$
5 .....	$390 \times 10^{-6}$	$65 \times 10^{-6}$
6 .....	$420 \times 10^{-6}$	$80 \times 10^{-6}$
Diameter of nucleus $360 \times 10^{-6}$ cm.		
1 .....	$370 \times 10^{-6}$	$5 \times 10^{-6}$
2 .....	$390 \times 10^{-6}$	$15 \times 10^{-6}$
3 .....	$410 \times 10^{-6}$	$25 \times 10^{-6}$
4 .....	$420 \times 10^{-6}$	$30 \times 10^{-6}$
5 .....	$440 \times 10^{-6}$	$40 \times 10^{-6}$
6 .....	$460 \times 10^{-6}$	$50 \times 10^{-6}$

probably a very great pressure, in the liquid at the surface of the solid. The author hopes to be able at some future time to give the numerical values of this surface pressure for various liquids in contact with glass.

In now appears that in all cases where condensation of moisture takes place at a solid surface, and at temperatures not below the dew-point, the thickness of the surface film varies from  $10 \times 10^{-6}$  to  $80 \times 10^{-6}$  cm. according to the substances used and the conditions of temperature and pressure, and for the water film on glass in saturated vapour at  $15^\circ$  C. the thickness is about  $13.4 \times 10^{-6}$  cm.

According to Prof. J. J. Thomson\* the mean radius of the drops formed by condensation in electrified gas is of the same order of magnitude, being  $81 \times 10^{-6}$  cm. for negatively electrified oxygen, and  $68 \times 10^{-6}$  cm. for positively electrified oxygen; the size of the nucleus is not known, but it is probably very small.

H.M. Dockyard School, Portsmouth.  
November 1902.

\* J. J. Thomson, 'The Discharge of Electricity through Gases' (1900).