CCCLXXXVIII.—*Adsorption of Vapour on a Quartz or a Glass Wall.*

By Andreas Smits.

Smits and Purcell (this vol., p. 2941) have shown that their " extrapolation method " enables one to find, not only the vapour density of the saturated vapour, but also the extent of adsorption by the walls of the apparatus. In the case of ammonium bromide, the change of the vapour-pressure curve of the saturated vapour into that of the unsaturated vapour (Boyle–Gay-Lussac curve) was not sharp, but took place over a temperature range of several degrees, *i.e.*, the saturated vapour-pressure curve was left at too low a temperature, and the Boyle–Gay-Lussac line was reached at too high a temperature. This continuous curve was found with both rising and falling temperatures, so there is no doubt as to its reality. Both quartz and Jena glass apparatus were used, and in order to keep the wall as smooth as possible, the apparatus had not been allowed to come into contact with water or water vapour.

These experiments were of great interest, since the results of McHaffie and Lenher (J., 1925, **127**, 1559) and of Lenher (J., 1926, 1785; 1927, 272) on the adsorption of water and benzene vapour on glass, silica, and platinum surfaces at temperatures near the saturation temperature had been criticised by Fraser, Patrick, and Smith (*J. Physical Chem.*, 1927, **31**, 897) on the ground that the walls of the apparatus were not plane, but had been etched by acid-cleaning. These authors had observed that for water and toluene the smoothness of the surface was very important, and that no adsorption of toluene on a plane surface could be detected by vapour-pressure determinations. At the time of publication of Fraser, Patrick, and Smith's paper, Rinse was completing investigations (this vol., p. 1442) in the author's laboratory which showed that mercuric iodide was adsorbed in layers 500 molecules thick at 300°, even though the glass walls had been kept as smooth as possible and had not been in contact with water or water vapour. Still more recently, J. W. Smith (this vol., p. 2045) has shown that a platinum vessel, of which the walls had been amalgamated in order to render them as plane as possible, adsorbs molecular layers, the number of which increases as the saturation temperature is approached: within the range of 30° the maximum number of adsorbed molecular layers was 40 in the case of water and 300 in the case of benzene. Further, de Boer (*Physica*, 1928, **8**, 145) has found that even at room temperature 30 molecular layers of iodine are adsorbed on calcium fluoride, and if it had been possible to approach the saturation temperature more closely, this number would probably have been much higher.

The author's application of the extrapolation method to find the degree of adsorption by the glass wall has been mentioned (Smits and Purcell, this vol., p. 2943) but not yet described. In the paper quoted, Fig. 6 shows the continuous change of the saturated into the unsaturated vapour-pressure curve, and on extrapolation the two lines intersect at a point corresponding to 379° and 49 cm. Hg. The vapour pressure measured at this temperature was, however, 48 cm. Hg, *i.e.*, 1 cm. too low. The bulb of the apparatus had a radius of 5·25 cm., so the surface was 346·36 cm.^{2}, or say 350 cm.^{2}. The bulb contained 0·3404 g. of ammonium bromide, so the decrease of 1 cm. in the vapour pressure corresponded with 0·0068 g., *i.e.*, the number of adsorbed molecules is $4{\cdot}23 \times 10^{19}$. From *X*-ray investigations on ammonium bromide it follows that in a crystal layer a molecule has a cross section of 25×10^{-16} cm.^{2}. On a surface of 350 cm.^{2}, therefore, 14×10^{16} molecules can be arranged in one layer, but since $4{\cdot}23 \times 10^{19}$ molecules were adsorbed, the number of adsorbed molecular layers would be 300. This result is very remarkable and of the same order as that obtained by Rinse and by Smith.

Although this phenomenon is being further investigated in this laboratory with various surfaces and substances, the following points may already be emphasised. Suppose we have a bulb containing a liquid or a solid volatile substance, and adsorption occurs on the wall of the vessel, which is a general phenomenon; the system wall + adsorption layer will then be a part of the whole equilibrium system. Equilibrium cannot be established before the glass wall has adsorbed so many molecular layers that the vapour pressure of the "wall-phase" (as we may call it) is the same as that of the solid or liquid phase in the bulb. Now, the various experiments seem to show that, depending of course on the nature of the substance, the wall-phase can consist of a large number of molecular layers, and if we accept this conclusion, the following considerations arise.

On increasing the temperature to the stage at which the last part of the solid or liquid phase has just disappeared, the wall-phase will still have a pressure equal to that of the saturated vapour at that temperature. Further increase of temperature causes the number of adsorbed molecular layers to become smaller and smaller. If the solid or liquid phase had still been present, the number of adsorbed molecular layers would have increased, so that now, the solid (or liquid) phase having disappeared, the number of adsorbed molecular layers is too small to give a pressure equal to that of the saturated vapour at the same temperature. The wall-phase will consequently give a lower vapour pressure, and the deficiency will increase continuously with rising temperature.

Finally, the wall-phase disappears, leaving behind probably a unimolecular layer, and the Boyle–Gay-Lussac line is practically reached.

Summary.

It is shown that experiments of other investigators and also of the author indicate that the adsorption films on a mercury surface and on glass or quartz surfaces, as plane as possible, formed in almost saturated vapour, can consist of a large number of molecular layers.

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