iron frame, but this binder cracked the glass, wrecking the whole apparatus. By putting a thin layer of litharge and glycerin between the plaster and the glass, the cracking was prevented.

The manometer was filled with mercury under a vacuum. A funnel with a long capillary tip was sealed into one side of the manometer. A ground-glass plug kept the mercury from running in while the manometer was being baked out and evacuated with a mercury diffusion pump. When the evacuation was completed the plug was lifted and the mercury allowed to run in. By cracking off the dome (see Fig. 1) the float and mirror were lowered into place with wires.

As is the case with nearly every instrument which is pushed to the limits of its sensibility, this manometer is somewhat difficult to work with. The zero point would sometimes shift, due to some unknown cause. At one time a steady shift was traced to a slow warping of the wooden brackets which supported the swinging table. When the brackets were covered with aluminum leaf and varnished, the shift stopped. By carefully watching the apparatus and discarding readings when the shifts took place good results were obtained.

Thanks are due to Drs. Shrader and Ryder for suggestions regarding the manometer, and to Professor T. W. Richards for invaluable help. The work was done with the aid of a fellowship from the National Research Council.

Summary

The sensitivity of the optical lever manometer of Shrader and Ryder has by a few changes been increased to about 0.0001 mm., with an accuracy of about 0.0002 mm. of mercury.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE ADSORPTION OF TOLUENE VAPOR ON PLANE GLASS SURFACES

BY EMMETT K. CARVER

Received August 31, 1922

The data on the adsorption of vapors, although they ought to furnish information of a decisive character regarding the nature of the intermolecular forces, are so complicated by unknown factors that it is difficult to draw trustworthy conclusions from them.

The important question of the thickness of the adsorbed layer is as yet not definitely settled. Most of the experimental work tends to show that this layer is many molecules deep, but Langmuir[1] points out that all such

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[1] Langmuir, THIS JOURNAL, 40, 1361 (1918).

data have been obtained with porous bodies in which the true adsorption is masked by the effect of the pores. He obtains some data for the adsorption of various gases on glass, mica and platinum which bear out his theory that the layer which is truly adsorbed is but 1 or 2 molecules deep. As his work was done at low temperatures and with gases which one might expect to be condensed by "free valences," it was thought worth while to work with some heavier, easily condensed vapors, to see whether a thick layer could be obtained. For this purpose toluene was selected. It was hoped to make measurements on glass, quartz and calcite, but only the measurements on glass were obtained.

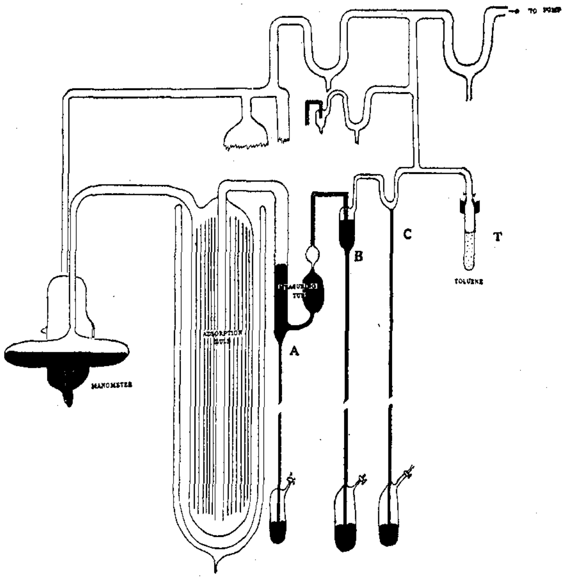

Fig. 1.

The apparatus is shown in Fig. 1. A known quantity of vapor was admitted to the bulb containing the adsorbing surface and the pressure rise was measured by the manometer. The difference between the pressure measured and that calculated must be due to adsorption. Then a like amount of vapor was admitted to a bulb on the other side of the manometer to bring it back to a zero reading. More vapor was admitted to the adsorption bulb, and the pressure change again measured. This was repeated, until the pressure had built up as much as was desired.

The manometer has been described in the article immediately preceding this.

The adsorption bulb was filled as closely as possible with concentric Pyrex tubes, giving a total area of 4277 sq. cm. The tubes were kept centered by small bosses, pressed into them while heated.

Before use, the bulb and tubes were washed for several hours with hot chromic acid cleaning solution, washed for a day with slowly-running distilled water, steamed for several hours, dried in a vacuum, and then outgassed at 200° with a mercury-vapor pump.

The apparatus for admitting the toluene vapor can be readily understood from the diagram. Liquid toluene was placed in the tube T, and was freed from air by boiling in a vacuum. Its vapor pressure was measured in the U-tube, C, by means of a cathetometer. Readings were taken in different parts of the tube, and a zero reading was taken when the toluene was immersed in carbon dioxide. By setting the mercury at various heights in Tube A, which had been carefully calibrated by weighing with mercury, and then by raising the mercury in Tube B, a known volume of toluene vapor under a known pressure could be shut off. Then by lowering the mercury in Tube A, this toluene could be admitted to the adsorption bulb, causing a pressure to be registered by the manometer. This pressure, when adsorption took place, was less than that calculated from the perfect-gas laws, and the amount of the adsorption could be calculated very simply.

TABLE I

ADSORPTION OF TOLUENE AT 0° ON GLASS WHICH HAD BEEN OUTGASSED AT 200° FOR 6 HOURS

Total pressure Mm. Hg	Amount adsorbed Moles per sq. cm. $\times 10^{12}$	Per cent. of surface covered[a]
0.0008	7.54	1.40
0.0015	15.1	3.47
0.00406	28.5	5.35
0.0203	48.6	9.12
0.0383	54.5	10.2
0.1281	62.0	11.6
0.2176	66.2	12.4

[a] Calculated on the assumption that the adsorbed film has the same density as the liquid, and that the molecules are spherical.

TABLE II

ADSORPTION OF TOLUENE AT 0° ON GLASS WHICH HAD BEEN OUTGASSED AT 200° FOR 12 HOURS

Total pressure Mm. Hg	Amount adsorbed Moles per sq. cm. $\times 10^{12}$	Per cent. of surface covered
0.0006	9.23	1.73
0.0025	22.9	4.30
0.0175	53.9	10.10
0.0850	124.4	23.35
0.1737	142.0	26.65
0.2629	151.2	28.38

The results are shown in Tables I and II and are plotted in Fig. 2. According to Freundlich's adsorption formula the logarithmic curves should be straight lines, but according to Langmuir's formula they should be concave downwards. Curve I shows data when the bulb had been outgassed for 6 hours at 200°. If it were extrapolated to the saturation pressure it would hardly reach the point at which the whole surface would be covered with toluene molecules. Curve II was obtained after outgassing the bulb at 200° for 12 hours. If it were extrapolated to the saturation pressure of toluene it might reach the point where the whole surface would be covered with toluene vapors. Curve III is a plot of Langmuir's simple adsorption formula, of the type $y = \frac{p}{c + p}$, where y is the amount adsorbed, p the pressure and c is a constant, with the values chosen arbitrarily to make it parallel to Curve II.

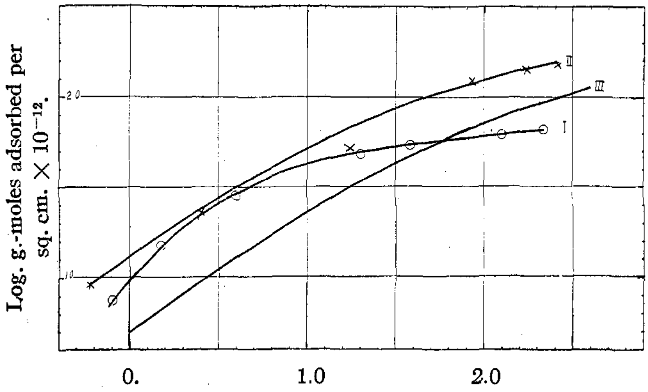

Fig. 2.—Log. total pressure × 10^3.

It would have been well if the curve could have been carried up to complete saturation, that is, up to the vapor pressure of toluene, but with the method used it would have been impossible, as errors in the vapor-pressure measurement and in volume would have accumulated to a larger amount than the total amount adsorbed.

The curves show definitely, however, that adsorption (at least the sort of adsorption which occurs largely at low pressure) will not produce layers of toluene greater than 1 molecule deep on glass. If the thicker layers obtained by other investigators cannot be accounted for by capillary condensation, some other effect must be sought. It is suggested that this effect might be the contact potential which appears to exist between unlike substances.

Adsorption measurements were made at 25° and with the adsorption tube outgassed at 100° instead of 200°, but the adsorption was exceedingly irregular and the amount small, almost beyond the scope of our instrument.

A run was made with hydrogen, instead of toluene, but no adsorption whatever could be observed. The fact that the calculated and observed pressures agreed so well (see preceding article) was taken to indicate that the manometer was correctly calibrated.

The work was done with the aid of a National Research Fellowship. Thanks are due to Professor T. W. Richards for timely help and criticism, and to Drs. Shrader and Ryder for suggestions regarding the manometer used.

Summary

Isotherms for the adsorption of toluene on plane glass surfaces at 0° have been obtained. They agree, in the main, with Langmuir's adsorption formula, and indicate that the adsorbed layer is not more than one molecule deep.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MARYLAND ACADEMY OF SCIENCES]

BLACK COLLOIDAL SUSPENSIONS IN PHOSPHORUS[1]

BY CLAUDE HAINES HALL, JR.

Received September 13, 1922

Bancroft,[2] in his list of problems in colloid chemistry, calls attention to the very confused condition of the literature relating to black phosphorus and suggests that the direct preparation of colloidal suspensions of mercury and other substances be investigated.

The confusion in the literature results chiefly from the indiscriminate use of the term "black phosphorus." At least 4 substances have at some time been given this name, namely Thénard's phosphorus, Bridgman's phosphorus, Hittorf's[3] phosphorus, and Svedberg's[4] colloidal phosphorus. Incidentally, there is really no excuse for calling Hittorf's phosphorus "black" phosphorus, although this term is used[5] as recently as 1919, as it is dark red in color.

In 1812 L. J. Thénard[6] announced that he had discovered a new variety of phosphorus, formed by heating yellow phosphorus to 50° and cooling rapidly. This substance was jet black and he believed it to be a true molecular modification.

Wild[7] independently announced a black phosphorus. Blondlot[8] at-

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[1] Presented before the Section of Physical and Inorganic Chemistry, 64th meeting of the American Chemical Society, September 4–9, 1922, at Pittsburgh, Pennsylvania.

[2] Bancroft, *J. Ind. Eng. Chem.*, **13**, 349 (1921).

[3] Hittorf, *Pogg. Ann.*, **126**, 193 (1865).

[4] Svedberg, *Ber.*, **39**, 1714 (1906).

[5] "Condensed Chemical Dictionary," Chemical Catalog Co., 1919, p. 374.

[6] L. J. Thénard, *Ann. chim. phys.*, **81**, 109 (1812); **85**, 326 (1813). "Traité de Chimie," Paris, **1**, 90 (1834).

[7] Wild, *Arch. Pharm.*, **129**, 262 (1854).

[8] Blondlot, *Compt. rend.*, **60**, 830 (1856); *J. pharm. chim.*, [4] **1**, 407 (1865); *Jahresber.*, **1865**, 134; *Compt. rend.*, **70**, 856 (1870); *J. pharm. chim.*, [4] **11**, 447 (1870); *Jahresber.*, **1870**, 278.