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## 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.

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

# BLACK COLLOIDAL SUSPENSIONS IN PHOSPHORUS[1]

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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-

[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.

tacked Thénard's theories and introduced evidence to show that the color was due to mercury. Ritter[9] claimed it to be due to arsenic. The whole matter was discussed at length by Blondlot,[10] Richardt,[11] P. Thénard,[12] Maumené,[13] Flückiger,[14] Dammer,[15] and Fittica.[16]

In 1910 Gernez[17] published a series of experiments from which he definitely showed that the production of black phosphorus was due to mercury (not phospho-mercuric compounds) and to mercury alone.

In 1914 Bridgman[18] published a description of the production of a black phosphorus by a very different method from those previously discussed. He heated pure yellow phosphorus to 200° under a pressure of 12,000 kg. per sq. cm. for a considerable period of time and obtained a homogeneous black material whose physical characteristics differ from those of Thénard's phosphorus. He presents practically conclusive evidence that his material is a new modification.

Additional proof, from vapor-pressure measurements and other criteria, that Bridgman's phosphorus is an allotropic modification has been given by Smits[19] and his co-workers.

## Experimental

It was decided that the simplest and most certain method of preparing a colloidal suspension in such a medium would be by a modification of Svedberg's method, namely, causing a high tension, low amperage arc to be formed in the melted medium. In the case of phosphorus it is, of course, necessary to exclude the air and to keep the current density low enough to prevent the formation of appreciable quantities of red phosphorus.

The apparatus consisted of an air-tight galvanized iron tank, 30 x 30 x 60 cm., fitted with 3 stopcocks; a U-shaped tube carried the necessary low-tension wires, sealed by filling the tube with insulating compound. The tank was also fitted with a plate glass window, drilled through the center to carry the high tension lead, and clamped tightly to the tank by four metal strips bearing on a heavy rubber gasket.

In the tank was an electric hot-plate and a thermo-couple. The phosphorus was

[9] Ritter, *Compt. rend.*, **78**, 192 (1874); *Bull. soc. chim. Paris*, [2] **21**, 151 (1874); *J. pharm. chim.*, [4] **19**, 279 (1874); *Jahresber.*, **1874**, 224.

[10] Blondlot, *Compt. rend.*, **78**, 1130 (1874); *J. pharm. chim.*, [4] **20**, 12 (1874); *Jahresber.*, **1874**, 225.

[11] Richardt, *Archiv. Pharm.*, **3**, 9, 442 (1876).

[12] P. Thénard, *Compt. rend.*, **95**, 409 (1882); *Jahresber.*, **1882**, 244.

[13] Maumené, *ibid.*, **95**, 653 (1882).

[14] Flückiger, *Archiv. Pharm.*, **230**, 159 (1892).

[15] Dammer, "Handbuch der anorganischen Chemie," Enke, **1894**, vol. 2, pt. 1, p. 95.

[16] Fittica, *Leopoldina*, **36**, 40 (1900).

[17] Gernez, *Compt. rend.*, **151**, 12 (1910); *Ann. chim. phys.*, [8] **21**, 11 (1910); *J. Phys.*, [1] **3**, 17 (1910).

[18] Bridgman, THIS JOURNAL, **36**, 1344 (1914); **38**, 609 (1916); *Phys. Rev.*, **3**, 184 (1914).

[19] Smits, *Pro. Acad. Sci., Amsterdam*, **18**, 992 (1916); **20**, 392 (1918).

contained in a porcelain casserole and the arc was formed between a copper plate, covering the bottom of the casserole and grounded on the tank, and a copper rod, held in the proper position by a glass support and connected to the lead wire through the window. Carbon dioxide was furnished from a cylinder of the liquefied gas.

The high tension current was supplied by a 10,000-volt transformer connected to a $^1/_2$ kw. synchronous converter. One high tension lead was grounded on the tank and the other was carried through the center of the window as previously mentioned.

The phosphorus was redistilled from the ordinary C. P. material supplied by the dealers and showed no traces of impurities.

The tank was filled with carbon dioxide and the switch of the hot-plate turned on. The phosphorus melted sharply at 45° to give a clear liquid without scum. The arc was started, while the stream of carbon dioxide was maintained, and was seen under the surface of the phosphorus as a blue light; it vaporized the phosphorus immediately around it and caused the evolution of clouds of dark material. After 15 minutes the current was cut off and the apparatus allowed to cool. Water was run in and the tank opened. The product was a black to reddish-black mass.

Other experiments were identical with the preceding except that they were run for 5, 10, and 25 minutes, respectively.

When the bottom of the casserole was covered with mercury and the experiment performed in the same manner the product was jet black.

The material obtained is perfectly homogeneous, readily inflammable, and has a specific gravity of about 1.9. When extracted with carbon disulfide it leaves a residue of extremely small black crystals (about 6.5 microns in length), or minute droplets in the case of mercury, and a few red flakes, evidently red phosphorus. The black crystals are copper phosphide, $Cu_3P_2$.

These products are evidently colloidal suspensions of copper phosphide and of mercury and have the same characteristics as the black phosphorus described originally by Thénard. Without doubt there would be no difficulty in preparing suspensions of almost any other metal.

This complements the proof given by Gernez that Thénard's material is not a true allotropic modification and bears out the conclusions arrived at in the preceding section.

## Summary

The literature relating to black phosphorus has been quoted to show that Thénard's phosphorus is a colloidal suspension of mercury, while Bridgmans' material is a true allotropic modification.

Two new colloids prepared by a modification of Svedberg's method are described.

A bibliography is given.

The author wishes to record his gratitude for the very valuable services rendered by Mr. Warren N. Crane in constructing the major part of the apparatus.

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