monomethylaniline, but it has not as yet been obtained in a pure enough state for identification.

Aniline and Diphenylamine.—Molecular quantities of these amines yield in benzene solution benzanilide, aniline hydrochloride, diphenylamine and unchanged benzoyl chloride.

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PIPERONAL AND HYDROGEN CHLORIDE: A TWO-COMPONENT THREE-PHASE SYSTEM.

BY F. J. MOORE.

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SINCE it appears from a recent paper by D. McIntosh,[1] that he is also studying the action of the halogen acids upon aldehydes, the following extremely incomplete observations are communicated at this time to avoid any possibility of collision.

While investigating the action of some organic compounds upon piperonal, the accidental observation was made that this substance liquefies when brought into contact with dry hydrogen chloride. When the liquid thus formed was exposed to the air on a watch-glass, crystals appeared. A melting-point determination showed that these consisted of piperonal. The explanation of these phenomena obviously is, that piperonal adds hydrogen chloride as long as the pressure of the latter upon its surface is about one atmosphere, but the vapor pressure of the product is so great that when the partial pressure of the hydrogen chloride falls, all the gas is liberated. In order to bring out these relations more clearly, the apparatus was devised which is represented in the accompanying diagram.

B is a small bulb about 35 mm. high and 7 in diameter—outside measurement. D is a much larger cylinder about 135 mm. long and 40 in diameter. E is a leveling-bulb connected with D by thick-walled rubber tubing.

Somewhat less than a gram of piperonal is first introduced into B. The most convenient way to do this is to melt some piperonal, and draw it in through A by suction. Mercury is next poured into the bulb E, and the latter is raised until the mercury fills D and reaches the point x, just leaving the tube C open. Meanwhile the piperonal in B is kept melted by means of a beaker of

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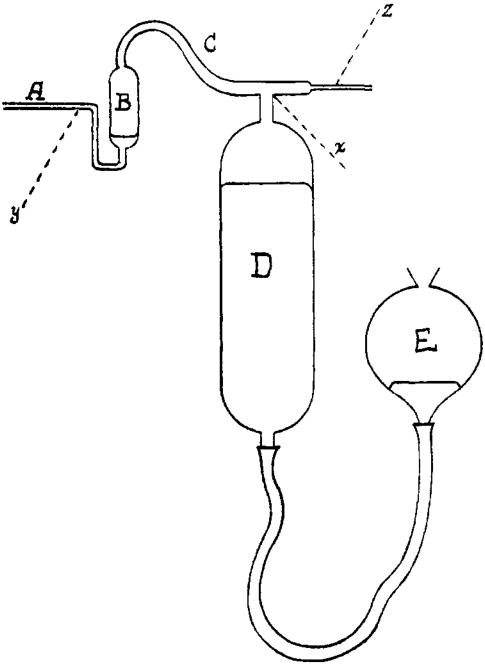
[1] This Journal, 28, 588 (1906).

warm water placed under it, and now a stream of dry hydrogen chloride is passed through the bulb, entering through A. As soon as the current is started, the warm water under B may be removed, and the gas is passed through until the crystals which at first begin to form have completely liquefied. The tubes A and C are now sealed off at the points *y* and *z*. The mixture in B is now in equilibrium with the hydrogen chloride above it at the prevailing temperature, and the whole system stands under the pressure of one atmosphere.



If, now, the bulb E be lowered, gas is evolved from the liquid in B, which begins to boil. Crystals soon appear upon its surface, and, if the quantity of piperonal has been appropriately chosen with reference to the dimensions of the apparatus, the contents of B solidify to a mass of crystals. If the bulb E be again raised, the gas is absorbed, the crystals rapidly lose their outline, and, in less than a minute, those on the surface have completely liquefied. After standing at a pressure of about an atmosphere for a few minutes, liquefaction is complete throughout the mass. These operations can, of course, be repeated indefinitely.

The conditions here seem analogous to those which obtain between calcium oxide, carbon dioxide and calcium carbonate at a temperature in the vicinity of 800°. As the action in the present case is so rapid, and can be so readily followed by the eye, it is suggested that the experiments just described might well find use in demonstrating to students this particular application of the "phase rule."

A rough measurement of the difference in level of the mercury in bulbs D and E, when both solid and liquid are present in B, shows that the dissociation pressure of the addition product is somewhere in the vicinity of 500 mm. This is but a rough approximation. An accurate measurement has not yet been attempted, as in the experiments hitherto made I could not be certain that the hydrogen chloride was free from air. Another form of apparatus has been designed to meet this difficulty, and when the work is resumed in the autumn, more accurate measurements will be made. The question whether the addition-product is a chemical compound or a solution will then be taken up, and the investigation extended to the action of hydrogen bromide and iodide as well as other compounds upon piperonal.

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BENZOYL-p-BROMPHENYLUREA: A BY-PRODUCT IN THE PREPARATION OF BENZBROMAMIDE.

BY F. J. MOORE AND A. M. CEDERHOLM.

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IN 1882, Hofmann,[1] while carrying on his celebrated investigation of the action of bromine and alkali upon amides, discovered acetbromamide. At the same time he made the observation that this substance reacts both with aniline and with phenol to form tribromaniline and tribromphenol respectively—acetamide being regenerated in accordance with the following equation.

$$C_6H_5.NH_2 + 3C_6H_5—CO.NHBr = C_6H_2(Br_3)NH_2 + 3C_6H_5CO.NH_2.$$

The chemical behavior of acetbromamide and analogous compounds has since been investigated by Seliwanow[2] and others,

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[1] Ber. 15, 410 (1882).

[2] Ibid. 26, 424 (1893).