

EXPERIMENTS WITH CAREFULLY DRIED SUBSTANCES.—By D. MC-INTOSH, M.A., D.Sc., Dalhousie University, Halifax, N.S.

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The great catalytic effect of small amounts of water on chemical reactions is familiar to all students of chemistry. The principal worker in this field, Baker, has made during the last thirty years many surprising discoveries. Among these may be mentioned the inertness of very dry mixtures of hydrogen and oxygen, of dry oxygen to sulphur, phosphorus, etc., and in particular the high boiling-points of super-dried liquids, such as ether, benzene and mercury. It seems probable that the physical properties of all pure liquids are greatly altered by the removal of the last traces of water, and that constants, such as the boiling and freezing points, solubilities, etc., will need to be revised in the light of this new knowledge. It is not surprising then, that other investigators such as Smits and Cohen, have studied this interesting group of phenomena, and have made notable contributions to both the theoretical and experimental sides.

During the last few years I have made some few experiments with carefully dried materials, by employing low temperatures. These have yielded no positive results, but, by giving an account of the method, some one may be induced to try similar experiments, and to improve the technique. The lack of success is due probably to difficulty in removing the film of water from the glass surface, although the apparatus was strongly heated and kept at low pressure.

1. The union of carbon monoxide and oxygen.

A mixture of these gases in the proportion of two molecules of the former to one of the latter is not ignited by an electric spark if the gases are dried by freshly distilled phosphoric anhydride. They may be dried by cooling to a low temperature in the following simple way. The tube shown in Figure 1 is exhausted by a mechanical pump, the lower part of the tube is surrounded by carbon dioxide and ether in a Dewar flask, and

the tube is filled with the gas mixture kept in a vessel over water. The upper part of the apparatus is always approximately at room temperature. Almost invariably the gases fail to explode after 15 hours, nearly always after 5 hours, and occasionally after only one hour's treatment.

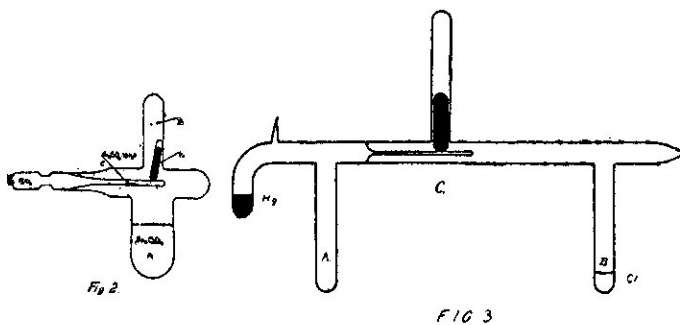
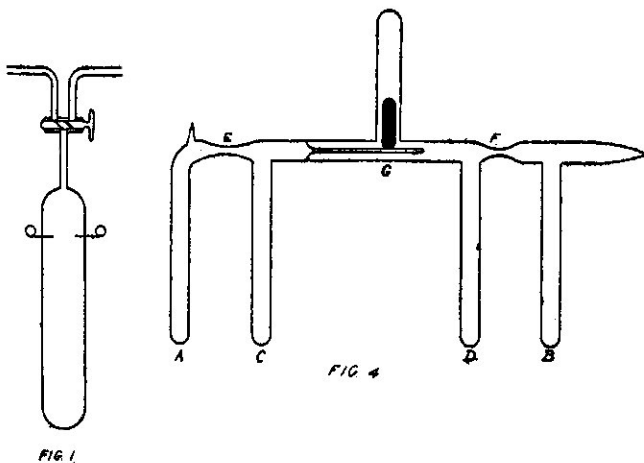
When the apparatus is allowed to warm slowly in a Dewar vessel containing cold ether, the gas explodes when the outside temperature is between -50° and -60° . Since the vapour pressures of the water at these temperatures are 0.03 and 0.01 mm., there is only one molecule of water present to some 40,000 molecules of the gas.

The amount of water is not, however, the sole factor influencing this reaction, for the energy of the spark and the gas pressure have been found by Bone to affect the amount of water vapour necessary to bring about partial combustion. I might mention here that a detonating mixture of nitrous oxide and carbon monoxide is always exploded by a spark when dried by cooling at -80° . These experiments were made in September, 1921, and I was not aware until a short time ago that the same method of drying the carbon monoxide mixture had been used by **Girvan**¹ in 1902.

2. I have attempted to dry sodium sulphate so completely as to destroy all crystals, and thus render it inactive in precipitating crystals from a supersaturated solution. The apparatus was almost the same as that used in some former experiments and is shown in Figure 2. The super-saturated solution was placed in A, the apparatus was heated to destroy any crystals, and C was exhausted by a diffusion pump, sealed and allowed to stand for several weeks. C was then opened, and finely ground air-dried sulphate introduced by a gentle stream of filtered air, so that the particles must have been very small. C was re-exhausted and the apparatus allowed to stand for six weeks. Crystallization occurred instantly when the particles were introduced into the super-saturated solution.

1 Proc. Chem. Soc. 236.

The experiment was varied by using glass hairs², rubbed gently over a crystal of sodium sulphate, in the inner tube, and by attaching a side-tube, not shown in the sketch, containing phosphoric anhydride, or which could be placed in liquid air. The results were in all cases the same; precipitation took place at once.



The precipitation may be due to the decahydrate or to anhydrous isomorphous crystals, as deCoppet suggested. In several experiments the tubes were heated to 45° for an hour.

² Professor Gowanloch has kindly measured the size of some of these particles. They had a mass not greater than 3×10^{-8} gram.

After cooling no precipitation occurred when the salt was introduced. This indicates that the crystallization was due to the decahydrate, for it would be destroyed by the heat, while the anhydrous crystals would probably not be affected. Apparently the small crystals hold moisture very tenaciously, although the vapour pressure of the ordinary crystals is about 15 mm.

3. The interaction of mercury and chlorine has been examined repeatedly, and even with the most careful drying a reaction seems to take place³. I have made some experiments on this in the following way.

Mercury and chlorine were placed in the two side tubes of the apparatus shown in Figure 3. The side containing the mercury was exhausted with a diffusion pump and the mercury gently boiled. The tube containing the chlorine was frozen by liquid air and exhausted to a low pressure with a mechanical pump. Tubes A and B were cooled in liquid air for 24 hours, and the separating tube C, broken. At -180° the vapour pressure of chlorine is quite appreciable, probably greater than 0.001 mm. At the low pressure of chlorine and water vapour there is no noticeable action on the droplets of mercury in 12 hours when they are examined with a magnifying glass. If the chlorine be allowed to rise in temperature, somewhere considerably below the temperature of solid carbon dioxide where the water vapour pressure is still very low, a reaction is evident.

4. The reaction between hydrobromic acid and ammonia.

The apparatus shown in Figure 4 was heated and exhausted. The end tubes were connected by rubber tubing to vessels containing liquid ammonia distilled from sodium, and hydrogen bromide respectively. The points were broken, so that the compounds distilled into A and B, which were cooled by liquid air. The apparatus was then exhausted and sealed. The acid and the ammonia were distilled into C and D at carbon dioxide temperature, and A and B were sealed off at E and F. C and D were kept at -80° for twenty-four hours. On breaking the

3 Germain, Jour. Phys. Chem. 28, 1218, 1924.

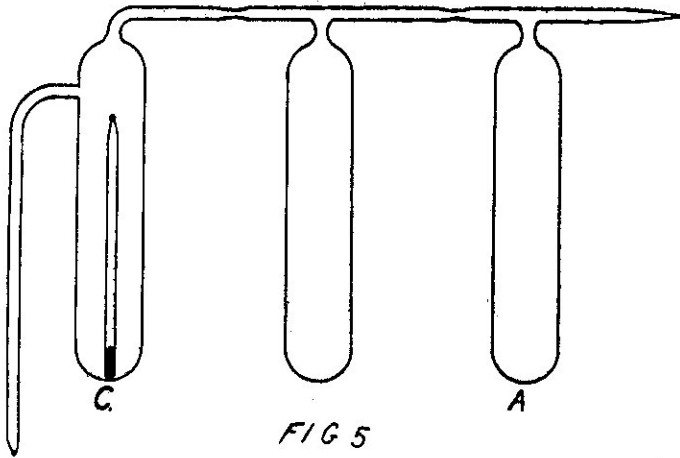
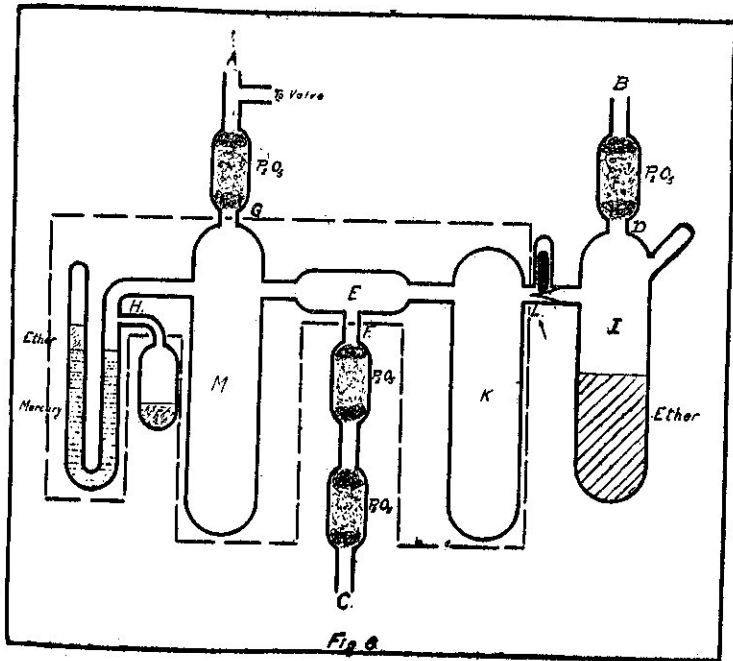


FIG 5



tube E, a cloud of ammonium bromide appeared, showing that the vapour-pressure of the water must be reduced below one one-thousandth of a millimeter to prevent interaction.

5. An attempt to dry ether.

In Baker's experiments the drying of ether was a matter of years. I have tried to make a high-boiling ether by distilling at a low temperature, since a comparison of the vapour-pressure curves of ether and water would seem to show that separation is more complete the lower the temperature.

The apparatus, shown in Figure 5, after remaining for some time exhausted to a low pressure, was filled with dry air. Ether, which had stood over sodium, was distilled into A, and the apparatus was exhausted and sealed. The ether was distilled at -80° into B and C, A and B being sealed off in turn. C was finally warmed in a water-bath to 36° , and the side tube was opened under freshly distilled mercury. The ether boiled at its normal temperature.

6. Drying ether by phosphoric anhydride.

This was done in the apparatus shown in Figure 6, which was constructed of Pyrex glass. It was exhausted by a diffusion pump for several hours being heated with a Bunsen burner to a high temperature, sealed and left for several weeks. The apparatus was opened at A and C, filled with dry air, phosphoric acid was distilled into E, and F sealed off. It was then re-exhausted through A, mercury distilled into the manometer, and the mercury bulb and phosphoric acid tube sealed off at H and G. The tube J, containing ether which had stood over sodium for several weeks, was then exhausted and the pentoxide tube sealed off at D. The valve connecting J with the main apparatus was broken, and the ether distilled at the temperature of solid carbonic acid into K, which was cooled with liquid air. The mercury in the manometer was frozen with carbon dioxide, the point of the manometer was broken, and ether introduced. This was boiled under reduced pressure until air was expelled, and the manometer was sealed. The apparatus, which is shown in the figure between the broken lines, was allowed to come to room temperature and the pressure read. The ether

was then distilled slowly through the phosphoric anhydride tube by cooling M with tap-water. After bringing to room temperature the manometer was read again, and this procedure was repeated each day.

Two experiments were made. In the first, a bubble or two of ether vapour passed from the manometer to M and the experiment was discontinued. The second trial seemed to be successful so far as the manipulation was concerned. The pressure however, equal at first on both sides of the manometer, increased on the dry ether side with each passage of the ether vapour through the phosphoric acid tube, and reached a difference of 5 centimeters at the 20th transference, and at the end of 6 months the oxide appeared quite moist. This increase of pressure may be due to decomposition of the ether into water and ethylene, which might possibly take place with ether not sufficiently dried in the beginning, or from water liberated from the glass when making the necessary seals.