ART. V.—*Explosive Properties of Methyl Nitrate;* by M. CAREY LEA, Philadelphia.

SEVERAL dangerous accidents have recently occurred in the manufacture of methyl nitrate, one of them unfortunately resulting in the death of Mr. Chapman. This, and the remarks recently published on the subject by M. Girard, the well-known French chemist (an abstract of which lately appeared in the pages of this Journal), leads me to make a few observations on this subject.

When I first attempted to prepare this substance by the only method published up to that time, I felt convinced that the chances were greatly in favor of an accident, though no warning was given in the text books. I therefore wore a mask, and operated cautiously with moderate quantities in a very large flask. A tremendous explosion followed, in which the flask entirely disappeared; no fragment of the body could be found. I then tried the use of urea in the same modified manner which I had proposed in the case of ethyl nitrate. The operation was entirely successful, and was many times repeated without any trouble or difficulty. And it is, I presume, in this way that it is now commercially manufactured on a large scale.

Within the last few days I have made the following experiments on its explosive properties.

Contrary to what has been stated, I do not find it liable to explode by percussion. Some extra thick filtering paper was saturated with it, was placed on a piece of iron, and forcibly struck with a hammer. This was repeated a dozen times, until the paper was broken to pieces, without explosion.

Five or six drops were placed in a test tube; this was placed in a deep cup, and a little alcohol poured into the cup and inflamed. In this way the flames played chiefly on the surface of the test tube above the liquid, thus preventing its escape by evaporation at low temperatures. A slight explosion followed, which did not break the test tube.

When ethyl nitrate was similarly treated, it quickly evaporated without explosion.

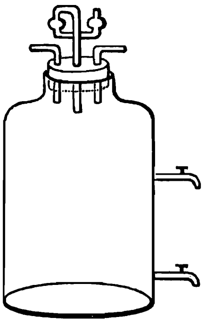
Twenty measured minims of methyl nitrate were then placed in the tube, and the experiment repeated. A moderate explosion followed, breaking the tube.

The same quantity as in the first experiment, five or six drops, was placed in the test tube, and dry sand added more than enough to absorb the liquid. The heat was applied in the same way as before, but the explosion was not greater than without the sand, except that the tube was broken.

When poured on filtering paper and inflamed, it burns quietly with a peculiar livid flame.

These trials do not seem to indicate a very violent explosive power. Nevertheless, the unfortunate experience which has been already gained sufficiently indicates that it is not a substance to trifle with. Indeed, a liquid whose vapor explodes at 150° C., as determined by Dumas and Peligot, cannot be otherwise than dangerous, especially when handled in large quantity. Having been the first person to prepare this substance in any quantity, and having had occasion to study carefully its conversion into the methyl ammonias, it occurs to me that as these substituted methyl compounds are now used on a large scale, a few suggestions toward a safe method of managing the operation for large quantities may be acceptable.

I would propose to construct a receptacle in which to receive the methyl nitrate vapors as they are distilled over, of the shape shown in the margin, a cylindrical vessel with a large mouth and two faucets, one near the bottom, the other a little above the middle.



To commence the operation, the vessel should be filled one-third full with lumps of ice. The cover should then be closely fitted on with a safety tube, and a third tube connecting with another similar vessel.

As the partly condensed mixed alcoholic and ethereal vapors come over, the products of distillation are cooled by the ice, and the water resulting from its melting precipitates the ether. This last can be from time to time drawn off by the lower faucet, into stoneware bottles already containing a proper quantity of strong ammonia and alcohol. When one-third full of the ingredients in the proper proportions, these bottles should be securely closed, and placed for several days at a temperature of about 90° F., until decomposition is complete.

The upper faucet shown in the cut is to draw off the mixed water and alcoholic distillate which accumulates in large quantities over the ether, and which otherwise would impede the operation.

In the process as above described, the methyl nitrate would be destroyed almost as soon as formed. As soon as any considerable quantity has passed over, it could be transferred into the vessels in which, by contact with ammonia, decomposition begins, and this without interrupting the distillation. If desired, sodium carbonate can be placed in the condensing vessel to remove any nitric acid that may adhere to the methyl nitrate. But the presence of a little acid is not important in the decomposing jar; it would be converted into ammonium nitrate, and as this salt is always formed to some extent by the action of methyl nitrate on ammonia, the presence of a fraction more or less would be unimportant.

I am inclined to believe that in the manner described, the danger in the preparation of this substance will be reduced to a minimum, a matter of some importance, as the quantity consumed in the manufacture of the methyl violet seems likely to be increasingly large. A good cooling apparatus between the retort or still and the receiver here figured would be necessary.

W. Weith has just published* an interesting communication on the formation of methyl-ammonias by the action of excess of methyl alcohol on sal ammoniac, which at 285° C. was completely converted into methyl ammonias. This method of methylizing ammonia may perhaps take the place of mine: it is, however, liable to two objections; first, that a considerable proportion of the methylic alcohol is, according to Herr Weith, lost by conversion into methyl ether; secondly, the high temperature and pressure necessary. I found that methyl nitrate, unlike ethyl nitrate, does not require pressure vessels, but reacts at or near the ordinary temperature and pressure. My own operations were performed in large stoppered vials set on the cooler part of a sand bath, where the temperature did not rise above 90°. The loss by formation of methyl ether may perhaps be compensated by the fact that in the formation of methyl nitrate there is always loss of both methylic alcohol and nitric acid.

Philadelphia, May 17, 1875.