XII.—*Interaction of Nitric Oxide with Silver Nitrate.*

By EDWARD DIVERS.

HAVING reason to think that silver nitrate might interact with nitric oxide if heated in it, and there being no information obtainable on this point, I have made some experiments on the action of nitric oxide on silver nitrate, as well as on other nitrates.

In the first place, something had to be ascertained as to the behaviour of silver nitrate when heated alone. Heated for 15 minutes in dry air or carbon dioxide, it suffers no chemical change until the temperature is close to the melting point of sulphur (444°), and the slight decomposition which occurs at that temperature, being accompanied by an action on the glass, may be due to that action. A minute quantity of oxygen seems to be liberated, and there is a very slight greying of the faintly yellow liquid; on cooling and dissolving, there is slight turbidity from the presence of silver, and a trace of nitrite can be detected. Only at a much higher temperature does the salt decompose with free effervescence, and then nitric peroxide accompanies the oxygen, and silver is deposited; even then, nitrite is present in the mass only in very small quantity at any time, there never being enough to remain undissolved when the nitrate is treated with a little water. This is sufficient, however, to show that the primary decomposition of silver nitrate by heat alone is into silver nitrite and oxygen, the instability of silver nitrite at much lower temperatures, although diminished by the presence of nitrate (Trans., 1871, 24, 85), accounting fully for its being found in such small quantity when the temperature is high, and for the production of nitric peroxide and silver instead. As determined by Carnelley, the melting point of silver nitrate is 217° .

The nitric oxide used for the experiments was prepared by the ferrous sulphate method, stored for 2 days in a glass gas-holder, and dried in its passage to the silver nitrate by a sulphuric acid column. At starting, the air in the drying apparatus and in the tube containing

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the silver nitrate was expelled by carbon dioxide, the silver nitrate being heated in the gas, in order to dry it. Interaction between the silver nitrate and the nitric oxide was recognised by the reddening of the gas, and at the end of an experiment the gases were expelled by carbon dioxide before opening the tube.

Silver nitrate, when heated in nitric oxide, is strongly affected by it, being freely decomposed at a much lower temperature than that at which it decomposes when heated alone, the nitric oxide becoming oxidised. The action commences, perhaps, at 150° , but this is doubtful; at the melting point of the salt, it becomes marked, and at the boiling point of mercury considerable, but even at this temperature it is a long time before the decomposition is complete, the progress of the change gradually becoming slower. For some time, the products are silver nitrite and nitric peroxide, $\text{AgNO}_3 + \text{NO} = \text{AgNO}_2 + \text{NO}_2$, but very little silver is liberated, the nitrite being almost wholly preserved for a long time, through combination with the undecomposed nitrate. But when, as the nitrate becomes decomposed, the nitrite is no longer unprotected, it suffers decomposition, as usual, into silver and nitric peroxide; finally, nothing but silver remains.

Theoretically, it is quite probable that nitric oxide does not, after all, act directly on silver nitrate. For, making the allowable supposition that, to a minute extent, silver nitrate decomposes into silver nitrite and oxygen, at temperatures much below that at which it does so sensibly, the nitric oxide may be regarded as being active by combining with this oxygen, and thus, by removing it, greatly hastening the spontaneous decomposition of the nitrate. This decomposition, thus assisted, and occurring at temperatures at which silver nitrite is comparatively stable in presence of nitrate, the nitrite remains, although at higher temperatures it decomposes almost as fast as it is formed from the nitrate. According to this theory, silver nitrate is not actually decomposed by nitric oxide, but only decomposes much more rapidly in its presence, in consequence of its interaction with one of the products of decomposition. For practical purposes, silver nitrate and nitric oxide may, however, be treated as acting on each other when heated together.

Nitric oxide has no action on sodium potassium or barium nitrate, even at the temperature of boiling sulphur.

Lead nitrate soon begins to decompose by heat alone, and nitric oxide seems to be without effect on its decomposition. According to Stas, lead nitrate begins to decompose somewhere above 200° ; I find that, for its fairly free decomposition, a temperature not much below 400° is required. At the boiling point of sulphur even, the decomposition proceeds at such a moderate rate that only after 10 minutes heating does the salt show distinct signs of fusing. No nitrite is pro-

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duced, but a very little peroxide of lead is formed. By washing the mass with cold water, and then boiling it out with water, the beautiful, crystalline, white salt, $\text{Pb}(\text{OH})\text{NO}_3$, can be obtained in abundance.