

Interaction of Nitric Oxide with Silver Nitrate.

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Having reason to think that silver nitrate might interact with nitric oxide if heated in it, and there being no information obtainable on the point, I have been induced to make some experiments with silver nitrate, as well as other nitrates, and nitric oxide.

First, something had to be ascertained of the behaviour of silver nitrate when heated alone. Heated for fifteen 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 its slight decomposition at that temperature, being accompanied by its action upon 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, being never enough to remain insoluble when the nitrate is dissolved in 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; since the instability of silver nitrite at much lower temperatures, though diminished by the presence

of nitrate (*J. Ch. Soc.*, 1871, **24**, 85) fully accounts for its being found only 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 two 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 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. At the end of an experiment the gases were expelled by carbon dioxide before opening the tube.

Silver nitrate heated in nitric oxide is greatly affected by it, being freely decomposed at much lower temperatures than those at which it decomposes by itself, while the nitric oxide becomes oxidised. The action commences perhaps at 150°, but this is doubtful; at the melting point of the salt it becomes marked and interaction at the boiling point of mercury considerable; but even at this temperature it is a long time before the decomposition becomes complete, the progress of the change growing slower. For some time the products are silver nitrite and nitric peroxide— $\text{AgNO}_3 + \text{NO} = \text{AgNO}_2 + \text{NO}_2$, with only very little silver, the nitrite being almost wholly preserved for a long time through combination with the undecomposed nitrate. But when by the consumption of the nitrate the nitrite gets unprotected it suffers spontaneous decomposition as usual into silver and nitric peroxide. At last, nothing but silver remains.

Theoretically, it is quite probable that nitric oxide does not, after all, act directly upon 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 active by combining with this oxygen and thus by removing it greatly hastening the spontaneous decomposition of the nitrate. This decomposition, thus assisted, occurring at temperatures at which silver nitrite is comparatively stable in presence of nitrate, the nitrite remains, though at higher temperatures it decomposes almost as fast as it gets 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 decomposition products. For practical purposes, silver nitrate and nitric oxide may however be treated as active upon each other when heated together.

Nitric oxide has no action upon 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 upon 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 ten minutes heating does the salt show distinct signs of fusing. No nitrite is produced, but there is formed a very little peroxide of lead. By washing the mass with cold water and then boiling it out with water, abundance of the beautiful, crystalline, white salt, Pb(OH)NO_3 , is obtained.