ON THE VOLATILIZATION OF PLATINUM IN CHLORINE GAS.

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Some years ago I tried the following experiment: a piece of thin platinum foil was placed in a tube of difficultly fusible glass, and heated to bright redness by a gas flame which surrounded the tube. A slow current of chlorine was then conducted through the tube, and continued without interruption for twenty-four hours. At the end of this time. it was found that the tube, behind the foil, was coated with crystals of platinum. The crystals showed the forms $\infty 0 \infty . 0, \infty 0, \frac{\infty 0 . n}{2}$, were beautifully developed, compact, lustrous, and the form could be recognized without the aid of the lense. Subsequently I tried the same experiment in a porcelain tube in a charcoal fire, but continued it for a few hours only. It furnished, again, crystals of the same form, only smaller. I sent a specimen of these crystals, in 1873, to Prof. R. Boettger, in Frankfort. Although the objection cannot be sustained that the platinum was mechanically transferred by the stream of chlorine, as it, in that case, would necessarily have assumed the form of an amorphous coating, I, nevertheless, recently tried the following experiment, to prove that platinum is volatile in an atmosphere of chlorine:

Some platinous chloride was placed in a small porcelain flask, with a very narrow neck. The flask was coated with loam, and, without closing the opening, heated to light redness in an ordinary portable furnace. After cooling and carefully breaking the flask, it was seen that the platinum had sublimed. A portion formed, in the lower part of the neck, a small sublimate of reticulated crystals, and below these the sides and bottom of the flask were coated with microscopic, but completely developed, platinum crystals which showed the lustrous faces above noted. It was evident that a white heat had not been entirely reached, as the platinum vapor would then have ascended to a higher point.

The experiments above communicated prove, with absolute certainty, that platinum is entirely volatile in chlorine gas. No platinous chloride was to be seen in either case. As, therefore, the hypothesis of a dissociation of chlorine in the experiments of V. and C. Meyer (Berl. Ber., **12**, 1426, and this JOURNAL, **1**, 313), rests, as they themselves remark, on the assumption that platinous chloride leaves, when heated, an *absolutely non-volatile residue*, the fact that, as above shown, this assumption is incorrect, deprives the hypothesis of a dissociation of chlorine of the sole foundation on which it rested, and makes it unnecessary for us to have recourse to the two hypothetical explanations which Ad. Lieben (Comptes Rendus, 89, 6, and this JOURNAL, 1, 453) offered on the presumption that the porcelain and platinum had evolved no gaseous substance. The fact, observed by the Messrs. Meyer, that the volume of the chlorine in their experiments was one-third greater than at lower temperatures, may be explained in perfect harmony with the observed facts, by the equation:

$$Pt_2Cl_4 = 2Cl_2 + Pt_2 = 6 \text{ vols.},$$

wherein 2 volumes are occupied by platinum vapor. The experiment gains additional interest from the fact that it represents just as well a determination of the vapor density of platinum as that of chlorine. It only remains to determine by quantitative experiment whether the molecule of platinum consists of one or of two atoms.

It is another question how we are to conceive that the platinum volatilizes in chlorine gas. A chemical action must take place, as platinum is not volatile at the same temperature in indifferent gases. It has already been proven by the experiments of Troost and Hautefeuille (Comptes Rendus, 84, 947), that when platinum is heated to 1400° C. in chlorine gas, it is deposited in crystals; and also, that when the gas is suddenly cooled, platinous chloride is deposited. They assume that the vapor at 1400° does not contain platinum, but platinous chloride, which, on cooling, dissociates and deposits platinum in crystals. If this view is correct, then, if the molecule of platinous chloride be Pt_2Cl_4, the vapor density of chlorine in the experiments of the Messrs. Meyer would be found to be greater than the normal figure; whereas, if the molecule be $PtCl_2$, it would be, at most, equal to it, and the probability of a dissociation in the experiments in question would thus be increased. We should, however, remain better in accord with the direct results of the experiments and with the phenomena of dissociation, if we should assume that the platinous chloride in the hot gaseous mixture is not stable, but in a condition of continual decomposition and recomposition. In this case there would always be present in the gaseous mixture platinous chloride, besides free platinum, the quantity of which would, at the temperatures employed by V. and C. Meyer, be so small, that it would have no perceptible effect on the volume. However that may be, there can be no thought of a dissociation of chlorine until it has been established that the gas experimented on is not contaminated with the vapors of other substances.