(2) Pressure bottle method of decomposition and analysis for explosive or volatile compounds capable of decomposition at temperatures below the boiling-point.

(3) Elaboration of methods for simultaneous recognition of hypophosphorous, phosphorous and phosphoric acids.

(4) Discussion of the source of hydrogen in the preparation of phosphine.

(5) Qualitative test for phosphine by ammonium molybdate.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.

VOLATILIZATION OF PLATINUM.

By G. A. HULETT AND H. W. BERGER.

Received August 15, 1904.

IN DETERMINING the effect of heat on barium sulphate[1] we observed a decrease in the weight of the platinum dish used. Heated to 1125° C. for four hours in an electric furnace there was a loss of 1.4 mg. and a platinum mirror was deposited on the cover of the furnace.

In 1852, Deville observed that noticeable amounts of platinum collected on the cover of the furnace in which he melted his platinum. Deville suggested that this might be due to volatilization. Aitken,[2] in 1879, in studying the formation of fog, observed that a platinum spiral glowed by an electric current gave off particles which produced a fog in an otherwise dust-free but moist atmosphere. The so-called "Zerstäubung" of electrically glowed platinum wires and points has been frequently observed, also that a metallic mirror is deposited on colder objects in the vicinity of the glowing wire. R. Nahrwold[3] paid particular attention to this phenomenon and was able to show that no "Zerstäubung" took place in an atmosphere of hydrogen or in a vacuum. It was necessary for oxygen to be present in order that the platinum wire lose weight when glowed by an electric current. Further evidence of the same nature has been obtained by W. Stewart,[4] and more particularly Holborn and Henning,[5] and Hol-

---

[1] *Ztschr. anorg. Chem.*, **40**, 209 (1904).

[2] *Nature*, **31**, 268.

[3] *Wied. Ann.*, **35**, 116 (1888).

[4] *Ibid.*, **66**, 88 (1898).

[5] *Sitzungsber. Berl. Akad.*, 1902, p. 936.

born and Austin,[1] have shown that platinum, iridium and rhodium all show this phenomenon. It is most marked with iridium, but it is only in oxygen or mixtures of gases that contain oxygen that the electrically glowed wire loses in weight and deposits the metal on colder objects. Palladium seems to behave differently from the others, losing weight independently of the gas and noticeably in vacuum. Palladium thus shows a true volatilization. The temperatures used by the above investigators ranged from 1050° C. to 1500° C.

We have made a few more experiments with the electric furnace, using a sheet of platinum foil 19.4 by 13.6 cm. wound in a loose coil so that it could be suspended in the heating cylinder of the electric furnace and also so that a slow current of air, free from carbon dioxide, might pass up through the coil. The total surface was some 530 sq. cm. We started at 900° C. (the temperature was measured as before)[2] and in two hours we found a loss of 1.6 mg., while we had hardly expected a loss at this temperature. A further two hours' heating at 900° showed a loss of 1.4 mg., and a third two hours' heating at the same temperature showed a loss of 0.9 mg. The foil was next heated for two hours at 1020° and lost 1.5 mg. The foil had now assumed a frosted appearance, such as is observed on platinum, which has been attacked by aqua regia. The foil was now treated with aqua regia until it had lost 220 mg., was rinsed, rapidly glowed, weighed and then heated in the furnace, as before, for two hours at 1020°. The loss was 5.6 mg. This decrease in loss on successive glowings has also been observed by Stewart,[3] and from this last result it seems that on removing the surface layer with aqua regia the subsequent glowing shows a maximum loss. Also burnishing with fine pumice has the same effect as treating with aqua regia, but the subsequent glowings show a decreasing loss for each successive glowing. The foil used was common platinum foil, 0.1 mm. thick, and evidently contained little iridium, as it dissolved completely in aqua regia; however, it seemed desirable to test pure platinum and we turned to the platinum manufactured by Heraeus for thermocouples, which contains no palladium or rhodium, hardly a trace of iridium and only 0.001 per cent. of

---

[1] *Sitzungsber. Berl. Akad.*, 1903, p. 245.

[2] *Ztschr. anorg. Chem.*, **40**, 209 (1904).

[3] *Loc. cit.*

iron.[1] A short piece of this wire, kindly loaned by Prof. E. D. Campbell, was rolled flat (except the ends) and then glowed in air by a current of 5.15 amperes. The flat portion, which only was at a white heat, was 38 cm. long and 1 mm. wide. Glowed for one-half hour the loss was 0.55 mg. The second half hour gave 0.27 mg. loss, and the third half hour gave 0.5 mg. loss. The ribbon was dipped in aqua regia, losing 0.2 mg. and then glowed, losing 0.8 mg. A current of 5.15 amperes was used for each glowing, but the temperature was probably not the same in all the glowings, as the resistance of the ribbon may have changed. However, the results show that this pure platinum behaves essentially as the foil.

Evidently the volatilization of platinum has little to do with the impurities present, nor are the impurities the cause of the very curious phenomenon of the decreasing losses of the successive heatings. It seems due to some condition of the surface brought about by volatilizaton of the metal and not to a condition of the surface due to a heating and cooling of the metal. The phenomenon presents an interesting problem in itself.

We wished especially to find the lowest temperature at which platinum loses weight. The above foil was, therefore, heated two hours at 810° with a slow air current passing up through the heating cylinder. The loss was 0.13 mg., while a second two hours at the same temperature showed a loss of 0.1 mg. At 870° the loss was 0.6 mg. when heated for two hours. The foil was now treated with aqua regia and then heated for two and one-half hours at 795°, but there was no detectable change in weight. It seems then that 800° is the lowest temperature at which the effect is noticeable. At 900° 100 sq. cm. surface loses about 0.25 mg. per hour as a maximum. At 1000° the loss amounts to 1 mg. per 100 sq. cm. surface.

In exact analyses where precipitates are glowed in platinum it is evidently advisable to check the weight of the platinum vessel used after the operation. The temperature in ordinary analytical work is considerably over 900°, as shown by the following experiment. A platinum crucible, supported by a platinum wire triangle, was provided with a perforated cover. The double-bored porcelain tube of the thermocouple extended through the cover and the junction of the couple rested on the bottom of the crucible.

---

[1] Mylius and Foerster : *Ber. d. chem. Ges.*, **25**, 683 (1892).

When the crucible was glowed by a good Bunsen flame, we observed a temperature of 960°. On blasting the crucible with foot bellows and lamp 1160° was observed, and now on changing back to the Bunsen burner, 975°. These temperatures are, of course, affected by a good many factors, but give an idea of the temperature ordinarily obtained and they are such that volatilization can very readily take place. The volatilization will depend, however, on the amount of. oxygen in the gases immediately in contact with the platinum.

The electric furnace used in our experiments consists of a vertical cylinder 6.5 cm. in diameter and 30 cm. deep. Around this cylinder is wound spirally a platinum foil. This cylinder is surrounded by a second larger cylinder, leaving an air-space of 1.5 cm. Here it will be noticed is an opportunity for the volatilization of platinum during the use of the furnace, for the foil and inner cylinder are at a very high temperature, while the surrounding cylinder is at a much lower temperature. On dismantling the furnace it was found that the inside of the outer cylinder presented a glistening appearance, due to innumerable tiny crystals of platinum. They were brushed off and some 30 mg. recovered, and perhaps as much more lost. Some of these crystals were $200 \times 100\ \mu = (0.2 \times 0.1$ mm.) and many well formed ones were $80\ \mu$ in diameter.

Platinum then begins to volatilize in air at about 800° C. where the effect is just perceptible and the rate increases markedly with the temperature. *In vacuo* or in an oxygen-free atmosphere there is no volatilization. The phenomenon is then due to the presence of oxygen and it seems probable that there are volatile compounds of the platinum metals which are stable at high temperatures, but decompose at lower temperatures, and such compounds would probably be endothermic. The existence of a volatile oxide of platinum which decomposes at 800° and below, but is stable above that temperature would account for all of the observed facts. The sprouting of molten platinum, when cooling, might well be due to the presence in solution of such a compound and as the temperature decreases decomposition takes place, with liberation of oxygen. The detection of compounds, which exist only at high temperatures, offers an interesting problem.

UNIVERSITY OF MICHIGAN,
August 10, 1904.