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THE RESISTANCE OF PLATINUM VESSELS TO HOT NITRIC ACID.

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In a recent research upon the atomic weight of selenium, Jannek and Meyer[1] have investigated the corrosion of platinum by hot nitric acid, and have made the astonishing statement that 10 cc. of halogen-free nitric acid distilled through a platinum condenser, upon evaporation in a platinum crucible yielded 0.00228 g. of non-volatile material. Since these investigators call attention to the fact that in a research by one of us[2] nitric acid was purified by distillation through a platinum condenser, and imply that the acid thus prepared was not pure, and since nitric acid has been thus purified in the Harvard Chemical Laboratories for many years, we have decided to renew the study of this subject, although the matter has several times before been considered, and this method of purification has been found to be adequate.

Evidence has already been published on the subject by Richards,[3] who states that nitric acid distilled through properly cleaned platinum leaves no weighable residue upon evaporation. Moreover, Richards and Willard[4] in an investigation upon the atomic weights of silver, lithium and chlorine, have found that a platinum dish when digested for some time with concentrated nitric acid did not lose appreciably in weight.

Our experiments upon this subject are described below: About 800 cc. of commercial C. P. acid were placed in a one-liter Jena glass flask with a constricted neck fitted to a quartz condenser. The condenser generally used for such purposes in this laboratory[5] consists of a 1 cm. tube, either of quartz or platinum, with a right angle bend about 5 cm. from one end. The short arm is inserted into the constricted neck of a Jena glass flask, making a joint which eventually becomes sealed with condensed liquid, and allowing a refluxing of the boiling liquid. Furthermore, liquid which condenses on the glass flows back into the flask instead of into the condenser. The long arm of the tube, about 30 cm., is water-jacketed to serve as a condenser. Two-thirds of the nitric acid was distilled off and rejected, since, as has been repeatedly shown in this laboratory, such treatment is necessary to remove the last traces of hydrochloric acid, even

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[1] *Z. anorg. Chem.*, **83**, 51 (1913).

[2] Baxter and Moore, THIS JOURNAL, **34**, 1644 (1912); *Z. anorg. Chem.*, **80**, 185 (1913).

[3] *Proc. Am. Acad.*, **26**, 248 (1891).

[4] *Publ. Carnegie Inst.*, No. **125**, 17; THIS JOURNAL, **32**, 18 (1910); *Z. anorg. Chem.*, **66**, 247.

[5] Richards, *Proc. Amer. Acad.*, **30**, 380 (1894); Richards and Willard, *Publ. Carnegie Inst.*, No. **125**, 15 (1910); THIS JOURNAL, **32**, 16; *Z. anorg. Chem.*, **66**, 245.

when the original acid is comparatively pure.[1] Next, the condenser was steamed out with nitric acid vapor for five minutes, and then 20 cc. of the distillate were collected in a weighed quartz crucible. After slow evaporation over an electric stove, no visible or weighable residue remained. During the evaporation the crucible touched nothing but a clean platinum triangle, and was carefully covered. A second experiment gave the same result. These observations are in perfect accord with similar experiments of Jannek and Meyer.

The purest nitric acid was now distilled in the same manner as before, but through a platinum condenser, well seasoned by more than twelve years' continual use, and was caught in a large, acid-seasoned quartz flask. After 300 cc. of this acid had been evaporated in a weighed quartz crucible, with all the precautions described above, only 0.00003 g. of whitish material remained. This experiment, in contradiction to the evidence of Jannek and Meyer, shows conclusively that practically nothing is extracted from pure, well-cleaned platinum by hot concentrated nitric acid.

Further experiments were carried out with an old platinum still of the goose-neck type, fitted with a second platinum condenser. The distillate was collected this time, however, in a well-seasoned platinum dish of 100 cc. capacity and about 40 g. weight, which had previously been twice cleaned by fusion with potassium pyrosulfate and subsequent boiling with nitric acid. After 200 cc. of distillate had been evaporated to dryness in this dish, a very slight brownish residue remained, and the dish weighed 0.00003 g. more than at first. It is evident that no important amount of material was extracted from the condenser. Gentle ignition for a moment caused the dish and contents to lose in weight by 0.00007 g., *i. e.*, the weight was now 0.00004 g. less than the original. The residue was now removed by warming with hydrochloric acid, and the dish was washed, dried and gently ignited. This treatment caused a further loss in weight of 0.00007 g., so that the total loss in weight of the dish was 0.00011 g. Undoubtedly a portion of this loss was caused by solution of the platinum in hydrochloric acid in the presence of air. These changes in weight are, however, scarcely greater than the probable error of weighing a dish of so large a weight and surface as this one. One can hardly believe that the nitric acid had an appreciable effect on either still or dish.

The slight, dark-colored residue obtained in the above experiment led us to suspect that the dish itself might have been attacked by the nitric acid. Therefore, 100 cc. of nitric acid, which had been distilled through a quartz condenser, was evaporated in it. Such acid has been shown above to be free from dissolved impurities. A residue identical in ap-

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[1] Jannek and Meyer do not state how hydrochloric acid was removed from their nitric acid.

pearance with the previous one was obtained, and the dish gained in weight by 0.00003 g. When this residue was rubbed off with a clean finger, and the dish carefully washed and ignited, the weight of the dish was found to be 0.00006 g. more than at first. As suggested before, fluctuations in weight of the magnitude of these are not significant. The fact that a similarly appearing residue was obtained by evaporation of both specimens of nitric acid, indicates, however, that the real source of the very slight residues was the dish and not the condenser.

The dish used in these experiments had been used for some time for various purposes, so that the more soluble surface impurities had undoubtedly been removed even before the cleaning with potassium pyrosulfate, to which we subjected it preliminary to our experiments. However, with platinum vessels which have not been subjected to drastic cleaning processes, there is no question that the danger of solution of surface impurities is not only real but serious. For instance, in one experiment 30 cc. of nitric acid which had been distilled through a platinum condenser was evaporated in a *new* platinum crucible, which had been merely washed and ignited. In this experiment the crucible gaintd 0.00030 g. And even after the crucible had been twice cleaned wieh potassium pyrosulfate, and boiled with nitric acid, in three repetitions of the experiment in which a quartz condenser was used, gains of 0.00018, 0.00002, and 0.00002 g. were observed.

In two cases the residues obtained in platinum were tested for iron with thiocyanate. Although traces of iron were found, the amounts were far too small to explain even the slight residues observed.

It is worth calling attention to the fact that the danger from surface impurities in the platinum has always been recognized in the Harvard Laboratories, and that new platinum vessels are always thoroughly cleaned before use, either by fusion with pyrosulfate or by sublimation of ammonium chloride from the vessel, according to Stas's suggestion, or by both methods.

The first fact established by these experiments is that, in harmony with the observations of Jannek and Meyer, concentrated nitric acid distilled through quartz contains no perceptible quantity of dissolved impurities; and the second that nitric acid distilled through well-seasoned platinum is of equal purity. The very small residues observed in the foregoing experiments came, no doubt, from the platinum vessels in which the evaporations took place, owing to the superficial oxidation of the baser metals. The surprisingly large residues reported by Jannek and Meyer are probably to be attributed either to the use of vessels of impure platinum, to inefficient cleaning of the platinum vessels, or to the presence of traces of hydrochloric acid in the nitric acid employed.

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