

gas pressure was less than before, showing that some oxygen had disappeared. The oxygen was pumped off; less was recovered than was put in (53.1 cc.) [analysis according to Franzen, *Ber.*, **39**, 2069 (1906)]. The sphere was then heated to -79° , whereupon the pressure increased. Some gas was pumped off and analyzed with barium hydroxide for carbon dioxide. The precipitate showed the presence of carbon dioxide (1.4 cc.).

The new effect may be considered analogous to the chlor-sensitized carbon-dioxide formation from carbon monoxide which has been studied by Bodenstein and co-workers. The effect is in interesting contrast to that reported in a brief note recently published by R. Livingston [*J. Phys. Chem.*, **34**, 2121 (1930)]. If his data are correct, one must assume that carbo-oxides (CO) are not oxidized in a bromine-sensitized reaction, whereas carbo-hydrides (C_2H_4) are oxidized to a slight extent. An energy chain propagated by the heat of formation of the water formed may account for this difference. Incidentally, the bromination of the hydrocarbon and its heat effects must be taken into account.

The bearing of this new type of reaction upon the use of the bromine pipet will be reported in a paper soon to appear.

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THE ALLEGED SELENIUM TRIOXIDE OF WORSLEY AND BAKER

Sir:

The method reported by Worsley and Baker¹ for the preparation of selenium trioxide has failed to yield that substance when carried out by Meyer and Pawletta,² and more recently Hoffman and Lenher³ have shown that the product is selenium dioxide contaminated with water and selenium oxychloride.

In 1927-1928 the Worsley and Baker experiment was repeated in this Laboratory. Selenium oxychloride was prepared by the dehydration of selenium hydroxychloride⁴ and redistilled twice under diminished pressure. This material melted at 9.4° and showed also by the test with cobalt carbonate⁵ that it contained traces of water. Highly purified selenium was dissolved in this solvent and oxidized with ozone (18 g. of O_3 per cu. meter of O_2). The precipitate obtained after thirty hours was examined. It contained traces of chlorides which could not be removed

¹ Worsley and Baker, *J. Chem. Soc.*, **123**, 2870 (1923).

² Meyer and Pawletta, *Ber.*, **60**, 985 (1927).

³ Hoffman and Lenher, *THIS JOURNAL*, **51**, 3177 (1929).

⁴ Muehlberger and Lenher, *ibid.*, **47**, 1842 (1925).

⁵ Lenher, *ibid.*, **43**, 32 (1921).

by washing with carbon tetrachloride and the selenium content was 61.52 and 61.60%. This substance did not liberate chlorine when boiled with hydrochloric acid⁶ and a precipitate was not formed when barium chloride was added to an aqueous solution of the material. Moreover, during the oxidation, the selenium oxychloride was dehydrated, as it no longer gave the characteristic reaction with cobalt carbonate. From these facts the authors conclude that the product formed by the ozone oxidation of Se-SeOCl₂ solution is not SeO₃ but SeO₂ contaminated with chlorides and water. This work was nearly completed before the authors were aware that a similar but more elaborate investigation had been carried out by Professor Lenher and his students. Announcement has been withheld until an account of the Wisconsin experiment has been published.⁷

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ACID-BASE REACTIONS IN PYRIDINE SOLUTION

Sir:

A preliminary study of the behavior of acids and bases in pyridine solutions has been made by us using a Hellige comparator and indicator solutions prepared by dissolving the solid dyes directly in pure pyridine.

In what follows the term apparent "*P_H*" referred to a pyridine solution simply means that a given indicator in the pyridine solution gives a color identical with that given by the same indicator in a water solution of that *P_H*, without implying that the acidity in pyridine is identical with that in aqueous solution.

In the first series of experiments, dilution curves for pyridine were obtained by making such indicator comparisons for the acids and bases under investigation for concentrations ranging from 0.00001 to 1.0 *M*. The results for trichloroacetic acid and diethylamine are shown in Fig. 1.

Since the change in apparent *P_H* with concentration is independent of the indicators used, it is obvious that the specific changes reside primarily in the activity coefficients of the acid and base studied.

In the second series we investigated the behavior of this acid and of this base in mixtures of water and pyridine. For this purpose indicator comparisons are reported in Fig. 2 for solutions containing a constant amount of acid or of base but with varying proportions of pyridine and water.

⁶ Gooch and Evans, *Am. J. Sci.*, [3] 50, 400 (1895).

⁷ For further details, see thesis submitted by C. L. Mehlretter in partial fulfillment of the requirement for the degree of Bachelor of Science in Chemistry at the Polytechnic Institute of Brooklyn in June, 1928.