

NOTES

A New Method of Preparing Phosphorus Pentafluoride.—It has been found that when a mixture of calcium fluoride and phosphorus pentoxide is heated, a gas is evolved, composed largely of phosphorus pentafluoride. The details of the method are as follows. A mixture of 25 g. of phosphorus pentoxide with approximately 55 g. of pure calcium fluoride (previously dried by heating in an iron crucible over a flame) was heated in a 2cm. iron pipe about 30 cm. long, capped at one end and connected to a 1cm. pipe at the other. Glass cannot be used. In order to reduce to a minimum the formation of hydrogen fluoride, the apparatus and materials had to be free from moisture. It was found necessary to bake out the apparatus, to use the best phosphorus pentoxide, to ignite the fluoride, to transfer it while still hot to the hot apparatus, and to measure out the materials rapidly (about 50 cc. of each) instead of weighing. The ingredients were mixed by shaking. The rate of gas evolution depended upon the temperature, and was quite rapid when a large flame was used. The gas fumed in moist air.

The vapor density of the resulting phosphorus pentafluoride was determined in the following way. The gas was allowed to pass under slight pressure for about 45 minutes through a tared bulb provided with two stopcocks. These were then closed, and the bulb was weighed, but not until one of the stopcocks was opened for a few seconds to liberate gas, of which some always escaped. The best value obtained gave a molecular weight of 119, instead of 126 required for PF_5 . If the main impurity was hydrogen fluoride, and if it was in the monomolecular form at the low concentration prevailing, the gas had an approximate composition of 94% of phosphorus pentafluoride and 6% of hydrogen fluoride. The absorption of a small amount of water by the phosphorus pentoxide accounts for the presence of hydrogen fluoride.

The probable reaction is $5\text{CaF}_2 + 6\text{P}_2\text{O}_5 \rightarrow 2\text{PF}_5 + 5\text{Ca}(\text{PO}_3)_2$. Although the gas is not pure, this method is superior to those previously described, since the necessary materials are easily available and the rate of gas evolution can be controlled.

Potassium fluoride is not a satisfactory substitute for the calcium salt since it is more difficult to obtain dry; moreover, it reacts too rapidly with the pentoxide.

We were unable to obtain any *iso*-amyl fluoride on passing phosphorus pentafluoride for one and one-half hours into boiling, anhydrous *iso*-amyl alcohol in a copper vessel under a copper reflux condenser.

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An Attempt to Prepare Aurous Oxide and to Measure the Potential of the Gold-Aurous Oxide Electrode.—The existing literature on the gold-aurous oxide electrode gives a value of its potential which is but a rough approximation. Various sources of error appear to have entered into the measurements, such as liquid potentials, and complex-ion formation, but the principal difficulty appears to lie in the uncertain nature and composition of the aurous oxide employed. A study was therefore undertaken, first to prepare aurous oxide, and second to measure a simple cell containing aurous oxide, namely: H_2 (g), H_2SO_4 (x-M), Au_2O (s), Au (s).

Preparation of Aurous Oxide.—Several methods recommended in the literature were tried.¹ The most nearly uniform and reproducible product was obtained by converting pure gold into potassium auribromide. It was found preferable to use only a slight excess of potassium bromide over the calculated amount, to prevent the reversal of the precipitation reaction later. The solution was diluted to about 1% strength in gold. One hundred cc. of this solution was cooled with lumps of ice, and reduction made with cold, dilute sulfur dioxide solution until the deep orange color of the auribromide had just faded out. More than a drop or two of the sulfur dioxide solution in excess invariably favors reduction to metallic gold. Precipitation of the oxide was accomplished with cold 2% potassium hydroxide solution, and a colloidal suspension of deep blue-black color was obtained. The colloid was readily coagulated by gently warming the solution, and the coarse precipitate could be filtered and thoroughly washed until free from bromides.

Attempts to identify this material as aurous oxide either by direct or indirect quantitative methods were not successful. When the product was dried over phosphorus pentoxide, it was found on ignition to contain 96.8% of gold. Although the solution in the course of reduction with sulfur dioxide is completely decolorized and no trace of metallic gold observed, it is probable, as Dr. R. H. Gerke (in a private communication) has suggested, that upon addition of the potassium hydroxide, any aurous oxide momentarily formed decomposes immediately into gold and auric oxide, the black color being due to colloidal gold on the surface of the particles.

Electromotive-Force Measurements.—The black precipitate so obtained (and assumed to be aurous oxide) was accordingly used to prepare a number of cells of the type mentioned above, and their potentials at 25° were measured. The potentials were rather discordant at the start, beginning at approximately 1.1 v. and tending to increase as time passed until a remarkably constant potential of 1.363 v. was reached as a limit. This voltage happens to check closely the potential of the corresponding cell involving auric instead of aurous oxide, as measured by Jirsa and

¹ Abegg, "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, 1908, vol. 2, pt. 1, p. 777.

Jelinek,² and appears to be evidence of the fact that the reaction $3\text{Au}_2\text{O} = \text{Au}_2\text{O}_3 + 4\text{Au}$ takes place. The constancy of the potential over a considerable period of time is considered significant, as well as the fact that the color of the blue-black precipitate had during this time changed to that of metallic gold. Dr. Gerke believes that the change in potential with the time can be accounted for by assuming that the electrode reaction is Au (colloidal) = Au (cryst.).

It is certain that the black precipitate does undergo a change with the time, suggesting considerable instability. Further work on this problem is planned to study other possible methods of preparation in an endeavor to establish conclusively whether or not aurous oxide is capable of existence, and to measure accurately the value of its electrode potential.

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FLUORESCEIN AND SOME OF ITS DERIVATIVES

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Fluorescein was first prepared by Baeyer² in 1871 by fusing a mixture of phthalic anhydride and resorcinol. Baeyer³ gave the formula $\text{C}_{20}\text{H}_{12}\text{O}_5 + \text{H}_2\text{O}$, to the *yellow* product precipitated from alkaline solution by acids, while for the product crystallized from ethanol as a dark *red* powder, he gave the formula $\text{C}_{20}\text{H}_{12}\text{O}_5$. In 1882, Baeyer⁴ assigned a lactoid structure to fluorescein (see Formula III below) and fluorescein dichloride. Bernthsen⁵ retained the lactoid structure for fluorescein, but assigned a quinoid structure to its salts and esters. Meyer⁶ proved that both hydroxyl groups in fluorescein were in the *para* positions to the methane carbon atom. Kehrmann and Dengler⁷ assigned an *ortho-quinoid* structure to fluorescein, holding that as it is colored it cannot be a dihydroxyfluoran, but must have a quinoid structure. Kropp and Decker⁸

² Jirsa and Jelinek, *Z. Elektrochem.*, **30**, 286, 534 (1924).

¹ From a dissertation presented by A. J. Hemmer to the Faculty of the Graduate School, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Baeyer, *Ber.*, **4**, 555 (1871).

³ Baeyer, *Ann.*, **183**, 1 (1876); see also Fischer, *Ber.*, **7**, 1211 (1874).

⁴ Baeyer, *Ann.*, **212**, 351 (1882).

⁵ Bernthsen, *Chem.-Ztg.*, **16**, 1956 (1892); *Ber.*, **26** [4], 376 (1893).

⁶ Meyer, *Ber.*, **28**, 428 (1895).

⁷ Kehrmann and Dengler, *Ber.*, **41**, 3440 (1908).

⁸ Kropp and Decker, *Ber.*, **42**, 578 (1909).