

since the latter represents both ozone and oxides of nitrogen. In the static experiment with 28.5 millicuries of radon decaying in a 4 O<sub>2</sub>:1 N<sub>2</sub> mixture, very little acid was produced.

The special experiment on the production of nitrous oxide in air confirmed Soddy<sup>15</sup> in its formation, although the yield was only 0.076 molecules per pair of ions, much lower than that of the acid-forming oxides.

The nitrous oxide was separated from the air by use of liquid air and was subsequently pumped off at  $-100^{\circ}$  into a miniature eudiometer tube. That the gas so separated was nitrous oxide was confirmed by explosion with a measured volume of pure hydrogen. The volume contraction corresponded approximately to that for the reaction  $N_2O + H_2 = N_2 + H_2O$  (liq.).

### Summary

1. Ozonization in oxygen flowing past an alpha-ray bulb is higher (per ion pair) the faster the rate of flow and the lower the intensity of ionization, that is, higher the lower the ozone concentration from either influence, owing to de-ozonization. This confirms D'Olieslager's results.

2. The maximum yields of ozone obtained per ion pair ( $M_{O_3}/N_{O_2}$ ) was not less than 1.5 and may be as high as 2-2.5.

3. De-ozonization appears to be due to a secondary effect of oxygen ions (or atoms), not to a primary impact with an alpha particle.

4. In mixtures of nitrogen and oxygen both ozone and acid-forming oxides of nitrogen are simultaneously formed; also a smaller amount of nitrous oxide (confirming Soddy). Nitrous oxide formation was investigated only for air.

5. The yield of acid-forming oxides diminishes with decreasing N<sub>2</sub>:O<sub>2</sub> ratio, while the total oxidizing power toward potassium iodide solution is little influenced. A theory is proposed for this.

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### NOTES

**An Application of the Thiocyanate Method for the Precipitation of Copper in the Confirmatory Tests for Cadmium and Antimony.**—The use of the thiocyanate anion as a means for the separation of copper from cadmium, after first having reduced the copper with sulfurous acid, has been suggested by Crookes.<sup>1</sup> This method has also been used for the quantitative determination of copper, but to the knowledge of the author it has not hitherto been applied to the qualitative scheme of analysis. The insolubility of cuprous thiocyanate in dilute sulfuric and hydro-

<sup>1</sup> William Crookes, "Select Methods in Chemical Analysis," Longmans, Green and Company, London, 1886, p. 332.

chloric acids and the ease of precipitation makes it well suited for this application.

The means for the separation of copper from cadmium in the confirmatory test for cadmium given by Noyes<sup>2</sup> has been found to be not quite satisfactory for class use due to the fact that many times the student does not obtain a thorough separation of the copper.

The thiocyanate method has been used in the classes in the Qualitative Laboratory of the University of New Hampshire and has been found to give very satisfactory results.

The procedure for this method is as follows. To the part of the ammonium hydroxide solution remaining after the ferrocyanide test has been made for the confirmation of copper add dilute sulfuric acid until acid to litmus, then 5 cc. of a normal solution of potassium thiocyanate. A brown coloration will result due to the formation of cupric thiocyanate. Heat to boiling, add about 0.5 g. of dry sodium sulfite and continue boiling for about one minute until the white precipitate of cuprous thiocyanate has coagulated. Filter off the precipitate and saturate the clear filtrate with hydrogen sulfide. If cadmium is present the characteristic yellow precipitate of cadmium sulfide will form.

This reagent has also been used to advantage to avoid the interference of copper in the test for antimony as given by Noyes,<sup>3</sup> which occurs in some instances when sodium polysulfide is used and very often when ammonium polysulfide is employed for the separation of the copper and tin groups. The above procedure may be used after the antimony and tin have been separated from the arsenic by concentrated hydrochloric acid, and the solution has been diluted to the proper acid concentration for the precipitation of the antimony sulfide.

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**An Improved Stopcock for Gas Analysis Burets.**—The usual type of buret stopcock used in both technical and exact gas analysis apparatus is of the three-way downward outlet type or a specially bored adaptation<sup>1</sup> of this when a compensator is attached. The objection to this type of stopcock lies not only in the difficulty of stopping the absorbent solutions exactly at the stopcock with its upward pointing outlet, but also in the

<sup>2</sup> A. A. Noyes, "Qualitative Chemical Analysis," The Macmillan Company, New York, 1928, p. 80.

<sup>3</sup> Ref. 2, p. 86.

<sup>1</sup> A. H. White, "Gas and Fuel Analysis," McGraw-Hill Book Company, New York, 1st ed., 1913, pp. 16, 73.

unpreventable draining of these solutions into the gas buret during the absorption process. Even in the hands of an expert an exact gas analysis apparatus becomes badly fouled in the course of a single complete analysis of a gas mixture such as water gas.

This difficulty is eliminated by the use of the special stopcock shown attached to a bulbed exact gas analysis apparatus<sup>1</sup> equipped with a single leg compensator<sup>2</sup> in Fig. 1. By placing

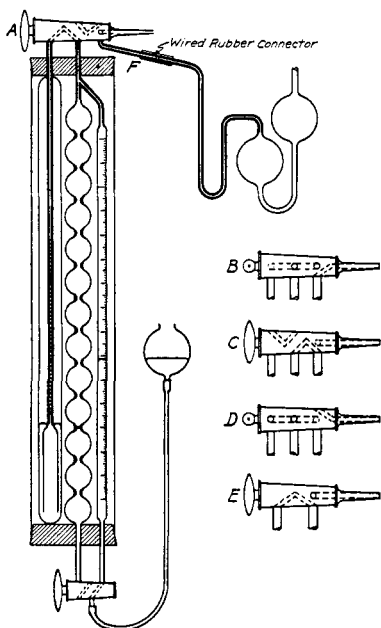


Fig. 1.

the outlet to which the absorption pipet is attached below instead of above the stopcock barrel, it is possible to bring the absorbent solution slowly up to the bore of the cock without any danger of spilling over into the buret. During the absorption of any constituent the solution adhering to the walls of the stopcock outlet then drains down away from the stopcock and buret. Four views of the stopcock are shown at A, B, C and D, each a quarter turn in the clockwise direction from the preceding position as shown in the sketches.

In the case of an uncompensated buret such as is used in technical analyses the simpler stopcock shown at E, suffices.

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<sup>2</sup> F. C. Vilbrandt, *Ind. Eng. Chem.*, **16**, 936 (1924)