

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

**GERMANIUM. XXXVII. GERMANIUM DIOXIDE GEL.
PREPARATION AND PROPERTIES¹**

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Introduction

Numerous investigations have shown that silicon dioxide can readily be prepared as a gel by several different methods and that this gel possesses high adsorptive power for the vapors of substances such as benzene, ethyl ether, carbon tetrachloride, water, etc. Important uses for silica gel based upon this property have been described. Since silicon and germanium are members of the fourth group of the periodic table of Mendelëff and their compounds have been found to possess many properties in common, it seemed worth while to try to prepare a pure germanium dioxide gel and to determine the adsorptive properties of this substance.

Unlike silicon dioxide, germanium dioxide is appreciably soluble in water. Pugh² found that 100 g. of water will dissolve 0.447 g. of the oxide at 25°. It is to be expected, therefore, that germanium dioxide will tend to build up crystals and will not form a gel as readily as silica does. Numerous investigators have demonstrated the crystalline nature of the dioxide formed by the ordinary methods. The only record of the formation of a gel was made by van Bemmeln,³ who passed carbon dioxide through a solution of sodium germanate. This gel, however, adsorbed sodium oxide strongly and after repeated washings with water it still contained one-fifth mole of sodium oxide per mole of germanium dioxide.

It appeared, therefore, that under certain conditions germanium dioxide precipitates as a jelly and under other conditions as a crystalline solid, but the available information was very meager. Accordingly, in this investigation, a preliminary comprehensive study was made of the formation of germanium dioxide, under various conditions.

Hydrolysis of germanium tetrachloride, germanium tetrabromide and germanium tetraiodide by water and by aqueous solutions of the corresponding hydrohalogen acids was investigated at temperatures varying from 0 to 75°, but the product always was crystalline. The same form of precipitate was secured when aqueous solutions of sodium germanate of varying concentration were treated with hydrochloric acid. A gelatinous precipitate was formed when carbon dioxide was bubbled through

¹ This article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Pugh, *J. Chem. Soc.*, 1537-41 (1929).

³ Van Bemmeln, *Rec. trav. chim.*, 6, 205 (1887).

0.10 to 0.75 molar aqueous solutions of sodium germanate, but this gel could not be washed free of sodium. Dialysis of an acidified solution of sodium germanate was unsuccessful because the colloidal oxide slowly went into true solution and passed through the membrane. Hydrolysis of germanium tetraethoxyl by water gave a metastable sol which was stabilized by adding alkali. The addition of alkali carbonate to this stabilized sol caused the formation of a gel but it could not be freed of sodium. Methods involving the use of aqueous solutions, therefore, seemed unsuitable for the preparation of such a gel.

Dearing and Reid⁴ have prepared silica gel by the action of the calculated amount of water on silicon tetraethoxyl in alcoholic solution and find that a very active product is thus obtained. Applying the method to germanium dioxide the authors found that the use of the proper amounts of germanium tetraethoxyl, ethyl alcohol and water yielded a firm gel, easily freed from alcohol.

Experimental

Preparation of Germanium Tetraethoxyl.—Germanium tetraethoxyl was prepared by the action of sodium ethylate on germanium tetrachloride.⁵ The preparation boiled at 187°.

Formation of Germanium Dioxide Gel.—Eleven grams of germanium tetraethoxyl was dissolved in 11 cc. of absolute ethyl alcohol (Solution A). This solution was cooled by immersing the container in ice for fifteen minutes; 1.60 g. of water (1.57 g. theoretically required for hydrolysis) was dissolved in 11 cc. of absolute alcohol (Solution B) and this solution also was cooled in ice for fifteen minutes. Solution B was then added to Solution A with very rapid stirring. The mixture set to a gel almost immediately. The test-tube containing this gel was corked and permitted to stand for one hour. Alcohol was then removed from the gel as slowly and uniformly as was possible with so small a sample. It was placed in an uncovered Petri dish in the bottom of a tall beaker, and the beaker was covered with a glass plate so that only the space between the cover and lip was open. The beaker was set in a cupboard at room temperature and under these conditions it took the gel five days to become hard and brittle. The gel was then broken up and placed in a container which could be evacuated by means of an efficient oil pump. The evacuation was carried on for five hours, after which time the gel was heated at 175–180° for four hours while dry air was passed over it. The resulting germanium dioxide was brittle and translucent. The lumps of gel were slightly reddish in color by transmitted light and were bluish-white by reflected light. This method is very satisfactory for preparing pure germanium dioxide gel and material made in this way was used in the following experiments.

Determination of Adsorptive Power of Germanium Dioxide Gel.—The adsorptive power of the gel prepared from germanium tetraethoxyl was tested by the method which Holmes, Sullivan and Metcalf⁶ used on certain silica gels. Air was passed through a flow-meter and was dried by calcium chloride, concentrated sulfuric acid and phosphorus pentoxide in the order named. The dry air was passed through two Friedrichs gas-washing bottles where it was saturated with the vapor to be adsorbed by the gel.

⁴ Dearing and Reid, *THIS JOURNAL*, 50, 3058 (1928).

⁵ Tabern, Orndorff and Dennis, *ibid.*, 47, 2039 (1925).

⁶ Holmes, Sullivan and Metcalf, *Ind. Eng. Chem.*, 18, 386 (1926).

The saturated air was led through a spray catcher to remove entrained liquid and was then passed through a tube containing a weighed amount of germanium dioxide gel. The gas-washing bottles, spray-catcher and gel tube were immersed in a thermostat held at $30 \pm 0.1^\circ$. The air stream was permitted to flow until the gel had reached constant weight.

The values obtained for the adsorption by germanium dioxide gel are given in Table I. For purposes of comparison, corresponding data reported by Holmes, Sullivan and Metcalf⁶ for "Patrick's silica gel" and "silica gel from iron" are also included.

TABLE I
GRAMS OF VAPOR ADSORBED PER 100 GRAMS OF GEL

Vapor adsorbed	Germanium dioxide gel First detn.	Germanium dioxide gel Second detn.	Patrick's silica gel	"Gel from Iron" (silica)
Benzene	47.2	47.2	32.2	62.0
Carbon tetrachloride	86.3	86.6	57.7	120.0
Ethyl ether	39.7	40.0	30.5	54.3

All of these values for germanium dioxide gel were determined on the same sample, since it was found that the adsorptive capacity of the gel could be restored completely by heating in a stream of dry air at a temperature of 175° for about thirty minutes. The results given in the table show that the adsorbing power of germanium dioxide gel for organic vapors is of the same order as that of silica gel.

Since germanium dioxide is appreciably soluble in water, it seemed worth while to determine the amount of water that could be adsorbed by germanium dioxide gel, and also to find out whether adsorption of water and its subsequent removal from the gel effected any change in the adsorbing power for organic liquids. A new sample of gel was made up by the method described above, except that it was not permitted to stand in a closed tube before removal of alcohol. Apparently this change made some difference in the structure since the sample here obtained adsorbed only 29.1% of its weight of benzene. When regenerated in the manner already described, this sample again showed the same adsorbing capacity for benzene. The lower adsorbing power did not interfere with the experiments, however, since only relative results were desired.

The adsorption of water by this gel was determined in the same manner as has been described for organic liquids. After twenty-eight hours equilibrium had not been reached, but further adsorption of water was very slow; 19.1% of water had been taken up. This water was removed by heating the gel to 200° and passing dry air over it. The adsorbing power of the revived gel for benzene vapor was found to be 23.0%. Since this value is appreciably lower than the previously determined adsorptive capacity of the sample, it indicates that the gel structure is probably altered in some way by the adsorbed water.

Summary

1. The physical properties of various preparations of germanium dioxide resulting from the hydrolysis of germanium tetrachloride, tetrabromide, tetraiodide and tetraethoxyl, and from the action of hydrochloric acid and of carbon dioxide on sodium germanate have been investigated.

2. Of the various methods for the preparation of germanium dioxide gel studied, the only procedure that yielded a satisfactory product was the hydrolysis of germanium tetraethoxyl by means of water, the reaction being carried out in alcoholic solution.

3. Germanium dioxide gel was found to possess an adsorptive power for the vapors of benzene, ethyl ether and carbon tetrachloride comparable with that of silica gel.

4. Germanium dioxide gel adsorbs water vapor but upon the removal of the adsorbed water the adsorptive power of the gel for benzene vapor was found to have decreased.

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THE EFFICIENCY OF THE REACTION $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$ AND ITS BEARING ON THE REACTION BETWEEN HYDROGEN AND OXYGEN¹

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The experiments by von Elbe on the photochemical reaction between hydrogen peroxide and hydrogen or carbon monoxide described elsewhere,⁴ and a careful estimate, from earlier measurements,⁵ of the intensity of incident radiation from the zinc spark, allow one to estimate a limit of the efficiency and the heat of activation of the reaction



The total number of quanta entering the reaction vessel per second was 2×10^{15} . Assuming that the absorption of hydrogen peroxide for the spectral lines used is 30%, calculated from the absorption measurements of Urey, Dawsey and Rice,⁶ and a quantum efficiency of $1\text{H}_2\text{O}_2$ decomposed per quantum absorbed yielding 2OH , the number of OH radicals formed (volume of vessel 86 cc.) was 1.4×10^{13} per sec. per cc.

The experimental data show that 5.6×10^{13} molecules of hydrogen reacted per second per cc. Thus, practically as many hydrogen molecules disappear per second as hydroxyl radicals are formed per second. The difference between the values 5.6×10^{13} and 1.4×10^{13} is apparently due primarily to the inaccuracy of the estimated light intensity. We note that the stationary concentration of OH must therefore be smaller or equal to about 5.6×10^{13} radicals per cc. In the latter case, the collision frequency between OH and H_2 at 40° is 3.9×10^{23} per sec. per cc. From these data we can conclude that at least 1 out of 7×10^9 collisions between OH and H_2

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⁴ G. von Elbe, *THIS JOURNAL*, **54**, 821 (1932).

⁵ Bernard Lewis, *J. Phys. Chem.*, **32**, 270 (1928).

⁶ Urey, Dawsey and Rice, *THIS JOURNAL*, **51**, 1376 (1929).