

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

ORGANOGEELS OF SILICIC ACID.

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As is well known Graham¹ was able to prepare silicic acid gels which contained large percentages of organic liquids, such as alcohol, ether, glycerine, and only very small amounts of water. Owing to the large percentage of organic liquids that were contained in the organogels, and from the ease with which he could replace one liquid by another by allowing the gel to soak in the liquid, *viz.*, transformation of an alcogel into an ether gel, Graham was led to some interesting conclusions: "The various organic liquids are capable of displacing the combined water of silicic acid hydrate, whether that hydrate is in the liquid or gelatinous condition, and give new products. The production of the compounds of silicic acid indicates the possession of a wider range of affinity by a colloid than could well be anticipated. Thus, of hydrated silicic acid the combined water leaves the acid to diffuse into the alcohol, and if the alcohol be repeatedly changed the *entire* water is thus removed, alcohol at the same time taking the place of the water in combination with the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Such changes illustrate the predominating influence of mass."

Because of Graham's experimental results and his conclusions which enjoy wide acceptance, the question arose whether we could prepare a hard gel composed of only silica and an organic liquid. This seemed very probable, since in the alcogel as prepared and analyzed by Graham there were 383 parts of alcohol to 1 part of water. It was thought that by heating the gel at a high temperature in a vacuum, an organic gel practically water-free could be obtained.

Preparation of the Gels.

The hydrogel of silica was prepared in the usual way from water glass and hydrochloric acid. The gel was washed free from chlorides, squeezed to remove as much water as possible, and then placed in 95% alcohol. Another sample was put into c. p. acetone. After the gel had remained in the alcohol for 24 hours it was squeezed dry of liquid and transferred to a fresh sample of alcohol. This treatment was repeated four times. The gel was then placed in a sample of alcohol that had been refluxed over lime for several days, and allowed to stand for two days. This treatment with the anhydrous alcohol was repeated four times.

¹ Graham, *J. Chem. Soc.*, 17, 318 (1864); *Pogg. Ann.*, 123, 529 (1864).

A sample of the gel that had undergone the above treatment was heated in a vacuum of 5 mm. for 1 hour at 80°, 1 hour at 120°, and finally for 1 hour at 270°.

The acetone gel was put through a similar process. It was given four treatments of 24 hours' duration in c. p. acetone, and finally four treatments at 48-hour intervals in redistilled acetone (b. p. 56.5°).

A portion of the alcogel as it came from the last soaking in alcohol was transferred to redistilled benzene and allowed to remain in this liquid for 2 days. This treatment was repeated six times, when a sample failed to give the iodoform test for alcohol. This benzene gel was heated in a vacuum like the others.

Analytical Results.

The three gels were analyzed by the regular combustion methods of organic chemistry. Towards the end of the combustion the boat containing the gel was heated to about 900° in order to drive all the water out of the gel. From the amounts of carbon dioxide and water formed, the percentages of alcohol, acetone, or benzene, as well as that of water in the gel were calculated. A typical analysis follows.

	I. G.	II. G.
Wt. of acetone gel	1.343	0.860
H ₂ O produced by combustion	0.111	0.0712
CO ₂ produced by combustion	0.115	0.0732
Calculated weight of acetone	0.0505	0.0322
Water from acetone	0.0470	0.0300
Excess water	0.0640	0.0412
% Acetone in gel	3.76	3.74
% Water in gel	4.76	4.78

The analytical results are tabulated below.

	% water.	%.
Alcogel	4.23	3.90 alcohol
Acetone gel	4.77	3.75 acetone
Benzene gel	4.31	3.82 benzene

Discussion.

From the above results it is apparent that Graham was in error when he stated that it is possible to replace all the water from a silica hydrogel by other liquids. We have shown in this laboratory that silica gel may be heated to 300° in a vacuum produced by a Gaede pump for a period of 6 hours without reducing the water content below 4.8%. It is not surprising, therefore, that soaking in anhydrous alcohol as above described does not remove all the water. It is evident that the residual small percentage of water in silica gel is held with a force that exceeds that exhibited between the atoms of many stable compounds. Subsequent work in this laboratory has shown that this water can be removed at high

temperatures without affecting appreciably the structure of the gel as exhibited by its adsorption ability.

Summary.

It is impossible to remove all the water from the hydrogel of silicic acid by repeated immersions in anhydrous alcohol, acetone, or benzene.

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COMPOUND FORMATION AND CONDUCTIVITY IN SYSTEMS OF THE TYPES FORMIC ACID:METAL FORMATE AND SULFURIC ACID:METAL SULFATE.

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In a recent investigation¹ on systems of the types acid:ester, acid:ketone and acid:acid it has been shown that the specific conductivities of such binary mixtures increase regularly with increasing compound formation between the components. Strong support was thereby obtained for the validity of the hypothesis, formulated in earlier articles,^{2,3} that ionization in solutions is primarily dependent upon the preliminary formation of unstable solvent-solute complexes. In subsequent communications^{4,5} it has also been established that compound formation in systems of the general type HX:RX increases in extent with increasing diversity in the positions of the radicals H and R in the electrode potential series. The present work continues the study of systems of this type by examining how far the parallelism between compound formation and conductivity can be traced in them. As experimental material, the two series previously investigated with respect to compound formation (metal formates in formic acid and metal sulfates in sulfuric acid) have naturally been chosen.

Very accurate determinations upon the conductivities of the alkali and alkaline earth formates in anhydrous formic acid have been carried out by Schlesinger and his co-workers,⁶ so that only a few additional data were required in this series. In the case of sulfuric acid:metal sulfate systems, the results of previous investigations proved to be much less dependable.

¹ Kendall and Gross, *THIS JOURNAL*, **43**, 1426 (1921).

² Kendall and Booge, *ibid.*, **39**, 2323 (1917).

³ Kendall and Gross, *ibid.*, **43**, 1416 (1921).

⁴ Kendall and Davidson, *ibid.*, **43**, 979 (1921).

⁵ Kendall and Adler, *ibid.*, **43**, 1470 (1921).

⁶ Schlesinger, *et al.*, *ibid.*, **33**, 1924 (1911); **36**, 1589 (1914); **38**, 271 (1916); **41**, 72, 1921, 1934 (1919).