

NOTES ON ISOMORPHISM IN OXONIUM COMPOUNDS.—By D. McINTOSH, M. A., D. Sc., Dalhousie University, Halifax, N. S.

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The two classes of oxonium compounds formed by the union of organic substances containing oxygen with the halogens and with the halogen hydrides show so many differences in their properties, that different constitutions must be ascribed to them. Since chemical constitution and isomorphism are sometimes related, I have, in this preliminary study, attempted to group those compounds having the same crystal form together, by finding the effect of one solid compound on the supercooled melt of another.

Crystallization is brought about in these supercooled solutions by low temperatures applied locally,—for example, a drop of liquid air or a piece of wire cooled in liquid air proves effective. But, if the solution be cooled to a low temperature uniformly, a glass is formed, and crystallization does not take place.

Gernez¹ showed many years ago that isomorphous salts promote crystallization in aqueous, supersaturated solutions, by precipitating magnesium acetate from its supersaturated solution by means of barium acetate. Boisbaudron confirmed this, but noted that often a greater supersaturation (or lower temperature) was necessary when an isomorphous salt was substituted for the salt in solution. A supersaturated solution of nickel sulphate was precipitated by zinc sulphate, but not by ferrous sulphate until further concentrated, and at times the crystal form varied with the isomorphous salt used.

As an example of the method of procedure, a mixture containing hydrogen chloride and ether in the proportion of one or two molecules of the former to one of the latter was prepared. This was cooled five degrees below its freezing tem-

¹Ostwald, Lehrbuch 2, 1, 740.

perature and was then "inoculated" with a few crystals of another compound, stirred gently and observed for some time. The compounds obtained from the following systems were examined in this way:

Ether with hydrogen chloride, bromide and iodide; alcohol, acetone and ethyl acetate with hydrogen bromide; ether, alcohol, ethyl acetate and acetone with bromine and chlorine; and methyl ether with hydrogen bromide and iodide.

Supercooled $C_4H_{10}O \cdot HCl$ is precipitated by its own crystals immediately, and also by $C_4H_{10}O \cdot HBr$ and by $C_4H_{10}O \cdot HI$, the latter after some little time, but not by the hydrobromide or iodide of methyl ether, nor by other salts such as acetone-hydrobromide or ether-chlorine. $C_4H_{10}O \cdot 2HCl$ is precipitated by its own crystals, by $C_4H_{10}O \cdot 2HBr$, but not by ether-hydrogen iodide (an additional proof to previous work that this is the only compound formed), nor by methyl ether-hydrobromide. The 5 HCl complex is not affected by any of the oxonium compounds, but must be precipitated by low temperatures.

The oxonium-chlorine compounds are precipitated by the corresponding bromine compounds, but not by other compounds of the halogen or acid classes.

From these experiments it seems probable that compounds of each class made with the same organic substances are isomorphous, while those made with different, though closely related, organic compounds are not.