In summary, it appears overwhelmingly probable that the S and R data apply not to an alloy of approximate composition Na_4Pb but to some other substance or substances as yet unidentified, and possibly of unknown constitution and structure.

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The Reaction of Chlorosilanes with Benzaldehyde

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Rochow and Gingold[1] recently stated that they did not succeed in combining chlorosilanes with aldehydes, including benzaldehyde, to form siloxanes, even on boiling for 3–4 days, the starting products being obtained again in unchanged form. In this respect I wish to report on work carried out on this reaction, though with different scope and aims.

Silicon tetrachloride reacts with benzaldehyde on being allowed to stand at room temperature, the reaction being expressed by the gross equation

$$SiCl_4 + C_6H_5COH \longrightarrow (SiCl_2O)_n + C_6H_5CHCl_2$$

If $SiCl_4$ is allowed to stand together with benzaldehyde, after a few weeks these liquids which mix well show an increase in viscosity which is somewhat accelerated by exposure to daylight. Demixing occurs in two phases after 2–3 months. This phenomenon is caused more rapidly at elevated temperatures. Likewise, in the gaseous phase $SiCl_4$ reacts with benzaldehyde within the sense of the above equation. The lighter one of the two layers consisted chiefly of excess benzaldehyde and benzal chloride as well as a small quantity of chloropolysiloxane while the heavy phase consisted to the major part of chloropolysiloxane. The latter was obtained as a residue in the fractional distillation. The determination of the molar weight estimate resulted in values between 1800 and 2000. The chlorine values of these polysiloxanes, calculated on hydrolyzable chlorine, were correspondingly around 60% with the silicon values around 26%. The index n in the formula $(SiCl_2O)_n$ thus appears to be in the order of 15.

While always an excess of benzaldehyde reacted with $SiCl_4$ in all the cases examined, the reaction did not proceed beyond the formation of a chloropolysiloxane. It appears to be probable, however, that the reaction will proceed to the formation of SiO_2 with sufficiently long periods of exposure or more critical conditions.

As shown by orientating qualitative experiments, the reaction is not limited to $SiCl_4$ but also proceeds in a corresponding manner in the case of organochlorosilanes, *e.g.*, phenyltrichlorosilane.

The reaction appears to take place in two stages. In a first stage the $SiCl_4$ will add on the CO double link of the aldehyde

$$Cl_3SiCl + O{=}CHC_6H_5 \longrightarrow Cl_3SiOCHClC_6H_5 \quad (1)$$

This product seems to react relatively rapidly with a further SiCl link to form

$$Cl_3SiOCHClC_6H_5 \longrightarrow Cl_3SiOSiCl_3 + C_6H_5CHCl_2 \quad (2)$$

No such products as result from equation 1 were isolated.

The apparent discrepancy with respect to the work of Rochow and Gingold can satisfactorily be accounted for by these two authors only having tried triphenylchlorosilanes with benzaldehyde.[2] In the case of this silane the reaction is strongly inhibited for steric reasons, and the reactivity of the SiCl linkages is unfavorably influenced by the three phenyl groups.

This suggestion is supported by the observed fact that already the $PhSiCl_3$ reacts with benzaldehyde somewhat slower than $SiCl_4$.

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(1) E. G. Rochow and K. Gingold, THIS JOURNAL, **76**, 4852 (1954).

(2) Private report by Prof. E. G. Rochow.

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Phase Diagram of the System $KNbO_3$-$KTaO_3$ by the Methods of Differential Thermal and Resistance Analysis

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$KNbO_3$ and $KTaO_3$ both exhibit the ABO_3 perovskite structure, but have widely separated Curie points. The unit cell size of both compounds, in the cubic state, differs only slightly.[1] On the basis of this, and the isomorphic nature of tantalum and niobium compounds, a strong possibility for solid solution interaction between the meta salts was seen to exist. If such an interaction takes place, it might be possible to prepare dielectric ceramics with Curie points ranging between 13 and 688°K., the Curie temperatures of $KTaO_3$ and $KNbO_3$, respectively.[2,3] Resolution of the diagram would provide needed information for the preparation of the necessary ceramic materials.

The solidus curve of a solid solution is generally more difficult to determine than the liquidus curve. The graphical extrapolation method employed by Tammann[4] and later modified by Campbell and Prodan[5] was found inapplicable because of the difficulties in attaining reasonable equilibrium throughout the cooling range. The standard heating curve techniques are at best laborious, and if not performed with the utmost care tend to give low results.[6] If applicable, quenching methods are invaluable, but in this system the tendency for crystallization to occur, even with small charges,

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(6) G. W. Morey, Jr., *Wash. Acad. of Sci.*, **13**, 326 (1923).