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

BY ALBRECHT ZAPPEL

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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

BY ARNOLD REISMAN, SOL TRIEBWASSER AND FREDERIC HOLTZBERG

RECEIVED APRIL 15, 1955

$KNbO_3$ 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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[1] P. Vousden, *Acta Cryst.*, **4**, 373 (1951).

[2] J. K. Hulm, B. T. Matthias and E. A. Long, *Phys. Rev.*, **79**, 885 (1950).

[3] G. Shirane, H. Danner, A. Pavlovic and R. Pepinsky, *ibid.*, **93**, 672 (1950).

[4] G. Tammann, *Z. anorg. Chem.*, **37**, 303 (1903).

[5] A. N. Campbell and L. A. Prodan, THIS JOURNAL, **70**, 553 (1948).

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

was so great that quenches could not be employed to fix solidus points. Consequently a procedure was sought which would enable closer approximation to static conditions in order to attain better equilibrium. Use of quasi static conditions would eliminate the one inherent difficulty attendant with presently employed methods.

Several investigators have reported the use of high temperature resistivity measurements for thermal analysis.[7-10] The methods employed were applicable only to thin metal wires. Glaser and Moskowitz[11] have recently reported a method for measuring resistivities of refractory hard metals, but because of the inherent difficulties of the method very large temperature gradients existed in the specimens. A procedure has been developed in this Laboratory which enables precise determination of solidus points by continuously measuring the conductivity of ceramic samples as a function of temperature. If two closely spaced platinum wires are imbedded in a ceramic disc, a sharp change in conductivity should be observed when the solidus is reached. Since the conductivity–temperature data are independent of heating rate, quasi equilibrium can be maintained throughout a determination.

Experimental Procedure

Reagents.—The tantalum pentoxide used was purchased from the Fansteel Metallurgical Company. This reagent is the company's T-400 grade and contained as the maximum impurity 0.001% TiO_2. The niobium pentoxide was purchased from the same company and contained as the maximum impurity 0.2% Ta. Reagent Grade Mallinckrodt potassium carbonate was dried at 400° for one hour to remove moisture. The potassium niobate was prepared according to the procedure developed in this Laboratory,[12] and was at least 99.9% pure. The potassium tantalate was prepared by a similar procedure to the niobate except that a final HF extraction was employed to remove small traces of Ta_2O_5.

Preparation of Samples.—Samples used for cooling curve experiments were prepared by fusing Nb_2O_5, Ta_2O_5 and K_2CO_3 until CO_2 evolution was complete. The validity of this procedure was determined by running mixed samples of pure $KNbO_3$ and $KTaO_3$ at the same mole percentages.

For heating curve experiments, very intimate mixtures of the oxides were fired approximately 30° below the expected solidus for two-hour intervals, until weight loss determination showed completion of the reaction. The samples were then ground, dried and refired and reground until X-ray spectrometer traces showed complete homogeneity of the solid solution. The total firing time was approximately 40 hours and normally only two grindings were necessary. As an alternative procedure, ceramics were prepared from the pure meta salts. The discs were ground to a fine powder and used for thermal analysis.

Conductivity measurements were made with ceramics having two B & S #28 platinum wires imbedded in them. The spacing of the wires was approximately 2 mm. These samples were prepared directly from the pure meta salts, and completeness of solid solution interaction was verified with X-ray spectrometer tracings. The intimately ground salts were pressed at 10^5 lb./in.^{2} without the use of binders. The samples were then fired approximately 30° below the solidus for eight hours, ground, repressed and refired until homogeneity and completeness of reaction were verified. The wires were imbedded in the final pressing.

Differential Thermal Analysis.—The heating and cooling curves were obtained using the apparatus previously described.[13] The only change in the equipment was that the top plug of the platinum furnace was wired with a platinum spiral. This modification increased the length of the uniform temperature zone. Previously described seeding and stirring techniques were employed during cooling experiments permitting the use of samples weighing approximately 10 g. for liquidus determinations. As the stirring was sufficient to prevent temperature gradients in the liquid, large heat effects could be obtained even with cooling rates of 0.7°/min. and Pt-Pt 10Rh couples. Two cooling curves were run at each of seven different mole %.

Heating curves were run using 15 g. of powdered solid solution. The thermocouples were centered in the powder and the heating rate was approximately 1°/min. These points were used to verify the data obtained from conductivity measurements.

Conductivity Analysis.—The measurements were made with a Mosely x-y recorder. The voltage developed across a small resistor in series with a dry cell and the sample is applied to the *x*-axis of the recorder as shown in Fig. 1a. The output of a thermocouple monitoring the temperature of the sample is connected to the *y*-axis. A Kanthal wound furnace, controlled by a variac drive was employed in these determinations and the temperature was rapidly brought up to about 25° below the solidus. The rate of temperature rise was then adjusted to approximately 0.5°/min. or less. A typical conductivity curve is shown in Fig. 1b. At least two determinations were made at each of the mole % studied, and the results obtained were within ±3° from one another.

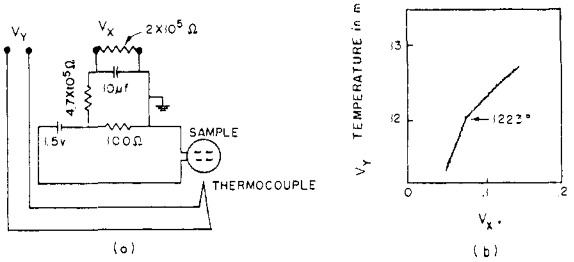

Fig. 1.—(a) conductivity circuit; (b) conductivity curve.

Discussion of Experimental Results

The data obtained by the different methods are listed in Table I, and are graphically depicted in Fig. 2.

TABLE I

THERMAL AND RESISTANCE ANALYSIS DATA

	Thermal analy.		Resistance analy.
Mole % $KTaO_3$	Av. temp. liquidus	Av. temp. solidus	Av. temp. solidus
0	1039	1039	
20	1136	1070	
30			1087
35	1194		
40			1115
50	1243	1141	1141
65	1282		
75			1223
80	1318	1247	
100	1357	1357	

The end members are seen to form a continuous series of solid solutions throughout the entire range of compositions. X-Ray analysis at room tempera-

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(7) M. R. Andrews, *J. Phys. Chem.*, **27**, 270 (1923).

(8) K. Becker, "Hochschmelzende Hartstoffe und ihre technische Anwendung," Verlag Chemie, Berlin, 1923.

(9) W. Espe and M. Knoll, "Werkstoffkunde der Hochvakuumtechnik," Springer Verlag, Berlin, 1936.

(10) W. H. Colner and O. Zmeskal, *Trans. ASM*, **44**, 1158 (1952).

(11) F. W. Glaser and D. Moskowitz, *Powder Met. Bul.*, **6**, 178 (1953).

(12) A. Reisman, F. Holtzberg, S. Triebwasser, M. Berkenblit, "Preparation of Pure Potassium Metaniobate," to be published.

(13) A. Reisman and F. Holtzberg, THIS JOURNAL, **77**, 2115 (1955).

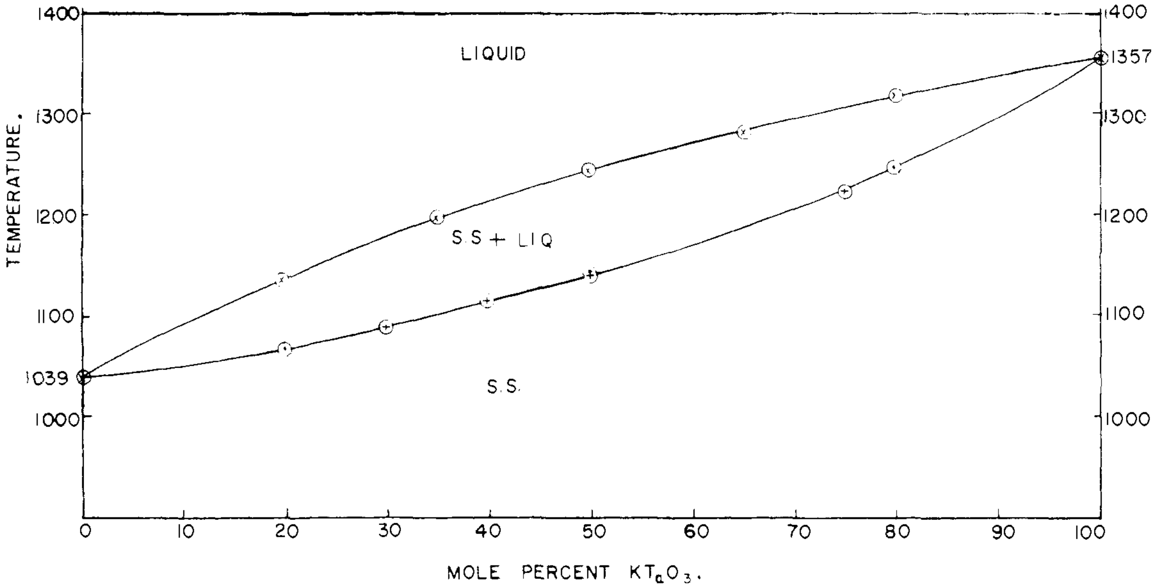

Fig. 2.—Phase diagram of system $KNbO_3$-$KTaO_3$: ⊗, cooling curves; ⊕, conductivity curves; ⊙, heating curves.

ture indicated that there was no low temperature exsolution.

The melting point of pure potassium tantalate as determined in this study was found to be 1357 ± 3°.

The method of conductivity analysis results in a clearly defined solidus transition. The data agree with thermal analysis measurements to within ±3°. Because of the definite change in slope and time independence, the new technique is apparently superior in defining the solidus.

Acknowledgment.—The authors wish to acknowledge the assistance given them by Mr. G. Burns who prepared the ceramics, Mr. K. Asai who prepared the potassium salts, Mr. M. Berkenblit for preparation of the charges and Miss M. Berry for X-ray analysis.

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The Electric Moments of Some Allylic Compounds and of Some Simple Halides

BY MAX T. ROGERS AND MORTON B. PANISH

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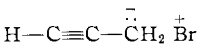
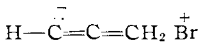
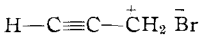
A study of the electric moments of some propargyl compounds[1] indicated that the acetylenic group is electron-attracting; to account for the electric moments of the propargyl halides it was proposed that the C–X bond moments in the halides were lowered below the normal values through the contribution of structures such as I and II.


$H{-}C{\equiv}C{-}\overset{\overset{-}{\cdot\cdot}}{C}H_2\ \overset{+}{Br}$

I


$H{-}\overset{\overset{-}{\cdot\cdot}}{C}{=}C{=}CH_2\ \overset{+}{Br}$

II

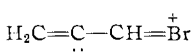

$H{-}C{\equiv}C{-}\overset{+}{C}H_2\ \overset{-}{Br}$

III

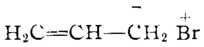
Since analogous structures may be written for allylic compounds, the electric moments of several have been investigated to determine whether they make an appreciable contribution to the normal states of allylic compounds. It is also of interest to find out whether or not structures such as III, which electric moment data indicate are not important in propargyl derivatives, are significant in the allylic series. We have, therefore, measured the electric moments of allyl bromide, allyl iodide, allyl cyanide, allylamine, allyl ethyl ether and benzylaminein benzene solution at 25°. The moments of bromoallene and *trans*-1-bromopropene-1 in benzene solution are also reported here and redeterminations of the moments of *sec*-butyl chloride, cyclohexyl chloride and cyclohexyl bromide have been made. Values have been reported previously[2] for the above three compounds and for allyl bromide.

Results

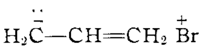
The electric moment of bromoallene (1.50) is about equal to those of bromobenzene[2] (1.55) and vinyl bromide[2] (1.44). It might be expected that resonance with structures such as IV would be about equal in importance in bromoallene and vinyl bromide and both moments are found to be about 0.5 below that of *n*-propyl bromide. It is a coincidence that bromoallene and its isomer, 3-bromopropyne, have identical electric moments so that all mixtures of these substances show the same molar polarization.[1]


$H_2C{=}\underset{\cdot\cdot}{\overset{-}{C}}{-}CH{=}\overset{+}{Br}$

IV


$H_2C{=}CH{-}CH_2\ \overset{-\ +}{Br}$

V


$H_2\overset{\overset{\cdot\cdot}{-}}{C}{-}CH{=}CH_2\ \overset{+}{Br}$

VI

The observed electric moments of allyl bromide, iodide and cyanide agree within experimental error

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[1] M. T. Rogers and M. B. Panish, THIS JOURNAL, **77**, 3684 (1955).

[2] L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948.