

sequently also be a function of θ . An exact evaluation of the changes which would be introduced into the calculated structure factors by this variation in scattering power cannot be made in the absence of a knowledge of the forms to be ascribed to the F curves for copper and aluminum atoms in crystals of CuAl_2 , but a qualitative estimate can readily be made and shows that the changes which would be introduced into S if the variation in scattering power were taken into account are in such a direction as to bring the calculated values of S^2 into better agreement with the observed intensities. The agreement is consequently thought to be satisfactory and since there is also good agreement with a Laue photograph which was taken with the incident beam of x-rays nearly perpendicular to the (001) plane of the crystal, it is concluded that the proposed structure gives a close approximation to the atomic arrangement in crystals of CuAl_2 . None of the other possible structures considered was found satisfactory.

The least distance between two copper atoms is 2.43 Å., between two aluminum atoms, 2.70 Å., and between a copper and aluminum atom 2.59 Å. These are somewhat less than the values 2.54 Å., 2.86 Å. and 2.70 Å. computed from the radii which copper and aluminum atoms have in metallic copper and aluminum.

Summary

The atomic arrangements in crystals of two of the intermetallic compounds formed by copper, Cu_2Mg and CuAl_2 , have been determined by x-ray methods.

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[CONTRIBUTION NO. 20 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

THE REACTION BETWEEN POTASSIUM CARBONATE AND SULFUR IN ALCOHOL SOLUTION

By TENNEY L. DAVIS AND JULIAN W. HILL

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In his "Experiments and Notes about the Producibleness of Chymical Principles," appended to the second English edition of "The Sceptical Chymist," Oxford, 1680, Robert Boyle discusses the possibility of transmuting or changing into one another the so-called elements of the alchemists. As evidence that "a disposition to be dissoluble in this or that liquor may be acquir'd by mixture," he points¹ to the fact that, whereas neither "salt of tartar" (potassium carbonate) nor sulfur is soluble in "spirit of wine" (alcohol), "yet if this Salt and Sulphur be mixt together, spirit of Wine will in less than an hour and sometimes in less than a quarter

¹ Robert Boyle, *op. cit.*, p. 4. Concerning the several editions of "The Sceptical Chymist," see *Isis*, 8, 71 (1926).

of that time dissolve enough of this matter to be richly color'd by it, and this without the help of external heat."

We have verified Boyle's observation. A mixture of powdered sulfur with anhydrous potassium carbonate does indeed impart a yellow color to alcohol after a few hours' standing. After a longer interval the color is deeper, and after three or four days no further change is apparent. With boiling alcohol the reaction is very rapid. We have not been able to find in the literature any explanation of this behavior or of the reaction itself—and have accordingly made experiments to determine the matter.

The deep yellow liquid is not a colloidal solution for it shows no Tyndall effect. On dilution with water it gives a precipitate of finely divided sulfur, about the same amount of precipitate as is produced by adding water to a saturated solution of sulfur in alcohol. On acidification it gives hydrogen sulfide and a precipitate of sulfur—evidence that it contains potassium polysulfide. On shaking with metallic mercury it is rendered colorless and produces black mercury sulfide. If air is bubbled through the yellow liquid or brought in contact with it by shaking in a capacious flask, the liquid quickly loses its color and deposits a precipitate of sulfur and potassium thiosulfate. These reactions are the same as those of an aqueous solution of potassium polysulfide except, of course, that potassium thiosulfate does not precipitate when the aqueous solution is oxidized.

The precipitate which was produced by agitating the yellow alcohol solution with air was collected, dried and freed from sulfur by washing with carbon disulfide. The white residue was recrystallized from water, in which it was very soluble, and was analyzed for potassium by fuming down twice with sulfuric acid, igniting with ammonium carbonate, and weighing as K_2SO_4 . Found: potassium 41.08%, 41.08%; calculated for $K_2S_2O_3$, potassium 41.11%. The thiosulfate was further identified by qualitative tests with hydrochloric acid, silver nitrate, ferric chloride and stannous chloride.

When powdered sulfur is allowed to stand at laboratory temperature with a strong aqueous solution of potassium carbonate, the liquid becomes pale yellow after about two weeks and does not become deeply colored even after long standing. In boiling water the reaction is more rapid, but still much less rapid than it is in boiling alcohol. Although potassium carbonate is readily soluble in water, sulfur is almost entirely insoluble, and the greater speed of the reaction in alcohol solution is due to the fact that alcohol dissolves an appreciable quantity of both reagents and that the mass-action product of the concentration of the reagents in that solvent is greater in consequence. We have found that absolute ethyl alcohol solutions saturated at 25° contain in 100 cc. 0.1114 g. of anhydrous potassium carbonate, 0.0088 g. of anhydrous sodium carbonate and 0.03926 g. of sulfur. When sodium carbonate and sulfur are boiled together in alcohol, the reaction is slight and the solution becomes only faintly colored.

We have attempted to isolate and analyze the pure potassium polysulfide from the alcohol solution. The yellow liquid was filtered and evaporated to dryness in a stream of dry nitrogen, and the residue was freed from sulfur by washing with carbon disulfide. Sulfur was determined by dissolving dried and weighed portions of the orange-brown material in water, oxidizing with bromine water, and precipitating as barium sulfate. Among many analyses several pairs of checks were obtained, but the checks were discordant with one another. Although the yellow alcohol solution did not smell of hydrogen sulfide, it was found that the vapors from its evaporation, even when the evaporation was carried out at laboratory temperature, contained hydrogen sulfide enough to blacken lead acetate paper. Alcoholysis evidently occurred, potassium ethylate was undoubtedly present in varying amounts in the residues from the evaporations—and an attempt at fractional crystallization of the polysulfide from alcohol was abandoned as impracticable.

Summary

The reaction between potassium carbonate and sulfur in alcohol solution is essentially the same as in water solution but is very much more rapid. Alcohol dissolves an appreciable amount of both substances, while water dissolves a large amount of one and exceedingly little of the other. The solubilities of potassium carbonate, sodium carbonate and sulfur in absolute ethyl alcohol at 25° have been determined.

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[CONTRIBUTION FROM THE UNIVERSITY OF VERMONT]

THE ODOR AND STRUCTURE OF CERTAIN CYCLIC ACETALS¹

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Verley² isolated an oil from jasmine blossoms that had as a principal constituent the cyclic acetal of phenylethyleneglycol and formaldehyde-1-phenyldioxolane. This compound was synthesized and found to have the same jasmine-like odor. The corresponding derivatives from acetaldehyde and valeraldehyde proved to have similar odors.

Shortly afterwards Hesse and Müller³ reported that no trace of this acetal was to be found in jasmine oil and that the odor was due to two compounds of unknown nature in addition to phenylethyl acetate and a terpene alcohol ester.

¹ For the odor evaluation of the products described in this paper the writers are indebted to Burton T. Bush, Inc., of New York City, particularly to Dr. Ph. Chaleyev of that Company.

² Verley, *Compt. rend.*, **128**, 314 (1899).

³ Hesse and Müller, *Ber.*, **32**, 565 (1899).