COMMUNICATIONS TO THE EDITOR

A NEW GROUP OF ISOMORPHOUS COMPOUNDS A_2XO_4

Sir:

X-Ray data show that alkali sulfates $Me^I_2SO_4$ constitute with alkali alkaline earth phosphates $Me^IMe^{II}PO_4$[1] and with calcium orthosilicate Ca_2SiO_4, modified by phosphate as in Bessemer and open-hearth furnace slags, principally at elevated temperatures, a new group of isomorphous compounds A_2XO_4 with a rather simple hexagonal unit cell containing two molecules. The space group D^3_{3d} and the atomic parameters have been determined for glaserite, $K_3Na(SO_4)_2$, the only substance known before to possess this particular lattice.[2]

TABLE I

Substance and temp. range of stability	Lattice dimensions, Å. a_0	c_0	c/a
α-K_2SO_4, above 590°	5.71	7.86	1.375
α-Na_2SO_4(I), above 239°[3]	5.38[4]	7.26[4]	1.350
Glaserite $(K, Na)_2SO_4$, room temp.	5.66[2]	7.33[2]	1.295[2]
α-$CaNaPO_4$, above 680°	5.23	7.13	1.364
α-$CaKPO_4$, above 705°	5.58	7.60	1.360
$SrNaPO_4$	5.48	7.36	1.34
$BaNaPO_4$	5.64	7.35	1.30
Calcium phosphato silicates, $Ca_x(SiO_4, PO_4)$:			
$(Ca_2SiO_4, {}^1/_2Ca_3(PO_4)_2)$[1,6,7]	5.38	7.05	1.310
$(Ca_2SiO_4, Ca_3(PO_4)_2)$[a]	5.21	6.90	1.32

[a] Allotropic form of silicocarnotite, $5CaO \cdot P_2O_5 \cdot SiO_2$.[5]

The group is expected to include chromates, vanadates, molybdates, tungstates, arsenates, selenates and other compounds A_2XO_4, particularly at elevated temperatures.

The high-temperature forms can be stabilized by the addition of substances which are insoluble in the low-temperature phase and therefore must be precipitated for transformation. More effective than additions of substances A_2XO_4, which are not isomorphous with the low-temperature forms of the compounds A_2XO_4 to which they are added, are compounds which deviate in composition from A_2XO_4, such as compounds A_2XO_3 (for instance carbonates), AXO_4 (for instance, alkaline earth sulfates), $A_3(XO_4)_2$ (for instance, alkaline earth phosphates) or others. Examples are $CaNaPO_4$–Na_2CO_3, $CaKPO_4$–K_2CO_3,[1] Na_2SO_4–Na_2CO_3,[4] Na_2SO_4–$CaSO_4$, Ca_2SiO_4–calcium phosphates and many others. The identity of the X-ray patterns of alleged "binary compounds," "$CaNa_8(SO_4)_5$"[5] or "$K_3Na(SO_4)_2$,"[2] with the pattern of one or both of their components, together with the known phase diagram of these systems, proves they actually are solid solutions of $CaSO_4$ in α-Na_2SO_4 and of Na_2SO_4 in α-K_2SO_4, respectively.

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(1) H. H. Franck, R. Frank, E. Kanert and M. A. Bredig, *Z. anorg. allgem. Chem.*, **230,** 1 (1936), and **237,** 49 (1938).

(2) B. Gossner, *Neues Jahrb. Mineral.*, **B**, **57A**, 89 (1928); "Structurbericht." 1913–1928, p. 378.

(3) F. C. Kracek and C. J. Ksanda, *J. Phys. Chem.*, **34**, 1741 (1930).

(4) L. S. Ramsdell, *Am. Mineral.*, **24,** 109 (1939).

(5) R. Klement and F. Steckenreiter, *Z. anorg. allgem. Chem.*, **245**, 236 (1940).

(6) G. Troemel and A. Koerber, *Arch. Eisenhüettenw.*, **7**, 7 (1933).

(7) G. Nagelschmidt, *J. Chem. Soc.*, 865 (1937).

EFFECT OF HYDROCYANIC ACID ON DISULFIDES

Sir:

The formation of mercaptans from disulfides by the action of cyanide in alkaline solution has long been recognized and interpreted as $RS—SR + NaCN \rightarrow RSNa + RSCN$ [I. Mauthner, *Z. physiol. Chem.*, **78,** 28 (1912); also H. T. Clarke in Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 915]. In discussing the mechanism of activation of such proteolytic enzymes as papain, etc., by hydrogen cyanide, Irving, *et al.* [G. W. Irving, T. S. Fruton and M. Bergmann, *J. Biol. Chem.*, **139,** 569 (1941)] pose the question whether a similar reaction can occur also in slightly acid solution since activation can be brought about at *p*H 5.

In an attempt to answer this question cystine and (—S—S—) glutathione were treated with hydrogen cyanide at *p*H 5 and different temperatures. After various time intervals, qualitative and quantitative tests for thiol groups and for cysteine specifically were performed (nitroprusside test, the Sullivan reaction [M. X. Sullivan, *Public Health Repts.*, **44,** 2, 1600 (1929). This method when applied to the determination of cysteine in the presence of cystine was found reliable when the cysteine comprised at least 10%

of the cystine; otherwise too high values are obtained] and the Mirsky and Anson modification of the Folin method) [A. E. Mirsky and M. L. Anson, *J. Gen. Physiol.*, **18**, 307 (1934). Correct values for cystine by this method are obtained only after removal of the hydrogen cyanide. This was achieved by evacuation with oxygen-free nitrogen passing through the capillary].

At 35° a slow formation of cysteine was noted in a 0.1 M citrate buffer solution (pH 5.0) containing 0.0025 mole of cystine and 0.0625 mole of potassium cyanide and hydrogen chloride per liter; 5% of the cystine was found to be reduced after twenty-four hours, 11% after seventy-two hours, 18% after six days. At 95° with 0.005 M cystine and 0.125 M hydrogen cyanide the reaction proceeded quite rapidly, the amount of cysteine formed within one hour corresponding to 49% of the cystine used. Further heating up to six hours caused a slow decrease in the yield of cysteine. When a cystine–hydrogen cyanide reaction mixture, after heating to 95° for one hour, was treated with sulfite to reduce any unchanged cystine, no significant increase in color intensity was found (beyond that due to the cysteine already formed), indicating the absence of any unreacted cystine. This, together with the fact that the yield in cysteine never exceeded 50%, is regarded as evidence that hydrogen cyanide, like potassium cyanide, does not cause reduction but "hydrocyanolysis" of the disulfide ($\text{RS—SR} + \text{HCN} \rightarrow \text{RSH} + \text{RSCN}$).

When a solution containing 0.01 mmole of (—S—S—) glutathione and 0.25 mmole of hydrogen cyanide was incubated at 35°, 22% of the glutathione was in the thiol form after three days. In the absence of the hydrogen cyanide no detectable amounts ($<0.5\%$) of thiol were formed under the same conditions. Also in control experiments in which the cystine–hydrogen cyanide reaction mixtures were kept at low temperatures (3 and −10°) for as long as eight days, no formation of cysteine could be detected. When cystine was heated at 95° and pH 5 in the absence of hydrogen cyanide, only 1.5% of the cystine yielded cysteine in six hours (by hydrolysis).

From these experiments it is concluded that hydrogen cyanide at pH 5 attacks disulfides, forming thiol groups more slowly but probably by the same mechanism as does potassium cyanide in alkaline solution. It is impossible to decide whether the rate of this reaction at 40° is sufficient to explain the activating effect of hydrogen cyanide on papain, etc., in the presence of small amounts of disulfide–sulfhydryl systems.

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2-PHENYLTETRALONE-1. A CORRECTION

Sir:

In the recently published article, by Plentl and Bogert [THIS JOURNAL, **63**, 989 (1941)], on "The Synthesis of Tricyclic Hydrocarbons Related to Stilbestrol," 2-phenyltetralone-1 is described as though it were a new compound, whereas it has been reported previously both by Newman [*ibid.*, **60**, 2949 (1938); **62**, 872 (1940)], and by Miss Crawford [*ibid.*, **61**, 608 (1939)]. Newman designated his products as "1-keto-2-phenyl-1,2,3,4-tetrahydronaphthalene" in his first paper, and "1,2,3,4-tetrahydro-1-keto-2-phenylnaphthalene" in his second, while Miss Crawford used the name "1-oxo-2-phenyl-1,2,3,4-tetrahydronaphthalene" in hers. This variation in nomenclature accounts in part for our failure to catch these articles in reviewing the literature. Our apologies are extended to these fellow investigators for this oversight.

While we all used the same initial material, *viz.*, α,γ-diphenylbutyric acid, the methods for its conversion into the tetralone differed. Newman gave the m. p. as 76–77°, Miss Crawford as 79–80°, and our product melted at 79°.

Our statement on page 991 of that article that 2-phenyltetralone-1 "did not react with semicarbazide hydrochloride" should be corrected. We ran the reaction only once, in an alcoholic solution containing sodium acetate as buffer, and failed to insolate a semicarbazone. On repeating the reaction, however, with what little tetralone we had left (38 mg.), we have been more successful, and have obtained a semicarbazone, which proved rather difficult to purify, as it was already somewhat discolored, and then melted at 254° (Anschütz total immersion thermometer), with some prior gas evolution and sintering.

Anal. Calcd. for $C_{17}H_{17}ON_3$: C, 73.1; H, 6.1. Found: C, 73.4; H, 6.4.

Newman, who prepared the semicarbazone without difficulty, found that it melted with decomposition at 250–251.4°, after sintering at 245°.