COMMUNICATIONS TO THE EDITOR

A NEW GROUP OF ISOMORPHOUS COMPOUNDS A_2XO_4

Sir:

X-Ray data show that alkali sulfates $Me^{I}_{2}SO_4$ constitute with alkali alkaline earth phosphates $Me^{I}Me^{II}PO_4$[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).

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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%