

Different Tastes of Enantiomorphic Hexoses

The recent report of Steinhardt, Calvin, and Dodd (1) on the difference in taste of α -D-mannose and β -D-mannose encourages us to report observations that have probably not been made before, at least not on pure substances.

It is well known that the D- and L-enantiomorphs of certain amino acids have different tastes, and the same might be expected of monosaccharides. Unfortunately, the "unnatural" L-forms of common sugars are not commercially available in pure form.

We recently had occasion to prepare L-glucose and L-mannose in pure crystalline form in fairly large amounts. A comparison of their taste with the corresponding D-compounds revealed that five people agreed in finding L-mannose distinctly less sweet than D-mannose, and in finding L-glucose not to be sweet at all but to have a slight salty taste. Three others, however, found L-mannose to be sweeter than D-mannose, and others found D-mannose bitter. Taste is obviously a complicated phenomenon.

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References and Notes

1. R. G. Steinhardt, Jr., A. D. Calvin, E. A. Dodd, *Science* **135**, 367 (1962).
2. This work was supported by research grants H1076 (C8), RG-4704 (C4), and RG-6939 (C1) from the National Institutes of Health and a research grant (NSF-G-15082) from the National Science Foundation.

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Tetragonal Iron Sulfide

Abstract. Studies of synthetic iron sulfides formed from aqueous solution at 25°C and atmospheric pressure have revealed the existence of a new phase, tetragonal FeS. This phase is formed as the initial corrosion product of metallic iron or steel in solutions of hydrogen sulfide. It has been discovered as an iron corrosion product in the sediments of the Mystic River at Boston, Massachusetts.

The initial product formed by the corrosion of steel in aqueous solutions of hydrogen sulfide has been reported as cubic FeS₈ (1). To this phase the name "kansite" was applied by F. Prange (1) to represent the H₂S corrosion product of steel pipes from sour crude oil wells in Kansas. In my study I obtained a corrosion product whose

x-ray diffraction powder pattern is essentially identical to that of "kansite" (Table 1). The product was formed by immersing reagent grade metallic iron wire in a saturated aqueous solution of H₂S for about 18 hours and collecting the loosened corrosion material. At all times care was taken to exclude air from the reaction vessel. Careful indexing of the x-ray powder photograph for this substance shows that it is not cubic but instead primitive tetragonal with $c_0 = 5.047 \pm 0.002$ Å and $a_0 = 3.679 \pm 0.002$ Å. The x-ray data are summarized in Table 1.

Similarity of relative intensities of powder diffraction lines of this tetragonal phase to those of tetragonal FeSe (2) suggests that the iron corrosion product might be tetragonal FeS. Because tetragonal FeSe was shown (2) to have the crystal structure of red PbO (3) calculations of relative intensities of individual forms (hkl), based on this structure, were undertaken. As a first approximation the following distribution of atoms in the unit cell was assumed:

2 Fe in (a): (000) ($\frac{1}{2}\frac{1}{2}0$)

2 S in (c): ($0\frac{1}{2}\frac{1}{2}0$) ($\frac{1}{2}0-\frac{1}{2}0$)

Temperature and absorption corrections were neglected. Good agreement was obtained between calculated relative intensities and those estimated visually from the powder photographs including absence of forms with a structure factor equal to zero (Table 1).

As a check on the chemical composition adduced on structural grounds several quantitative chemical analyses were made for HCl-soluble iron and sulfide sulfur by a modification of the evolution method used for the determination of sulfur in steel (4). The fine-grained character and extreme ease of oxidation precluded weighing prior to analysis. The results can, therefore, only be expressed as the atomic ratio, Fe:S²⁻. Iron was determined spectrophotometrically with *o*-phenanthroline. The average of three analyses is Fe:S²⁻ = 1.05 ± 0.02 , which agrees well with the composition FeS. The probable cause of the small excess of iron is air oxidation prior to analysis. Some of the excess iron may be present actually in the structure analogous to the reported 4 percent excess of iron in tetragonal FeSe (5). I conclude that the initial corrosion product of metallic iron in aqueous solutions of H₂S at room temperature and atmospheric pressure is a tetragonal phase whose composition is essentially FeS.

Table 1. X-ray powder diffraction data for tetragonal FeS (unfiltered FeK radiation) and "kansite."

“Kansite”*		Tetragonal FeS			
$d_{\text{meas. A}}$	$d_{\text{meas. A}}$	$d_{\text{calc. A}}$	hkl	$I_{\text{obs.}}^\dagger$	$I_{\text{calc.}}$
			100	‡	0
5.05	5.03	5.04	001	10	190
2.99	2.97	2.97	101	8	69
	2.60	2.60	110	2	15
2.32	2.305	2.31	111	8	94
			102	‡	0
	1.835	1.839	200	6	56
1.80	1.805	1.811	112	8	103
1.73	1.723	1.728	201	6	42
	1.677	1.681	003	2	8
	1.564	1.564	211	4	17
1.54	1.527	1.530	103	2	8
1.42	1.410	1.412	113	3	16
1.31	1.298	1.300	220	5	20.5
1.26	1.258	1.261	004	5	10
		1.257	221		15
	1.239	1.241	203	3	16
	1.190	1.192	301	1	5.5
	1.174	1.176	213	2	11.5
1.14	1.133	1.134	311	5	29
			310	‡	0
	1.055	1.056	312	8	100

* Data from Meyer *et al.* (1). † Relative intensities by visual estimation from powder photographs. ‡ Absent.

Tetragonal FeS has been discovered in the sediments of the Mystic River, Boston, Mass. Its x-ray powder pattern is identical with that of tetragonal FeS synthesized in the laboratory. It is formed by the reaction of H₂S with iron trash. The H₂S is produced from sulfate in sea water by the activity of sulfate-reducing bacteria. Sewage and industrial wastes serve as a food and energy source for the bacteria.

Some properties of synthetic tetragonal FeS are: black color when wet, soluble in concentrated HCl, unattracted by an ordinary hand magnet. Under the microscope tiny ($<1\mu$), opaque, brassy-colored crystals of imperceptible outline can be seen. The wet material oxidizes rapidly in air to γ FeOOH (lepidocrocite) and orthorhombic sulfur.

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