

The Polymorphism of Cu₂S, and the Relations Between the Solid Phases in the System Cu₂S–CuS

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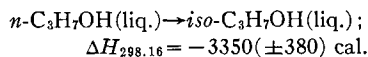
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"accuracy error" in our final result to be ± 300 cal. per mole.

Using Rossini's "best value" for *n*-propanol¹ and this new result for isopropanol, we now find for the isomerization reaction



By the third law of thermodynamics, $\Delta S_{298.16} = -3.1(\pm 0.5)$ e.u.⁸ for this reaction; and hence

$$\Delta F^\circ_{298.16} = -3350 + (298.16)(3.1) = -2430(\pm 420) \text{ cal.}$$

GEORGE S. PARKS
GEORGE E. MOORE

Department of Chemistry,
Stanford University, California,
September 22, 1939.

¹ Rossini, Nat. Bur. Stand. J. Research 13, 189 (1934).

² Richardson and Parks, J. Am. Chem. Soc. in a forthcoming issue.

³ Parks and Kelley, J. Am. Chem. Soc. 47, 2089 (1925).

⁴ Washburn, Nat. Bur. Stand. J. Research 10, 525 (1933).

⁵ Baxter, Guichard, Hönigschmid and Whytlaw-Gray, J. Am. Chem. Soc. 61, 223 (1939).

⁶ Swietoslawski, J. Am. Chem. Soc. 42, 1092 (1920).

⁷ Rossini, Chem. Rev. 18, 233 (1936).

⁸ Parks and Huffman, *The Free Energies of Some Organic Compounds* (The Chemical Catalogue Co., New York, 1932), p. 109.

The Polymorphism of Cu_2S , and the Relations Between the Solid Phases in the System $\text{Cu}_2\text{S}-\text{CuS}$

The literature relating to the polymorphism of chalcocite and to the more general relations between the solid phases in the system $\text{Cu}_2\text{S}-\text{CuS}$ contains numerous diverse conclusions. Because the solid phases in the system $\text{Cu}_2\text{S}-\text{CuS}$ are of importance to mineralogists, a systematic x-ray study of them was undertaken. A special camera was designed to make x-ray photographs of powder-samples at high temperatures. This camera allows the specimen to remain heated continuously, and the heat

treatment can be controlled as in a furnace. Samples were made up of annealed mechanical mixtures of the two end-members. The Cu_2S end-member came entirely from a single, homogeneous, pure orthorhombic crystal from Bristol, Connecticut. The CuS was chemically pure synthetic material which gave the covellite powder pattern.

The phase diagram for the system $\text{Cu}_2\text{S}-\text{CuS}$ is shown in Fig. 1. This contains three compounds and six phases. The compounds are:

Chalcocite, ideally Cu_2S

Digenite, ideally $4\text{Cu}_2\text{S} \cdot \text{CuS} = \text{Cu}_9\text{S}_6$

Covellite, CuS

Several authorities have inferred that, on heating, chalcocite inverts from an orthorhombic to a cubic modification at about 91°C . In the present investigation it was found chalcocite undergoes three transformations, and none of the high temperature phases is cubic up to at least 250°C . The revised inversion scheme is:

above	105°C , nonisometric completely disordered basic structure
78°C to	105°C , nonisometric partially disordered basic structure
52°C to	78°C , nonisometric ordered basic structure
below	52°C , orthorhombic superstructure.

These temperatures are probably accurate to $\pm 4^\circ\text{C}$. The 52° inversion is easily detectable by x-ray diffraction records, and makes itself known by the disappearance of superstructure lines on the powder photograph. The other inversions take place without obvious changes in the powder pattern except for certain intensity changes. The temperatures of these inversion points were determined by accurate thermal measurements. The superstructure phase is capable of dissolving up to 8 atomic percent CuS , while the ordered basic structure can dissolve only 2 atomic percent CuS . The solution of CuS by Cu_2S crystals almost certainly takes place by omission of Cu atoms from the Cu_2S structures.

The experimental evidence indicates a hitherto unrecognized compound, Cu_9S_6 , whose powder pattern is

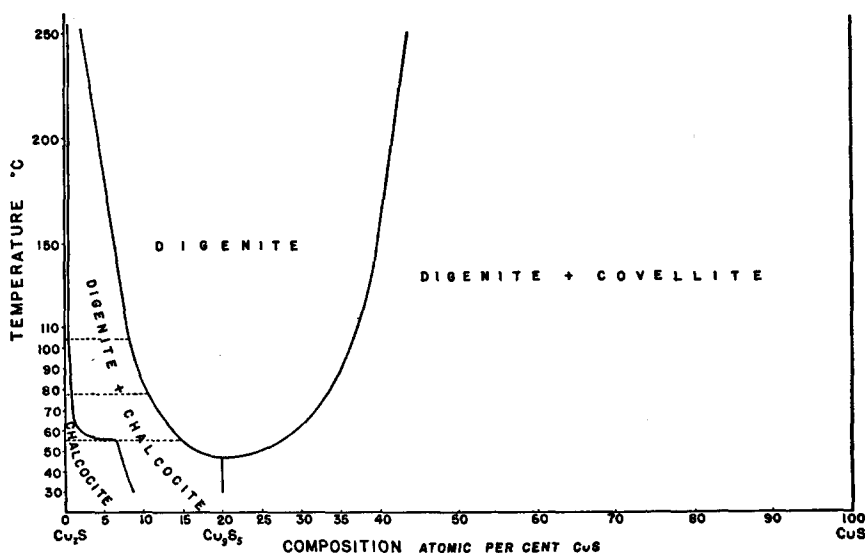


FIG. 1.

essentially identical with that of the discredited mineral digenite, to which the formula $2\text{Cu}_2\text{S} \cdot \text{CuS} = \text{Cu}_5\text{S}_3$ had been assigned. Below approximately 47°C digenite has the ideal composition Cu_5S_3 but above this temperature it takes increasing amounts of either Cu_2S or CuS into its composition. The mechanism of this solution is undoubtedly a variation in the number of copper atoms in the crystal structure. At 170°C , it is known that the copper atoms of this compound are in disorder. It is likely that at a temperature of 47°C or lower, the copper atoms in digenite become ordered and give rise to another modification.

Evidently digenite has been regarded as the phase of chalcocite stable above 91°C . Actually, the heat effect in this region is due to the transformation of ordered high chalcocite into the disordered high chalcocite, which is not isometric. The vanishing of this heat effect in preparations containing 8 percent and more by weight of CuS is evidently due to the fact that a heating run passes out of the chalcocite-digenite two-phase region and entirely into the digenite field before the chalcocite transformation is reached.

A full discussion of this investigation will appear elsewhere.

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Dipole Variation of Ether

Recently Byers¹ showed that the Cellosolves, whose structural formula resemble both ethers and alcohols, behave very similarly to the alcohols in respect to variation of dipole moment and not like the symmetrical ethers. The author stated that he was unable to find values for the electric moments of unsymmetrical ethers but predicted that these would vary in the manner of the Cellosolves and alcohols.

Reference to the values given in Table I shows that

TABLE I.

MIXED ETHYL ETHERS COMPOUND	MOMENT $\times 10^{18}$	MIXED PHENOL ETHERS COMPOUND	MOMENT $\times 10^{18}$
Ethyl alcohol	1.70	Phenol	1.70
Diethyl ether	1.14	Anisole	1.20
Ethyl butyl ether	1.2	Phenetole	1.0
Ethyl isoamyl ether	1.2	Diphenyl ether	1.05
Ethyl phenol ether	1.0		

Byers' prediction, with respect to unsymmetrical ethers is true. There is an initial decrease in moment from ethyl alcohol to ethyl ether and from phenol to anisole, the decrease being due to the increased repulsion over the repulsion between an ethyl or phenyl group and hydrogen. Further lengthening of the chain does not alter its bulk in the neighborhood of the oxygen atom and therefore the moments remain sensibly the same. Essentially the same reasoning was applied by Smythe to account for the constant moment of the alcohols and by Byers for that of Cellosolves. The values given in the table are taken from Smythe.² The only exception is that of ethyl butyl ether

which is taken from unpublished measurements from this laboratory. This unsymmetrical ether was prepared from interaction between butyl bromide and sodium ethylate. The product is purified by refluxing with sodium and repeated fractional distillation. The physical constants agree very well with those reported by Norris and Rigby.³

Meyer and Büchner⁴ redetermined the moment of propyl ether and found it to be 1.16 ± 0.06 . This value agrees with the electric moment of diethyl ether and together with the value of 1.0 for the moment of di-isoamylether,² indicates that even the symmetrical ethers shows similar dipole variation as that of unsymmetrical ethers.

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August 10, 1939.

¹ W. H. Byers, J. Chem. Phys. **7**, 175 (1939).

² Smythe, *Dielectric Constant and Molecular Structure* (Chemical Catalogue Co., New York, 1931).

³ Norris and Rigby, J. Am. Chem. Soc. **54**, 2097 (1932).

⁴ Meyer and Büchner, Physik. Zeits. **33**, 390 (1932).

Erratum: The Vapor Pressures of Ortho- and Para-hydrogen and Ortho- and Paradeuterium

KARL COHEN AND H. C. UREY,
(J. Chem. Phys. **7**, 157 (1939))

During a conversation with Professor E. Teller on our paper on the vapor pressures of *o*- and *p*- H_2 and *o*- and *p*- D_2 ¹ he was kind enough to point out an error in the calculation of the centrifugal stretch of the rotating molecules. The stretch should be expressed as $\delta_c/c = 8B_0^2/\omega_0^2$, and not $4B_0^2/\omega_0^2$ as we had calculated. Since, in our view, the difference in heats of sublimation of 0°K caused by van der Waals attraction, ΔE_A , is proportional to this stretch, the calculated differences become doubled. Thus

$$\begin{aligned}\text{for } \text{H}_2 \quad \Delta E_A (\text{calc.}) &= -3.36 \text{ cal./mole,} \\ \text{for } \text{D}_2 \quad \Delta E_A (\text{calc.}) &= -2.32 \text{ cal./mole,}\end{aligned}$$

while

$$\begin{aligned}\text{for } \text{H}_2 \quad \Delta E (\text{exp.}) &= -1.78 \text{ cal./mole} = E_{o-\text{H}_2} - E_{p-\text{H}_2}, \\ \text{for } \text{D}_2 \quad \Delta E (\text{exp.}) &= -1.78 \text{ cal./mole} = E_{p-\text{D}_2} - E_{o-\text{D}_2},\end{aligned}$$

where ΔE is the difference in sublimation heats computed from vapor pressure data, and naturally includes contributions from repulsive forces.

The corrected result is more satisfactory than the previously reported one. If, on the one hand, the stretch of rotating molecules increases their mutual attraction, on the other hand, the resultant increased penetration of the electron shells will also increase the repulsive forces. Thus a part of the increased binding energy caused by the increased van der Waals attraction will be canceled by the increased repulsion, and one must have $|\Delta E_A| > |\Delta E|$ if our explanation is to hold good.

If we calculate the required values of E_R to give agreement with experiment, namely $\Delta E_R = \Delta E - \Delta E_A$, we find

$$\begin{aligned}\text{for } \text{H}_2: \quad \Delta E_R &= 1.58 \text{ cal./mole,} \\ \text{for } \text{D}_2: \quad \Delta E_R &= 0.54 \text{ cal./mole;}\end{aligned}$$

this agrees with the idea that ΔE_R will be larger for hydrogen because of the twice larger stretch.

¹ K. Cohen and H. C. Urey, J. Chem. Phys. **7**, 157 (1939); **7**, 438 (1939).