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Chemical Reactions in the Roasting of Copper Sulfides

By I. D. Shah and S. E. Khalafalla

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CHEMICAL REACTIONS IN THE ROASTING OF COPPER SULFIDES

by

I. D. Shah[1] and S. E. Khalafalla[2]

ABSTRACT

The Bureau of Mines investigated the sequence of principal chemical reactions taking place during the roasting of covellite (CuS). Practically all covellite is converted to digenite ($Cu_{1.8}S$) before oxidation to Cu_2O begins. Part of the Cu_2O is then converted to CuO, which in turn forms $CuSO_4$ through $CuO \cdot CuSO_4$ as an intermediary. $CuSO_4$ and $CuO \cdot CuSO_4$ decompose at 600° to 700° C to yield CuO and SO_3 (g) as final products. An overall mechanism is proposed for chemical reactions occurring at different interfaces of partially oxidized CuS pellets.

INTRODUCTION

The roasting process is widely used in extracting copper from its sulfide ores. At present the development of a new process for winning copper from pelletized chalcocite concentrate is underway at the Bureau of Mines Twin Cities Metallurgy Research Center. In this process, the dead roasting of sulfide is followed by the reduction of oxide to metallic copper by a reducing agent such as hydrogen. This work revealed a scarcity of fundamental information connected with the chemistry, kinetics, and mechanism of the oxidation of copper sulfides.

The broad objectives of the research are to investigate the sequence of the principal chemical reactions and the kinetics and mechanism of chemical reactions involved, and to find a method to improve the roasting process. The present report deals only with the chemistry of the process.

According to Kullerud (<u>12</u>),[3] covellite (CuS) begins to break down to digenite ($Cu_{1.8}S$) and sulfur at 235° C in an inert atmosphere. Digenite is stable up to 550° C and then breaks down to chalcocite (Cu_2S) and sulfur.

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[1] Metallurgist.

[2] Supervisory research chemist.

The authors are with the Twin Cities Metallurgy Research Center, Bureau of Mines, Minneapolis, Minn.

[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Buerger (2) investigated the phase diagram of the Cu_2S-CuS system and reported the presence of three compounds and four phases. The compounds are chalcocite, ideally Cu_2S; digenite, ideally $Cu_{1.8}S$; and covellite, CuS. The phases are high chalcocite, low chalcocite, digenite, and covellite. According to Buerger and Wuensch (3), in high chalcocite the sulfur atoms are substantially fixed in hexagonal close-packed structure, while copper atoms are mobile through the interstices of this structure. This high disorder was apparent from the investigation of Jensen (9), who observed that the diffusion rate of copper in low chalcocite increased rapidly as the temperature approached the transformation temperature and was much higher throughout the high-chalcocite range. The activation energy for diffusion was about 0.15 ev, an extremely low value compared with the 1 to 2 ev usually found for metal-atom diffusion in close-packed compounds. According to Ray (16), digenite is known to be only a p-type semiconductor and imperfection in its crystal structure is mainly due to copper deficiency. Figure 1 summarizes the Cu-S phase diagram, while figure 2 shows a portion of that phase diagram, based upon the work of Roseboom (17).

Martinez and Hollander (13) studied the thermal decomposition of CuS to $Cu_{1.8}S$ in N_2 by differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) but were unable to explain the thermograms satisfactorily, due to the presence of impurities in the starting material. According to Kulikova (11), at 425° to 500° C in an inert atmosphere, covellite dissociates into digenite and partially into β-chalcocite and gaseous sulfur is liberated.

Ashcroft (1) reported that the oxidation of copper sulfides proceeds with an intermediary stage of the formation of copper sulfate which subsequently dissociates into copper oxides and SO_3 gas. Peretti (15) has conclusively shown that a layer of Cu_2O appears directly adjacent to the Cu_2S during the roasting of cylindrical briquets of copper(II) sulfide under conditions where sulfates will be formed. Above 663° C, CuO was the only final product, but below 663° C, increasing amounts of sulfates were found mixed with the CuO. McCabe and Morgan (14) supported Peretti's claim (15) that Cu_2O is formed directly from Cu_2S. Wadsworth and coworkers (19) studied the oxidation of natural chalcocite in oxygen and their results were in general agreement with those of McCabe and Morgan (14) and Thornhill and Pidgeon (18).

EXPERIMENTAL WORK

Methods and Apparatus

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) techniques were used in this study. The DTA (model KA H) and TGA (model TGA 5-B) were supplied by Tracor Company,[4] Austin, Tex. Stainless steel powder-sample holders and Inconel liquid-sample holders were fitted with platinum versus platinum-10 percent rhodium thermocouples. The reference and sample holders were cylindrical, 0.25 inch in diameter and 0.25 inch deep. The apparatus was equipped with a recorder, controller, amplifier, and heating-rate

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[4] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

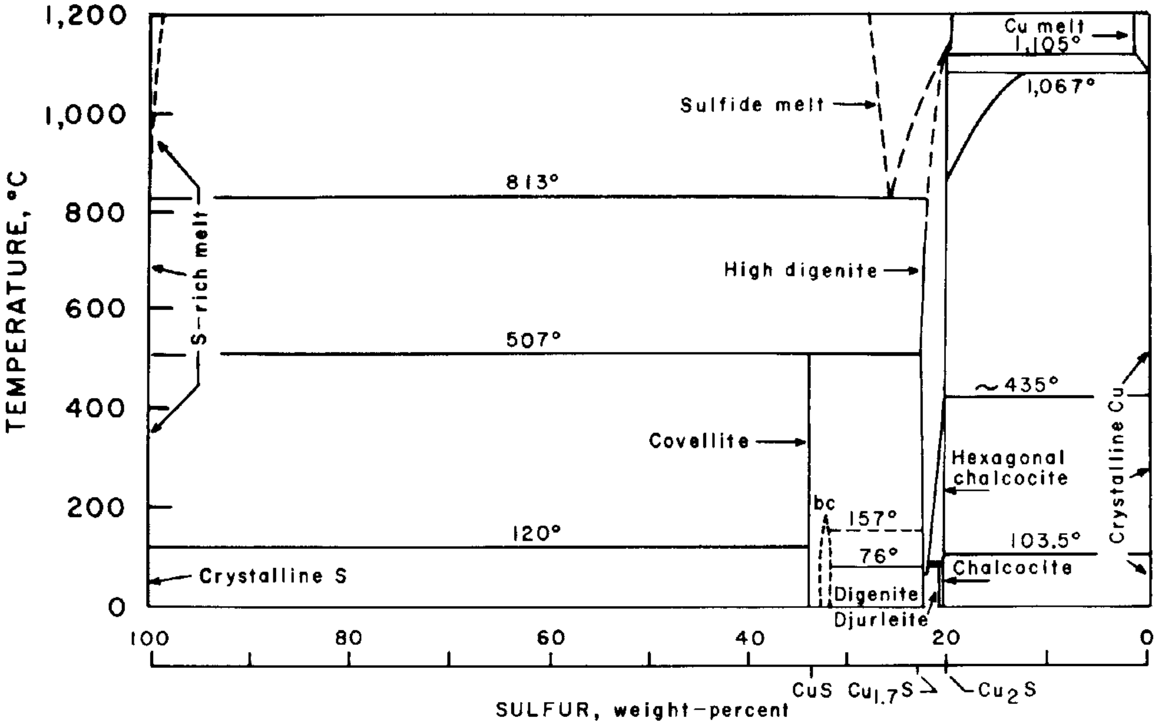

FIGURE 1. - Phase Diagram of Cu-S System. All phases shown coexist with vapor. Data obtained from reference 17.

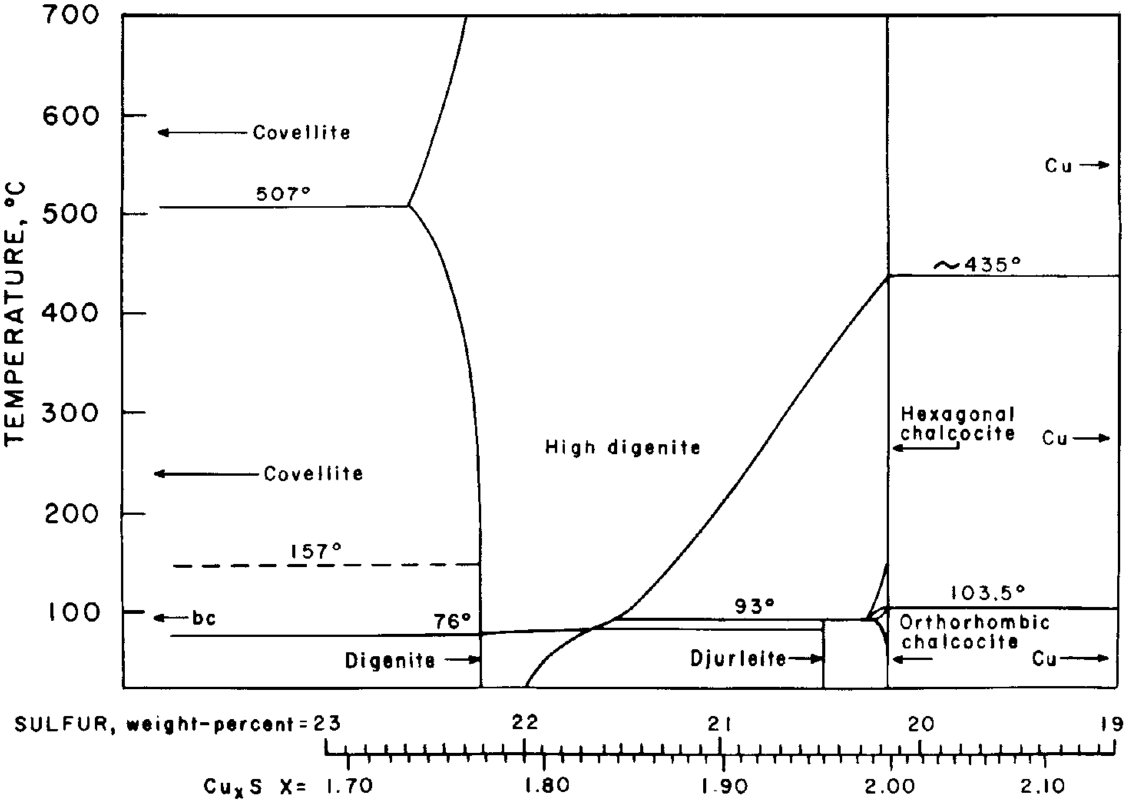

FIGURE 2. - Expanded Portion of Figure 1.

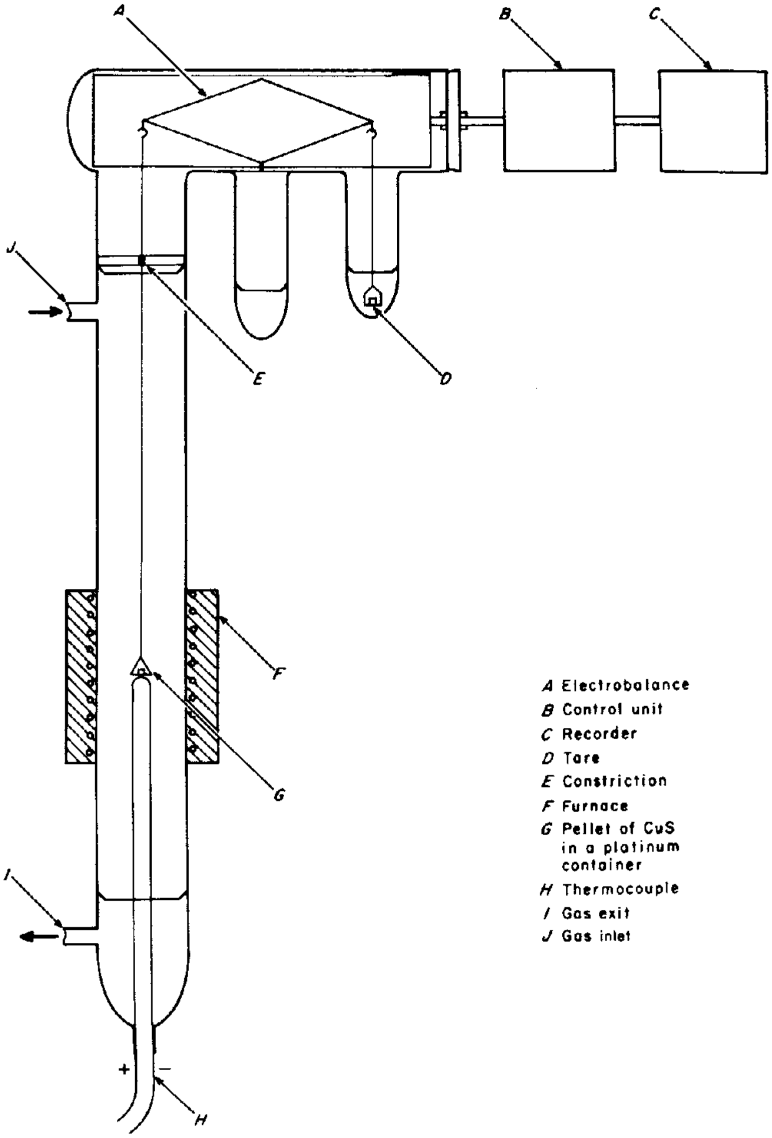

FIGURE 3. - Schematic Drawing of Thermal Gravimetric Analysis Equipment.

programer. A platinum versus platinum-10 percent rhodium thermocouple was placed in the center of the sample block and connected to the programer, recorder, and controller to program the linear heating rates and to record and control the block temperature. The programer gave a maximum of 2 percent deviation from linearity over any 100° C interval.

The TGA apparatus was equipped with a Cahn RG automatic electrobalance assembled such that the DTA control unit could be utilized with this apparatus. A small resistance furnace supplied by Tracor was used throughout this study. A platinum versus platinum-10 percent rhodium thermocouple made from 0.0001-inch-diameter reference-grade wire was enclosed in a small-diameter quartz protection tube and placed just under the platinum bucket, as shown in figure 3. This thermocouple was used for programing as well as recording and controlling the sample temperature. The sample holder was enclosed in a 19-mm-inside-diameter Vycor tube with a gas inlet near the top. The sample holder was connected to the weighing mechanism by a platinum wire. A ground-glass joint with gas outlet was connected to the bottom of the tube to facilitate the insertion of the thermocouple.

Materials and Reagents

Copper(II) sulfide powder was obtained from A. D. Mackay, Inc., and Matheson, Coleman and Bell. The manufacturer reported the following upper limits for impurities in the Matheson, Coleman and Bell reagent-grade CuS: alkali salts, 1.0 percent; chloride, 0.01 percent; and iron, 0.1 percent. A. D. Mackay, Inc., did not provide results of chemical analysis on their reagent-grade CuS. Table 1 contains the chemical analyses of the copper sulfides. According to these data, Matheson's product (hereafter referred to as covellite A) was 99 percent CuS, while the Mackay product (covellite B) was about 84 percent CuS. X-ray diffraction analysis showed the presence of $CuSO_4 \cdot 3H_2O$ as an impurity in covellite B. From the chemical analysis, it was estimated that covellite B contained a substantial amount of $CuSO_4 \cdot 3H_2O$.

TABLE 1. - Chemical analysis of copper(II) sulfide from two suppliers

CuS	H_2O lost at 105° C, percent	Before ignition analysis, percent				Loss on ignition at 1,000° C minus H_2O at 105° C, percent	After ignition analysis, percent		
		C	S	Cu	S[1]		Cu	Fe	S
Matheson (A).....	0.18	<0.10	33.1	65.8	1.9	18.20	81.2	<0.10	0.007
Mackay (B).....	3.28	.12	28.1	58.2	3.2	23.70	78.9	.88	.027

[1] Elemental.

Anhydrous copper(II) sulfate was supplied by Fisher Scientific Co. The chemical analysis supplied by the manufacturer is given in table 2. Copper(II) oxysulfate ($CuO \cdot CuSO_4$) was prepared by heating Fisher $CuSO_4$ powder at 650° C for 36 hours in air, with frequent rabbling. The X-ray diffraction analysis of the product showed $CuSO_4$ as a trace impurity. The high-purity nitrogen and filtered air used were passed through Drierite before entering the reaction chamber. Cylindrical pellets of different heights but of a constant radius (0.113 inch) were made from CuS powder. Pellets made at a pressure of greater than 150,000 psi had an average density of 94 percent of the theoretical density for CuS.

TABLE 2. - Chemical analysis of anhydrous copper(II) sulfate

Impurity	Weight, percent
Insoluble matter........	0.005
Chloride................	.003
Ferrous iron............	.04
Nitrate.................	.02
Alkalies and earths.....	.06
Heavy metals............	.001
Zinc....................	.0005

EXPERIMENTAL RESULTS AND DISCUSSION

Conversion of Covellite to Digenite

Figures 4 and 5 represent typical DTA thermograms obtained when samples of covellite B and A, respectively, weighing in the range of 10 to 30 mg, were heated in the powder-sample holder at 12° C/min from room temperature to 800° C in flowing N_2 at 150 cm^3/min. The presence of impurities in covellite B

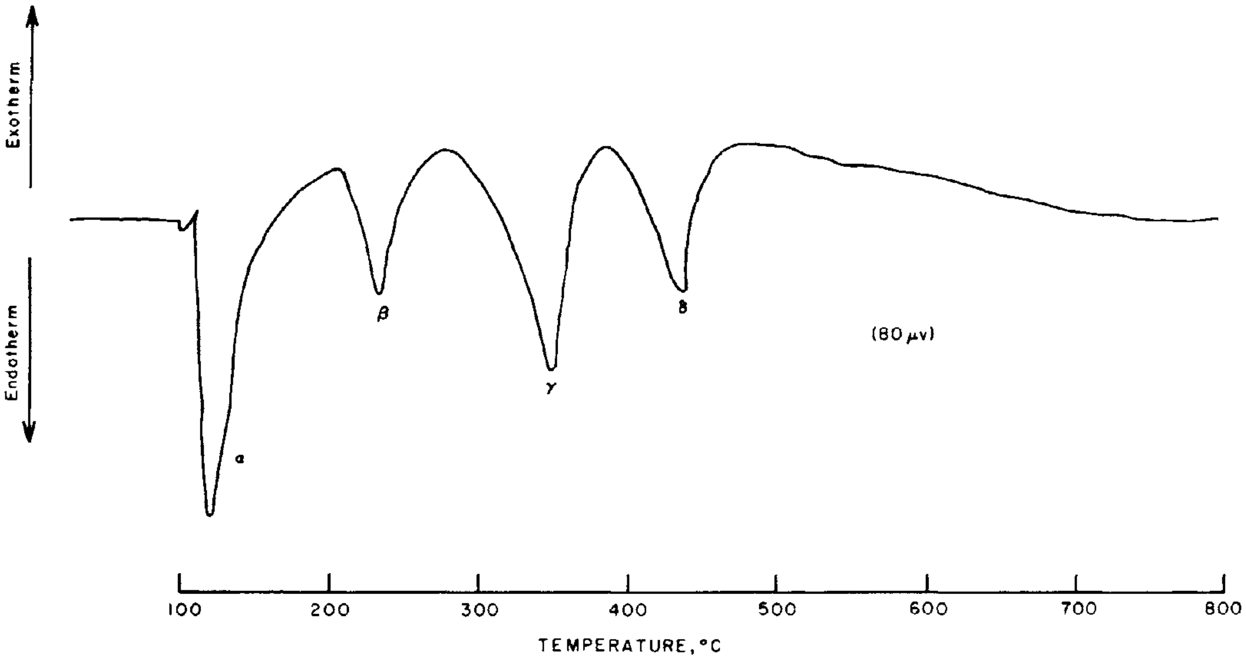

FIGURE 4. - Differential Thermal Analysis (DTA) of CuS (B) in N_2 at 150 cm^3/min.

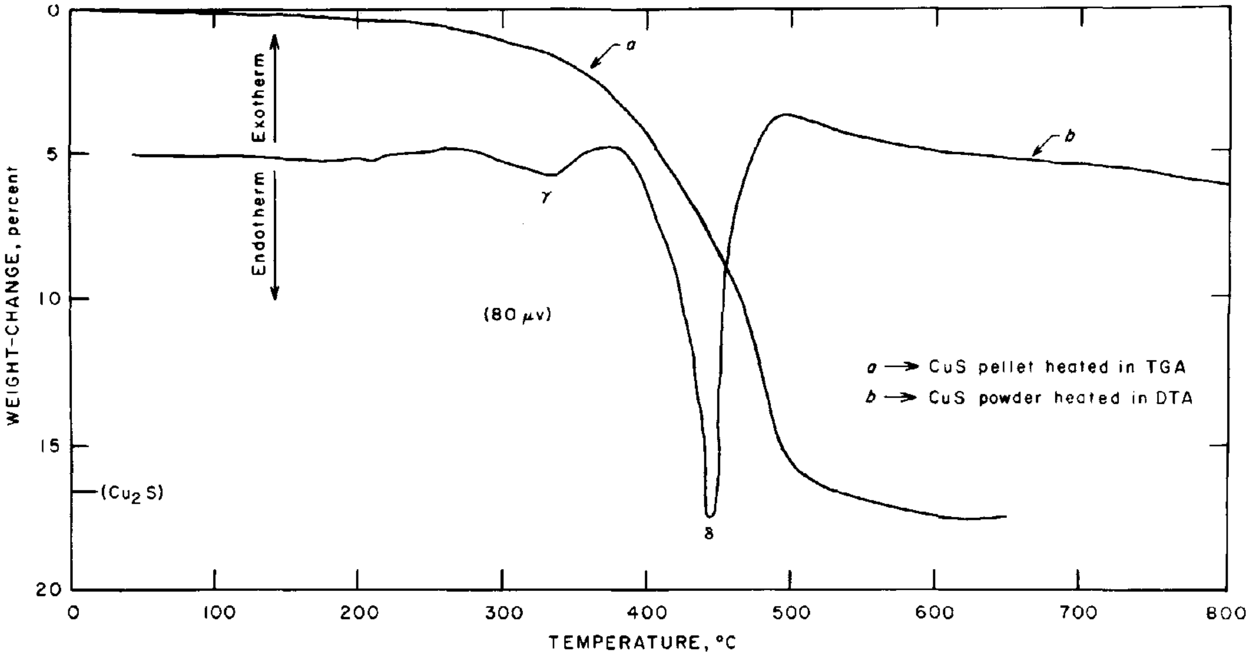

FIGURE 5. - Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) of CuS (A) in N_2 at 150 cm^3/min.

and the noticeable difference in the roasting thermograms (10) were found only after some experimental work with covellite B had been done. It is believed that the comparison of the results obtained with covellites A and B will be educational in revealing the effects of impurities on the results. For ease of reference, Greek letters are used to designate the various endotherms and exotherms. Various DTA runs were made from room temperature to various halt temperatures, and the product when cooled to room temperature was analyzed by X-ray diffraction. Typical results are summarized in table 3. Curve a in figure 5 represents the TGA thermogram obtained when a pellet made from covellite A was heated at 5° C/min from room temperature to 670° C in flowing N_2 at 190 cm^3/min. The weight loss obtained, as indicated on the thermogram, is very close to the theoretical value as predicted by the following equation:

$$2CuS \rightarrow Cu_2S \text{ (digenite)} + S. \qquad (1)$$

During the process, some sulfur deposited on the colder part of the reaction tube. Cazafura and Dobovisck (4) heated CuS in N_2 and obtained only one endotherm (420° to 470° C) in their DTA thermogram, similar to the peak in figure 5. With the aid of present results and the knowledge of the impurities in the starting material, the peaks due to Cu-S interactions in figures 4 and 5 can be reasonably interpreted as follows:

α endotherm: Dehydration of free absorbed moisture.

β endotherm: Dehydration of structural water attached to $CuSO_4 \cdot 3H_2O$.

γ endotherm: This may be due to the removal of the elemental sulfur and/or to the removal of the remaining structural water.

δ endotherm: Conversion of covellite to digenite.

TABLE 3. - X-ray identification of DTA product of CuS in nitrogen (150 cm^3/min)

Halt temperature, ° C	DTA product	Remarks
345.........	$Cu_{9-x}S_5$ (digenite)[1]	Held at 345° C for 2 hr.
490.........	$Cu_{9-x}S_5$, $Cu_{1.96}S$...	Held at 490° C for 2 hr.
600.........	$Cu_{9-x}S_5$, $Cu_{1.96}S$...	Heated to 600° C and cooled to room temperature.

[1] Digenite, a defect structure of chalcocite, occurs naturally as $Cu_{2-x}S$ with x ranging from 0.12 to 0.45 and an average analysis of $Cu_{1.8}S$.

Similar DTA experiments were performed at various halt temperatures in flowing air at 150 cm^3/min. The products were analyzed by X-ray diffraction and are summarized in table 4. Covellite is converted to digenite at lower temperature when heated in air. This can be explained by shifting reaction 1 to the right by rapid oxidation and removal of liberated sulfur as SO_2. The overall reaction can be represented by

$$2CuS + O_2 \rightarrow Cu_2S + SO_2. \qquad (2)$$

Ganguly and Mukherjee (5) have also shown that while covellite decomposes to a negligible extent at 340° to 360° C in the absence of air, its decomposition is appreciable in the presence of air.

TABLE 4. - X-ray identification of DTA product of CuS in dynamic air (150 cm^3/min) at lower temperatures

Halt temperature, ° C	DTA product	Remarks
190.......	CuS............	Held at 190° C for 30 min.
260.......	CuS, $Cu_{1.96}S$...	Held at 260° C for 30 min.
[1]300.......	CuS, $Cu_{1.96}S$...	Heated to 300° C and annealed in air.

[1] This test was run in static air.

There is considerably less agreement with regard to the products of reactions involving copper, sulfur, and oxygen and the temperatures at which they occur. To make any intelligent prediction, an understanding of the thermodynamics of the system is a necessary prerequisite. To assess the thermodynamic feasibility of the various reactions involved in the roasting of copper(II) sulfide, predominance-area diagrams of Cu-S-O systems were constructed at various temperatures from the data reported by Ingraham (7). Figures 6 and 7 represent the equilibrium-phase diagrams of Cu-S-O systems at 800° and 950° K, respectively. With the aid of figures 6 and 7, the most probable reactions taking place during the roasting of CuS in air could be generalized as follows:

$$2CuS = Cu_2S \text{ (digenite)} + S. \tag{1}$$

$$S + O_2 = SO_2. \tag{3}$$

$$Cu_2S + \tfrac{3}{2}O_2 = Cu_2O + SO_2. \tag{4}$$

$$Cu_2S + 4O_2 = 2CuSO_4. \tag{5}$$

$$SO_2 + \tfrac{1}{2}O_2 = SO_3 \tag{6}$$

$$Cu_2O + \tfrac{1}{2}O_2 + 2CuO. \tag{7}$$

$$Cu_2O + SO_3 + \tfrac{1}{2}O_2 = CuO \cdot CuSO_4. \tag{8}$$

$$Cu_2O + 2SO_3 + \tfrac{1}{2}O_2 = 2CuSO_4. \tag{9}$$

$$2CuSO_4 \rightleftarrows CuO \cdot CuSO_4 + SO_3. \tag{10}$$

$$CuO \cdot CuSO_4 \rightleftarrows 2CuO + SO_3 \tag{11}$$

The thermodynamic conditions of these reactions are such that the temperature and the partial pressure of SO_2 and O_2 will determine which of the solid phases are stable. If the roasting is carried out under nonequilibrium

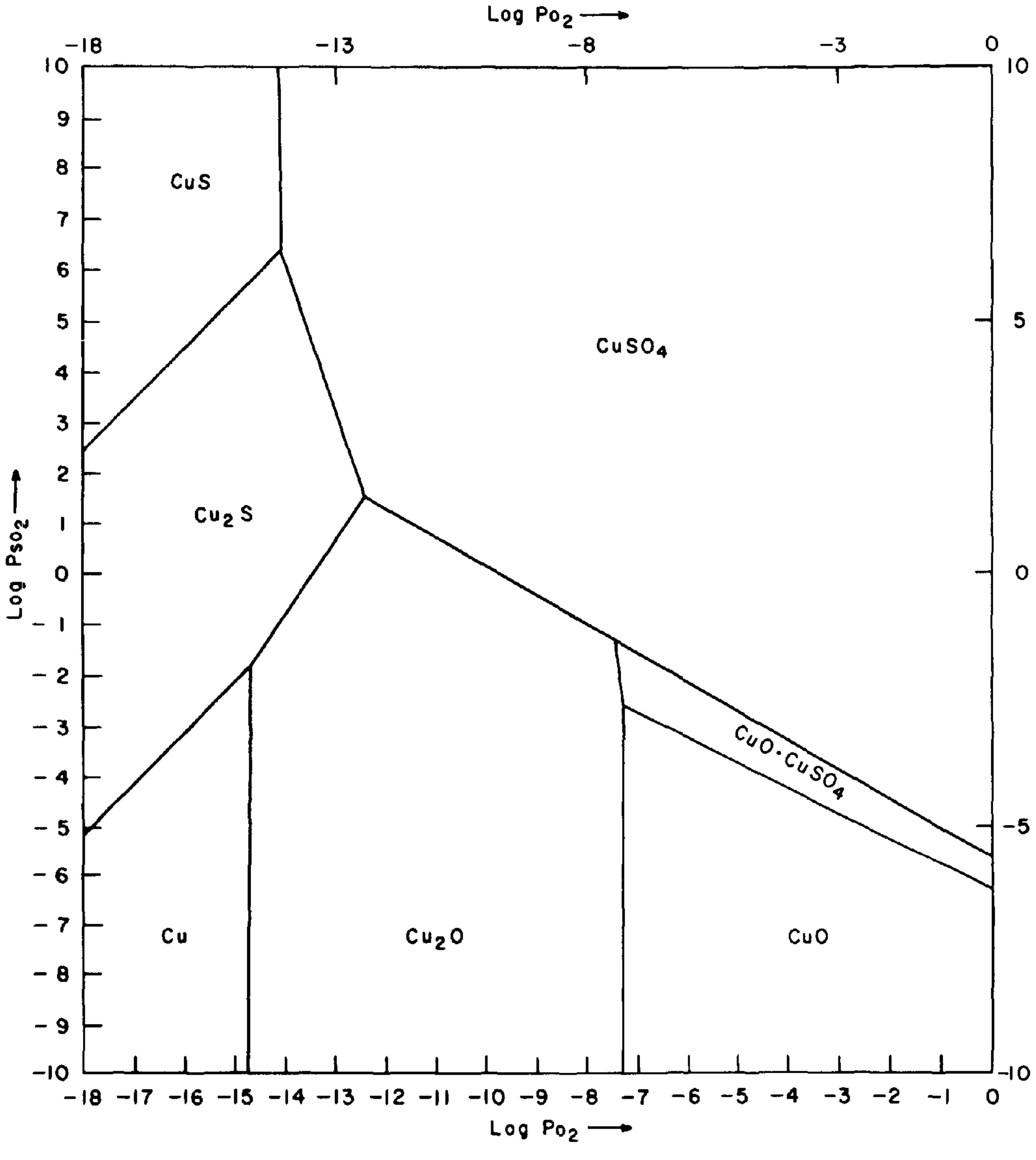

FIGURE 6. - Predominance-Area Diagram of Copper-Sulfur-Oxygen System at 800° K. Data obtained from reference 7.

conditions, which is usually the case, the kinetics and the mechanism of the reaction will play an important role in determining the various phases present in the roast product.

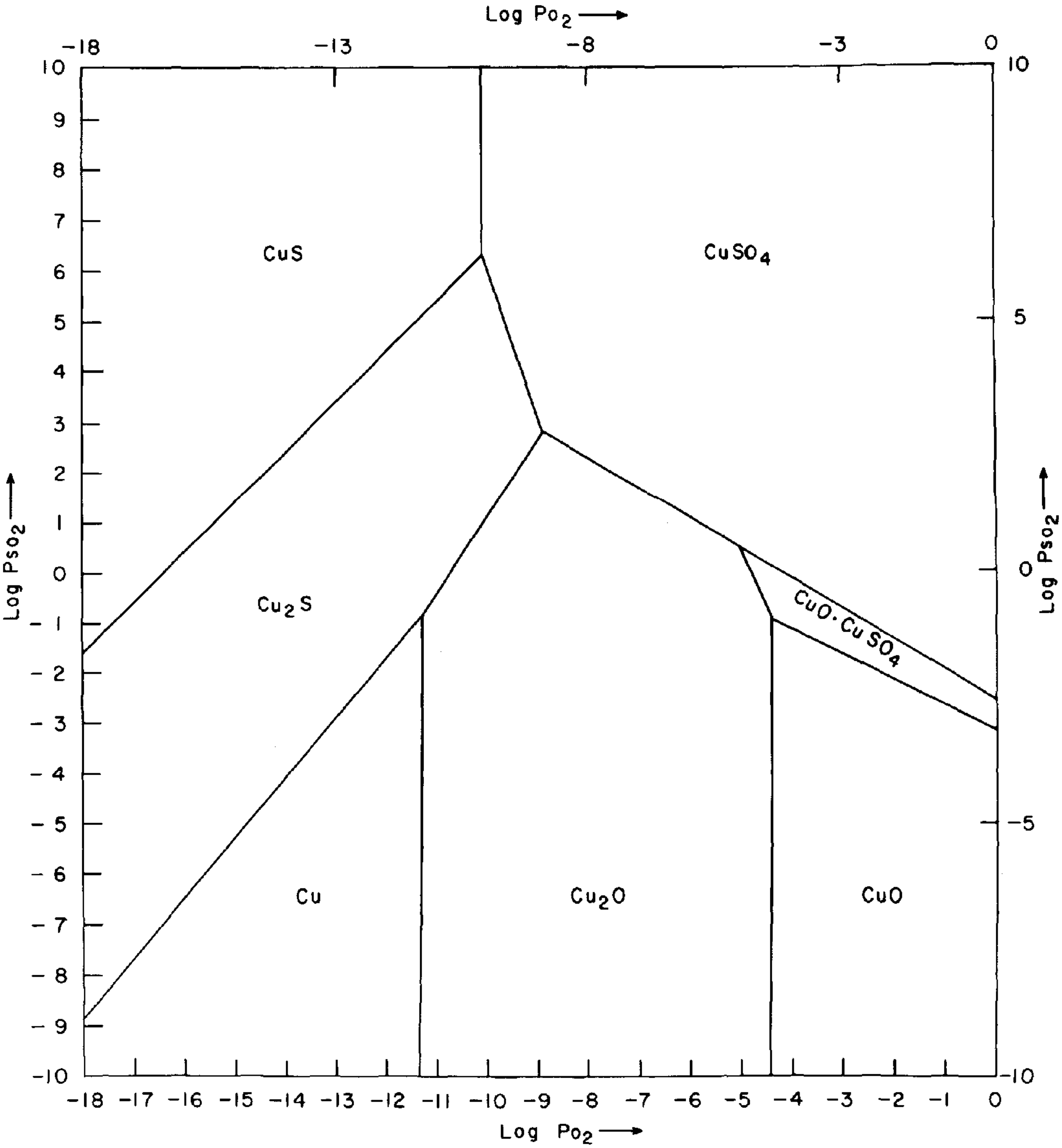

FIGURE 7. - Predominance-Area Diagram of Copper-Sulfur-Oxygen System at 950° K. Data obtained from reference 7.

Figure 8 represents a typical DTA thermogram obtained when covellite B was heated at 12° C/min in dynamic air flow at 150 cm^3/min in a powder-sample holder. Figure 9 represents a typical DTA thermogram obtained when covellite A, mixed with an equal amount of minus 100-mesh alumina, was heated at 12° C/min in a liquid-sample holder in which flowing air at 300 cm^3/min

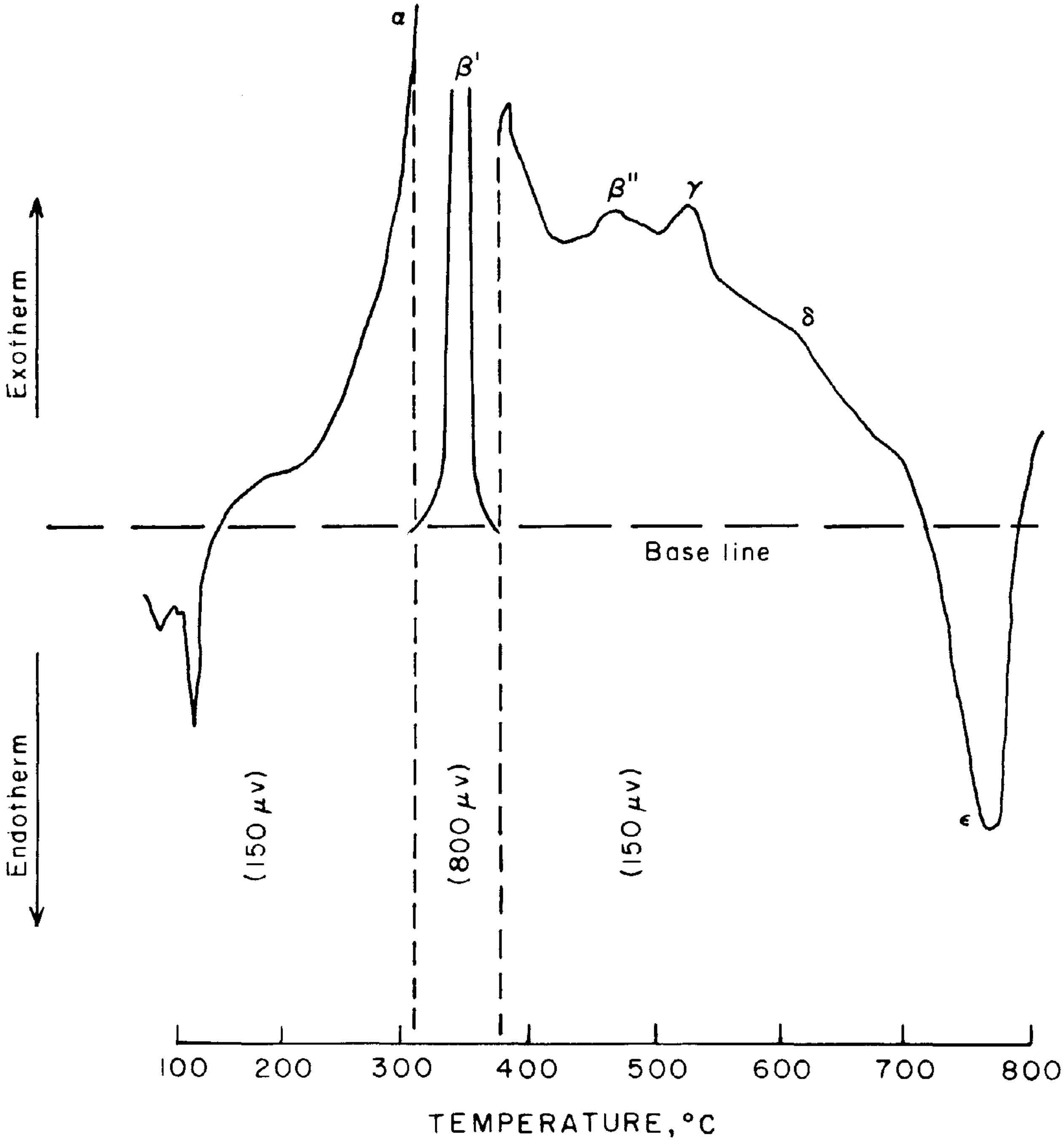

FIGURE 8. - Differential Thermal Analysis of CuS (B) in Dynamic Air.

surrounded the sample cups. In order to identify the reactions taking place at various peaks, covellite B was heated to various halt temperatures and the product was cooled to room temperature and analyzed by X-ray diffraction. These results are summarized in table 5.

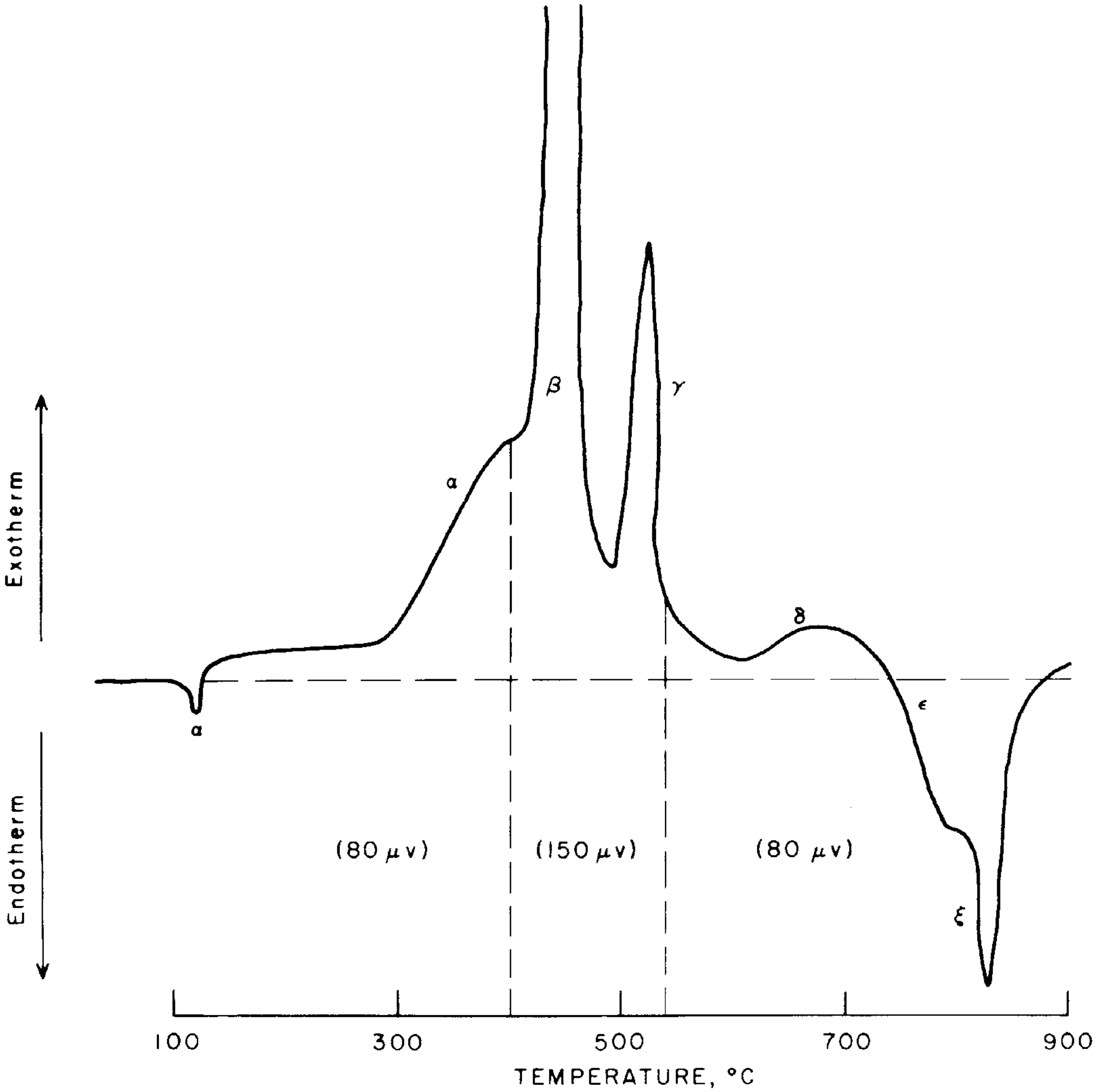

FIGURE 9. - Differential Thermal Analysis (DTA) of CuS (A) in Flowing Air.

TABLE 5. - X-ray identification of DTA product of CuS in flowing air (150 cm^3/min)

Halt temperature, ° C	DTA product	Remarks
265.............	$CuSO_4$, trace Cu_2O (sulfides)[1]	Held at 265° C for 2 hr.[2]
280.............	$CuSO_4$, trace Cu_2O, sulfides..	Held at 280° C for ½ hr.
335.............	$CuSO_4$, trace Cu_2O, sulfides..	Held at 335° C for ½ hr.
340.............	$CuSO_4$, trace Cu_2O, CuO.......	Held at 340° C for 2 hr.[2]
410.............	$CuSO_4$, Cu_2O[1].................	Held at 410° C for ½ hr.
460.............	$CuSO_4$, $CuO{\cdot}CuSO_4$.............	Held at 460° C for ½ hr.
490.............	$CuO{\cdot}CuSO_4$, $CuSO_4$ and Cu_2O[1]...	Held at 335° C for 2 hr[2] (1). Held at 490° C for 2 hr (2).
490.............	CuO, $CuO{\cdot}CuSO_4$, trace Cu_2O...	Heated in N_2 up to 490° C and held at this temperature for 1½ hr in air.[2]
510.............	$CuSO_4$, $CuO{\cdot}CuSO_4$.............	Held at 510° C for 10 min.
515.............	$CuSO_4$, $CuO{\cdot}CuSO_4$.............	Held at 515° C for ½ hr.
600.............	$CuO{\cdot}CuSO_4$, CuO, $CuSO_4$........	Sample immediately cooled to room temperature.[2]
610.............	$CuSO_4$, $CuO{\cdot}CuSO_4$, Cu_2O.......	Sample immediately cooled to room temperature.

[1] X-ray identification of this component was not conclusive.

[2] Sample was sandwiched between two porous alumina disks.

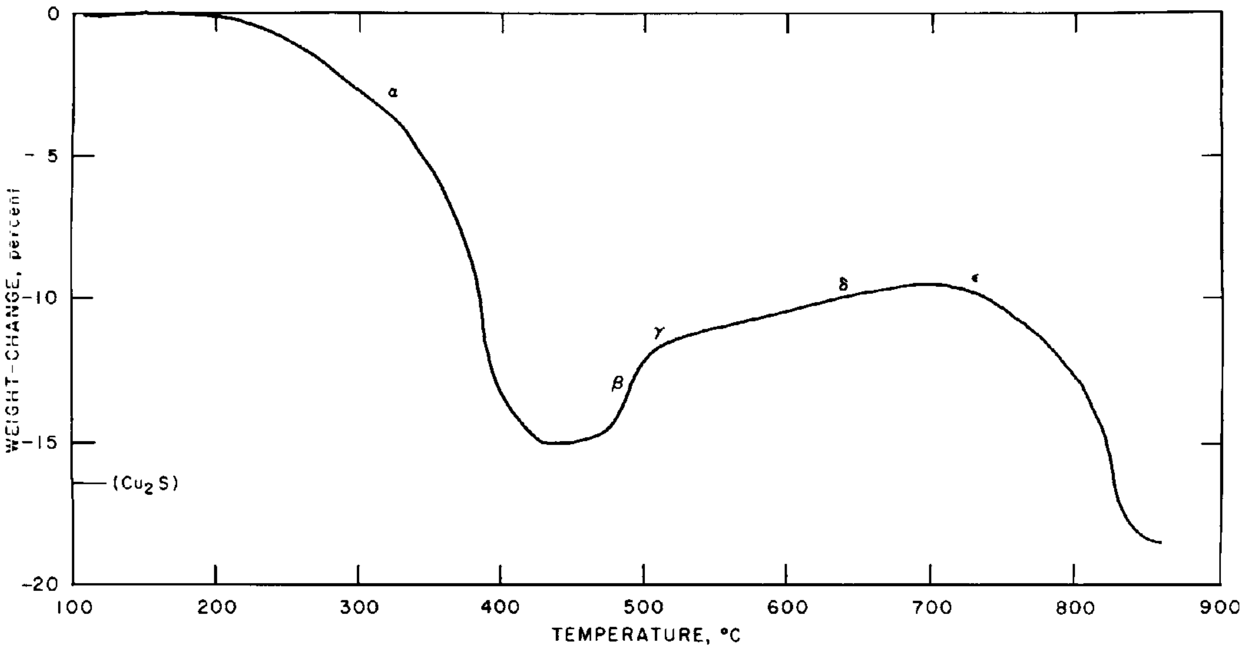

FIGURE 10. - Thermal Gravimetric Analysis (TGA) of CuS (A).

A typical TGA thermogram obtained when pellets made from covellite A were heated at 5° C/min from room temperature to 800° C in flowing air at 190 cm^3/min is shown in figure 10. Here the α portion of the curve represents the conversion of CuS to Cu_2S. The increase in weight in β section is due mainly to the formation of sulfates. Various other TGA runs were made at different halt temperatures under different conditions. The polished cross sections of the heated pellets were examined under microscope, and the products were analyzed by means of X-ray diffraction. Table 6 summarizes the X-ray diffraction analyses of these runs. The X-ray diffraction analyses did not show the presence of $CuO \cdot CuSO_4$ at lower temperatures because of the poor crystallinity of $CuO \cdot CuSO_4$.

TABLE 6. - X-ray identification of TGA product of CuS (A) pellet in flowing air (190 cm^3/min)

Halt temperature, ° C	TGA product	Remarks
300	$CuSO_4$, Cu_2S, Cu_2O	Held at 300° C for 1 hr.
305	$CuSO_4$, Cu_2S, Cu_2O	Sample immediately cooled to room temperature.
450	$CuSO_4$, Cu_2O, Cu_2S, $CuO \cdot CuSO_4$, CuO.	Heating rate was erratic.
460	$CuSO_4$, Cu_2O, CuO	Held at 285° C for ½ hr, then heated to 460° C and held for 45 min.
900	CuO	Sample immediately cooled to room temperature.
350	$CuSO_4$, $Cu_{1.8}S$, Cu_2O	Heated in N_2 up to 350° C (1). Air replaced N_2 and heating continued at 350° C until no apparent increase in weight is observed (2).
350	$Cu_{1.96}S$	Heated in N_2 up to 350° C (1). Air replaced N_2 and heating continued until CuS → Cu_2S appeared to be complete (2).

In another set of experiments during the kinetic studies, CuS pellets were heated in N_2 to 350° C, and air then replaced the N_2. The heating was continued until the reaction appeared to have ceased, as indicated by the constant weight in section <u>a</u> of the TGA thermogram in figure 11. A very thin skin of $CuSO_4$ was formed on the outermost surface of the pellet. The inner part of this skin was always orange-colored and was identified as $CuO \cdot CuSO_4$. When the temperature was increased to 485° C, a further increase in weight took place as indicated by section <u>b</u> in figure 11. The microscopic examination of the pellet showed a comparatively larger amount of $CuO \cdot CuSO_4$ under the $CuSO_4$ skin. This new $CuO \cdot CuSO_4$ forms inside the outer sulfate layer. It appears that as the chemical potential of SO_3 decreases within the pellet and

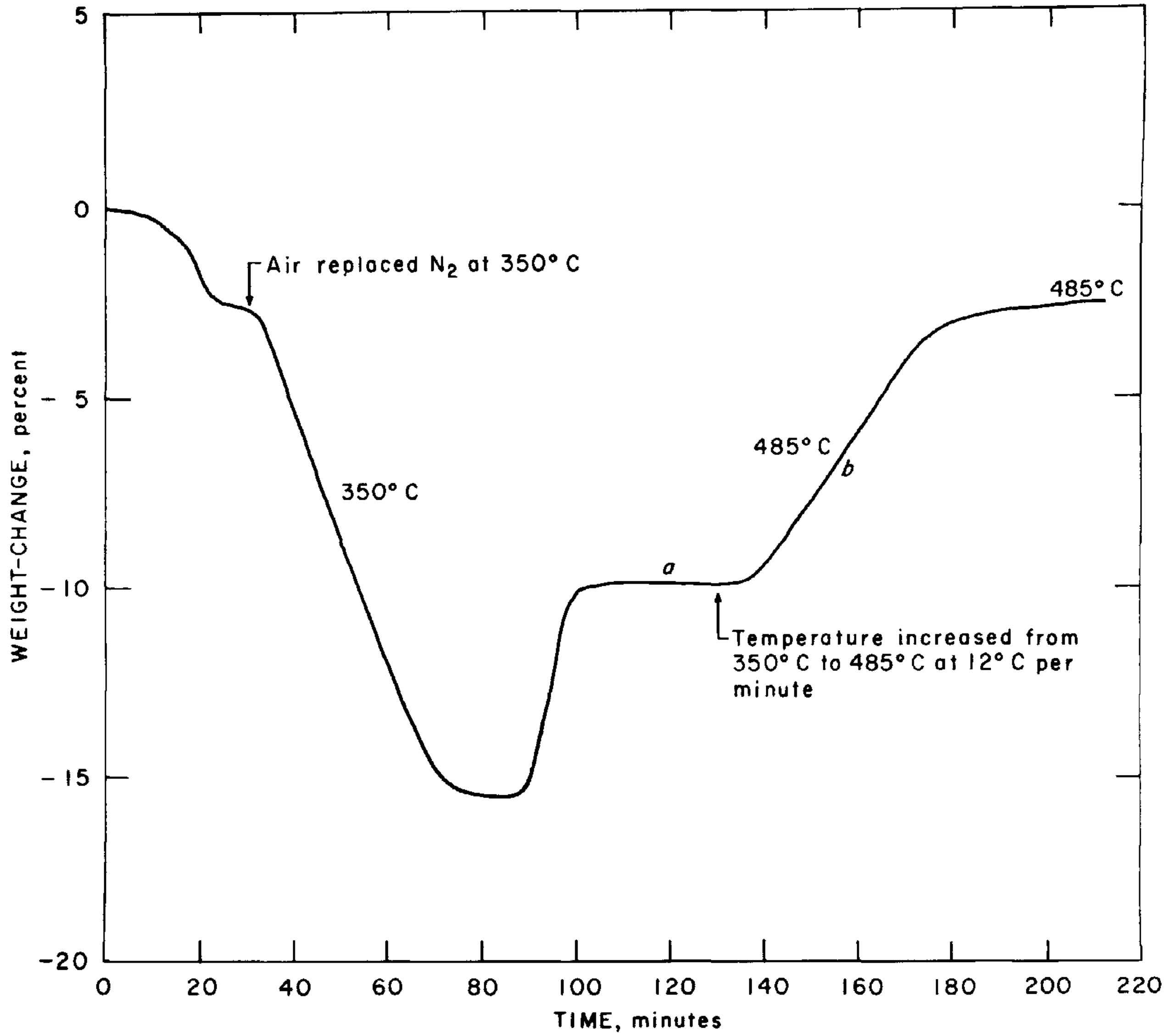

FIGURE 11. - TGA Thermogram Showing Formation of Copper(II) Sulfate and Copper(II) Oxysulfate.

as the temperature rises, $CuO \cdot CuSO_4$ becomes more stable than $CuSO_4$ and the amount of $CuO \cdot CuSO_4$ increases within the $CuSO_4$ skin. Similarly, when the chemical potential of SO_3 is further diminished within the pellet, Cu_2O formed initially will be converted to CuO under the oxysulfate layer. The presence of CuO at 450° to 460° C, which is well below the decomposition temperature of $CuO \cdot CuSO_4$, has been indicated by X-ray diffraction analyses, the results of which are shown in table 6. From these results we conclude that $CuSO_4$ is formed from CuS by the following sequence of steps:

$$CuS \rightarrow Cu_{1.8}S \rightarrow Cu_2O \rightarrow CuO \rightarrow CuO \cdot CuSO_4 \rightarrow CuSO_4. \qquad (12)$$

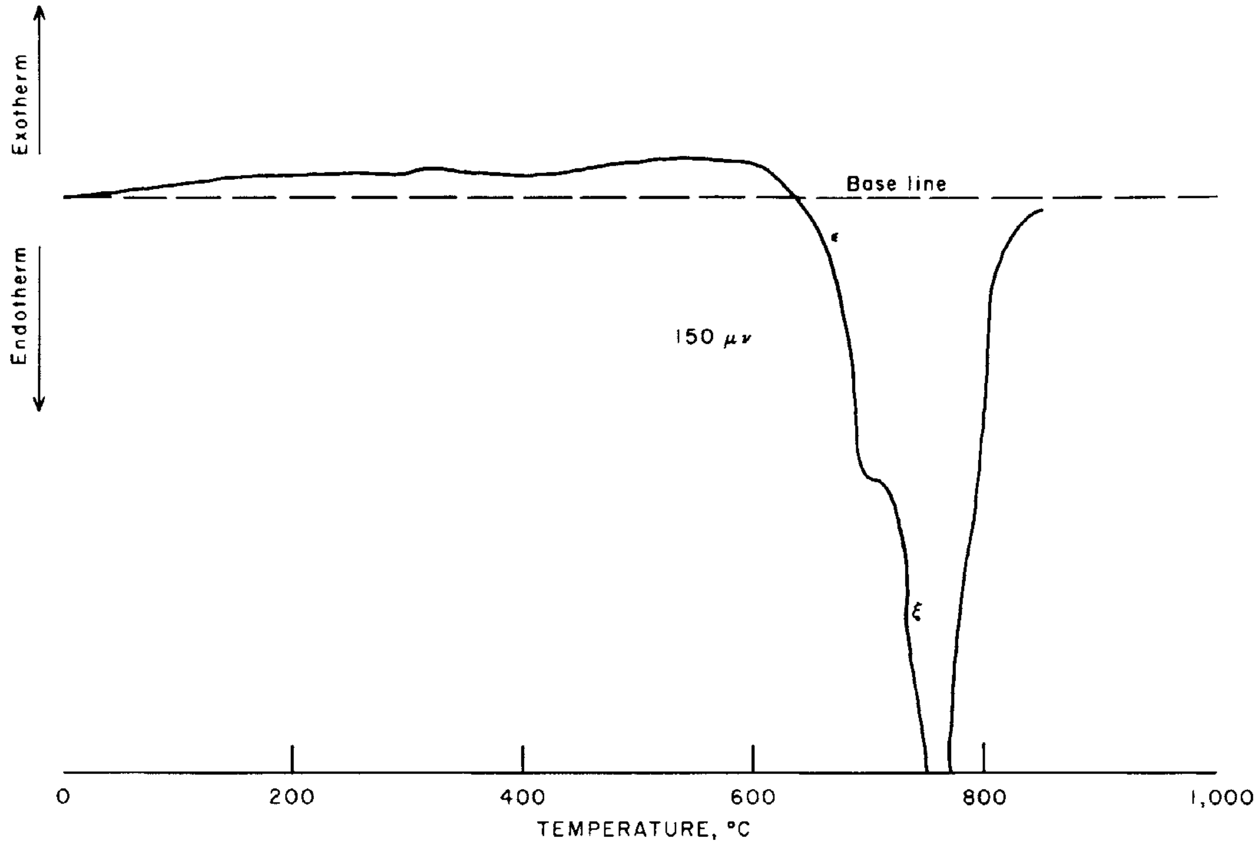

FIGURE 12. - Differential Thermal Analysis of Anhydrous $CuSO_4$ in Dynamic Air at 150 cm^3/min.

Figure 12 shows the DTA thermogram of $CuSO_4$ powder heated at 12° C/min in a powder-sample holder in dynamic air flow at 150 cm^3/min. This figure is comparable with sections ϵ and δ in figure 8. Figure 12 clearly indicates that at about 600° C, $CuSO_4$ decomposes to $CuO \cdot CuSO_4$ and that at about 670° C, $CuO \cdot CuSO_4$ decomposes to CuO (equations 11 and 12). Furthermore, freshly formed $CuSO_4$ on the CuS pellet starts decomposing at about 490° C.

The various peaks in figures 8 and 9 and the different sections in figure 10 can now be explained as follows with increase or decrease of weight shown by the notation ($+\Delta w$) or ($-\Delta w$), respectively:

α endotherm: The dehydration of moisture ($-\Delta w$).

α exotherm: This transformation can be represented by the following equation:

$$1.8\ CuS + 0.8\ O_2 \rightarrow Cu_{1.8}S + 0.8\ SO_2\ (-\Delta w). \qquad (13)$$

β exotherm: This represents the formation of $CuSO_4$ through $CuO \cdot CuSO_4$ as indicated by equation 12 ($+\Delta w$).

β' exotherm: Represents primarily the formation of $CuO \cdot CuSO_4$ as

$$Cu_{1.8}S \rightarrow Cu_2O \rightarrow CuO \rightarrow CuO \cdot CuSO_4 \ (+\Delta w). \tag{14}$$

γ exotherm: This probably represents the formation of Cu_2O and $CuO \cdot CuSO_4$, as indicated by equations 4 and 14. Depending upon the extent of formation of $CuO \cdot CuSO_4$ and Cu_2O, the change in weight would be positive or negative ($\pm\Delta w$).

δ exotherm: This represents primarily the formation of CuO as

$$Cu_2S \rightarrow Cu_2O \rightarrow CuO \ (+\Delta w). \tag{15}$$

ϵ endotherm: This represents the decomposition of $CuSO_4$ (equation 10). The partial decomposition of $CuSO_4$ also takes place in γ and δ regions ($-\Delta w$).

ζ endotherm: This represents the decomposition of $CuO \cdot CuSO_4$ as indicated by equation 11 ($-\Delta w$).

Reaction Sequence in Roasting

Figure 13 represents the individual steps leading to the formation of CuO from CuS, as deduced from the present results and from some of the reported mechanism for the formation of some Cu-S-O compounds (6).

The following reactions are probably taking place at various interfaces:

$$0.8\ Cu^+ + 0.8\ e^- + CuS \rightarrow Cu_{1.8}S \text{ (at interface a)}, \tag{16}$$

and

$$Cu_{1.8}S \rightarrow 1.8\ Cu^+ + 1.8\ e^- + S \quad \text{(at interface b)}. \tag{17}$$

$$S + O_2 \rightarrow SO_2. \tag{18}$$

When covellite is present, Cu^+ and e^- diffuse through the $Cu_{1.8}S$ layer and react with CuS at interface a, according to equation 16; and when covellite is consumed, the following reaction takes place at b:

$$2\ Cu^+ + 2\ e^- + 0.5\ O_2 \rightarrow Cu_2O. \tag{19}$$

When digenite is present,

$$Cu^+ + e^- + \tfrac{1}{2}\ O_2 \rightarrow CuO \text{ (at interface c)}. \tag{20}$$

When digenite is consumed,

$$Cu_2O \rightarrow CuO + Cu^+ + e^-. \tag{21}$$

$$SO_2 + \tfrac{1}{2}\ O_2 \rightarrow SO_3. \tag{22}$$

$$Cu^+ + e^- \text{ (diffuse through CuO)} + \tfrac{1}{2}\ O_2 \rightarrow CuO \text{ (at interface d)}, \tag{23}$$

$$2CuO + SO_3 \rightarrow CuO \cdot CuSO_4, \tag{24}$$

and

$$CuO \cdot CuSO_4 + SO_3 \rightarrow 2CuSO_4 \text{ (at interface e)}. \tag{25}$$

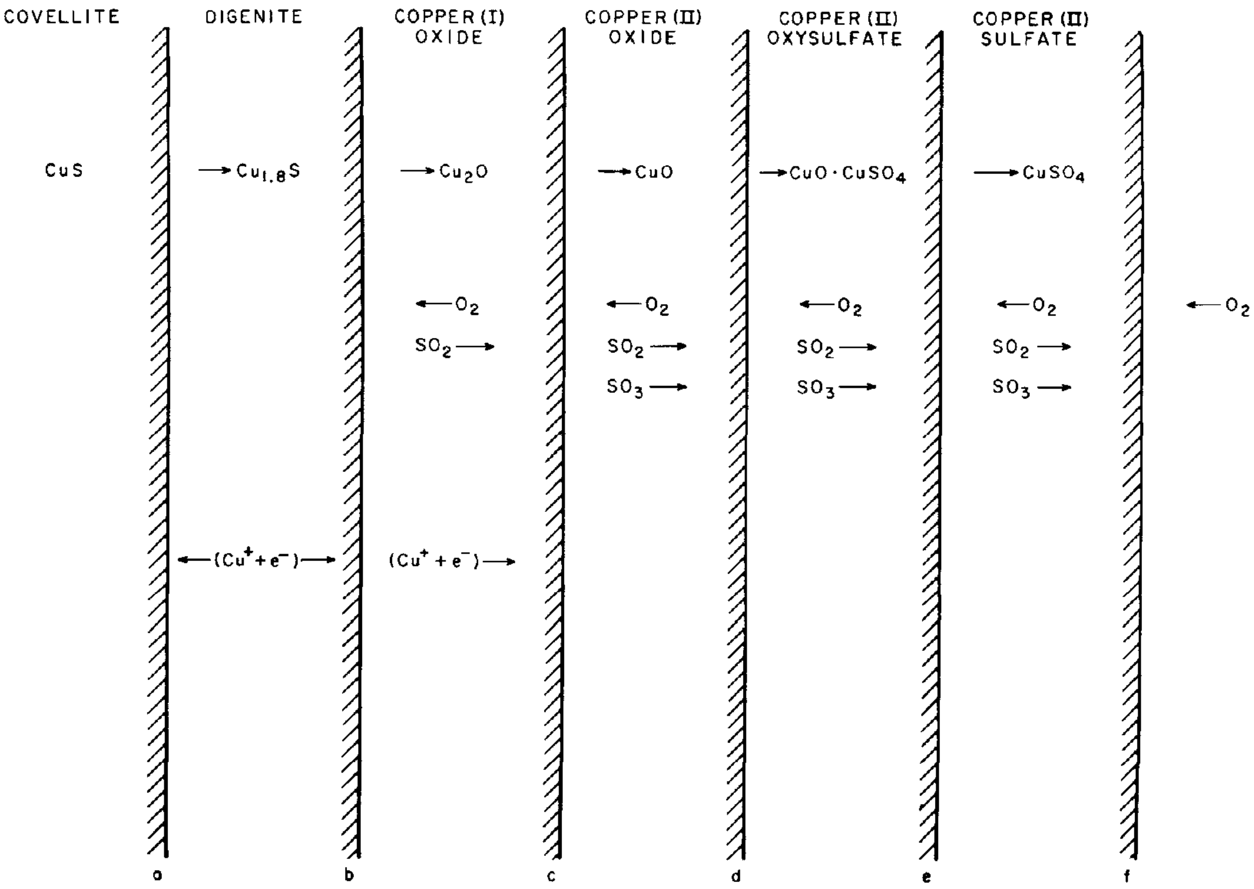

FIGURE 13. - Schematic Representation of Sequence of Reactions in CuS Roasting.

At higher temperatures, first $CuSO_4$ and then $CuO{\cdot}CuSO_4$ decompose at interface f, as indicated by equations 10 and 11.

Wadsworth and coworkers (19) and Hocking and Alcock (6) have studied the kinetics and mechanism of sulfate formation on copper(I) oxide and have reported the formation of the product layers in the following order:

$$Cu_2O \rightarrow CuO \rightarrow CuO{\cdot}CuSO_4 \rightarrow CuSO_4. \tag{26}$$

This sequence is in agreement with the present results wherein CuS was oxidized to CuO.

On the basis of the products observed on quenching, Wadsworth and coworkers (19) and McCabe and Morgan (14) have reported that when Cu_2S is roasted, $CuO{\cdot}CuSO_4$ arises from the thermal decomposition of $CuSO_4$ and the CuO formed arises from the thermal decomposition of sulfates. Accordingly, they suggested the formation of product layers in this order:

$$Cu_2S \rightarrow Cu_{1.8}S \rightarrow Cu_2O \rightarrow CuSO_4 \rightarrow CuO{\cdot}CuSO_4 \rightarrow CuO. \tag{27}$$

Their proposal is difficult to reconcile with the thermodynamics of the Cu-S-O system and with the present experimental results. It has been conclusively shown here that $CuO \cdot CuSO_4$ forms under a skin of $CuSO_4$. Ingraham and Marier (8) have shown conclusively that when $CuSO_4$ decomposes, the interface $CuSO_4/CuO \cdot CuSO_4$ migrates into the pellet at a uniform rate at constant temperature. Thus $CuO \cdot CuSO_4$, if formed only by thermal decomposition of $CuSO_4$, should form outside the $CuSO_4$ layer. The sequence of chemical reactions taking place during the roasting of CuS in air, as suggested in this paper, is in general agreement with the thermodynamic probability that can be deduced from figures 6 and 7.

SUMMARY

When covellite (CuS) obtained from different sources was heated in N_2 and air, various endotherms and exotherms on DTA thermograms and different sections of TGA thermograms were identified with various reactions taking place in the Cu-S-O systems. The order of the principal chemical reactions taking place when CuS is heated in flowing air from room temperature to 800° C was established, and a mechanism for the various reactions taking place during the roasting of CuS pellets was suggested. It has been conclusively established that $CuO \cdot CuSO_4$ forms prior to the formation of $CuSO_4$ during the roasting of CuS.

REFERENCES[5]

1. Ashcroft, E. A. Sulfate Roasting of Copper Ores and Economic Recovery of Electrolytic Copper From Chloride Solution. Trans. Electrochem. Soc., v. 23, 1933, pp. 23-44.

2. Buerger, N. W. The Chalcocite Problem. Econ. Geol., v. 36, 1941, pp. 19-44.

3. Buerger, M. J., and B. J. Wuensch. Distribution of Atoms in High Chalcocite, Cu_2S. Science, v. 141, 1963, pp. 276-277.

4. Cazafura, Krsto, and Bogo Dobovisck. Kemizem prazenja bakrovih in zelezovih sulfidov. (Chemistry of Roasting Copper and Iron Sulfides.) Rudarsko-Met Zbornik, v. 4, 1956, pp. 193-210.

5. Ganguly, N. D., and S. K. Mukherjee. Studies on the Mechanism and Kinetics of Oxidation of Copper Sulfide - 1. Oxidation of Copper Sulfide in a Fixed Bed. Chem. Eng. Sci., v. 22, 1967, pp. 1091-1105.

6. Hocking, M. G., and C. B. Alcock. The Kinetics and Mechanism of Formation of Sulfates on Cuprous Oxide. Trans. AIME, v. 236, 1966, pp. 635-642.

7. Ingraham, T. R. Thermodynamics of Thermal Decomposition of Cupric Sulfate and Cupric Oxysulfate. Trans. AIME, v. 233, 1965, pp. 359-363.

8. Ingraham, T. R., and P. Marier. Kinetics of the Thermal Decomposition of Cupric Sulfate and Cupric Oxysulfate. Trans. AIME, v. 233, 1965, pp. 363-367.

9. Jensen, M. L. Diffusion in Minerals. Ph.D. Thesis, Dept. of Geology, Massachusetts Inst. of Tech., 1951, 103 pp.

10. Khalafalla, S. E., and I. D. Shah. Oxidative Roasting of Covellite With Minimal Retardation From the $CuO \cdot CuSO_4$ Film. Metallurgical Trans., v. 1, 1970, pp. 2155-2156.

11. Kulikova, L. A., T. Yu Gol'dshtein, M. P. Asanova, and A. I. Okunev. (Experimental Study of Oxidation and Decomposition of Covellite.) Tr. Ural Skogo Nauchn-Issled i Proektn. Inst. Modn. Prom., v. 6, pp. 217-226; Chem. Abs., v. 60, 1964, p. 15597g.

12. Kullerud, G. The Cu_2S-CuS System. Carnegie Institution of Washington Yearbook, v. 55, 1955-56, pp. 180-181.

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[5] Titles enclosed in parentheses are translations from the language in which the item was originally published.

13. Martinez, E., and M. L. Hollander. Reactions of Metal Oxides and Sulfur Studied by Thermoanalysis: Copper Oxides. Trans. AIME, v. 229, 1964, pp. 300-306.

14. McCabe, C. L., and J. A. Morgan. Mechanism of Sulfate Formation During Roasting of Cuprous Sulfide. J. Metals, v. 8, 1956, p. 800A.

15. Peretti, E. A. A New Method for Studying the Mechanism of Roasting Reactions. Disc. Faraday Soc., v. 4, 1948, pp. 174-179.

16. Ray, Hans. Defect Equilibria in Cubic High Temperature Copper Sulfide (Digenite). J. Phys. Chem. Solids (Pergamon Press), v. 28, 1967, pp. 903-916.

17. Roseboom, E. H., Jr. An Investigation of the System Cu-S and Some Natural Copper Sulfides Between 25° and 700° C. Econ. Geol., v. 61, 1966, pp. 641-672.

18. Thornhill, P. G., and L. M. Pidgeon. A Microscopic Study of Sulfide Roasting. J. Metals, v. 9, 1957, pp. 989-995.

19. Wadsworth, M. E., K. L. Leiter, W. H. Porter, and J. R. Lewis. Sulfating of Cuprous Sulfide and Cuprous Oxide. Trans. AIME, v. 218, 1960, pp. 519-525.