A NEW METHOD FOR STUDYING THE MECHANISM OF ROASTING REACTIONS

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Received 20th May, 1948

In the extraction of several of the important non-ferrous metals from their ores, roasting is practised as an intermediate operation, e.g., in the production of copper, lead, zinc and mercury. If we let M represent a divalent metal, the most probable reactions taking place can be generalised as follows:

$$MS_2(s) \rightleftharpoons MS(s) + \tfrac{1}{2}S_2(g) \tag{1}$$

$$\tfrac{1}{2}S_2(g) + O_2(g) = SO_2(g) \tag{2}$$

$$MS(s) + 1\tfrac{1}{2}O_2(g) = MO(s) + SO_2(g) \tag{3}$$

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \tag{4}$$

$$MO(s) + SO_3(g) \rightleftharpoons MSO_4(s) \tag{5}$$

$$MSO_4(s) \rightleftharpoons MO\,.\,ySO_3(s) + (1 - y)\,SO_3(g) \tag{6}$$

$$MO\,.\,ySO_3(s) \rightleftharpoons MO(s) + ySO_3(g) \tag{7}$$

At the temperatures commonly used for roasting, reactions (2) and (3) for the metals mentioned possess such large free-energy changes that the SO_2/O_2 equilibrium ratios need not be considered. For example, by using FeS in reaction (3) a thermodynamic calculation results in the following (nomenclature of Lewis and Randall [1]):

$$\Delta F^\circ = -113{,}000 + 9{\cdot}5T\log T - 1{\cdot}965 \times 10^{-3}T^2 - 6{\cdot}7T \tag{8}$$

and at 1100° K. the equilibrium constant, K, is $1{\cdot}12 \times 10^{18}$. Kelley's [2] standard free-energy equation for reaction (2) yields a K of $2{\cdot}76 \times 10^{13}$ at 1100° K. This means, then, that at these temperatures for eqn. (2) and (3) the oxide and sulphur dioxide will be the stable phases in the presence of even small amounts of oxygen. On the other hand, the thermodynamics of (4), (5), (6) and (7) are such that the temperature and the partial pressure of sulphur trioxide determine which of the solid phases are stable. The respective equilibrium constants are

$$K_4 = \frac{f_{SO_3}}{f_{SO_2} \times \sqrt{f_{O_2}}} \tag{9}$$

$$K_5 = \frac{1}{f_{SO_3}} \tag{10}$$

$$K_6 = f_{SO_3}^{(1-y)} \tag{11}$$

$$K_7 = f_{SO_3}^{y} \tag{12}$$

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[1] Lewis and Randall, *Thermodynamics* (McGraw-Hill Book Company, 1923).
[2] Kelley, *U.S. Bur. Mines*, Bull. 406, 1937, 13.

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Applying the phase rule [3] we find that a system in which SO_2, O_2, SO_3, MO, MSO_4 and MO . ySO_3 are in equilibrium is nonvariant, and this will be at the point where

$$f_{SO_3} = K_4 . f_{SO_2} . \sqrt{f_{O_2}} = \frac{1}{K_5} = K_6^{\left(\frac{1}{1-y}\right)} = K_7^{\frac{1}{y}} \quad . \quad . \quad (13)$$

For the coexistence of gas and (*a*) MSO_4 and MO, (*b*) MSO_4 and MO . ySO_3, (*c*) MO and MO . ySO_3, the systems are univariant.

There are two degrees of freedom for the stability of gas and any single solid phase. The solid will be:

(*a*) MSO_4, if $f_{SO_3} > \frac{1}{K_5}$ and $> K_6^{\left(\frac{1}{1-y}\right)}$,

(*b*) MO, if $f_{SO_3} < \frac{1}{K_5}$ and $< K_7^{\frac{1}{y}}$,

and (*c*) MO . ySO_3, if $f_{SO_3} < K_6^{\left(\frac{1}{1-y}\right)}$ and $> K_7^{\frac{1}{y}}$.

If the roasting operation is carried out under non-equilibrium or changing conditions, which is probably the actual case most of the time, the solid phases present in an industrial calcine may be determined largely by the rate of the various reactions and the mechanisms by which they proceed. Of the seven general reactions listed, all but two are of the heterogeneous solid-gas type for which the mechanism is difficult to determine by the methods usually used for homogeneous reactions because diffusion of gases to and from the reaction interface is very often the rate-controlling factor.

Roasting experiments are usually performed by heating an extremely large number of small particles in a stream of gas. As a result it is almost impossible to analyse an individual piece to determine the sequence of phase formation. The employment of a single lump of mineral is discouraging because of the difficulty of cutting many specimens to a given size and shape and because of the tendency to cracking. It is believed that the technique to be described overcomes these objections.

Experimental

As an example, let us consider the roasting of CuS. Relatively pure specimens of the mineral can be obtained or an artificially prepared compound can be used; we chose the latter, Fisher's C.P. cupric sulphide, which was all minus 100 mesh. Forty-seven grams of the sulphide were placed in a steel mould and made into a cylindrical briquette under a pressure of 3500 lb. $in.^{-2}$. The compresses measured 2·86 cm. diam. by 2·86 cm. long and had sufficient strength to be handled without breaking. From three to five of the briquettes were placed in an electrically-heated muffle furnace whose temperature was automatically controlled to within ± 5° C. of the desired value. The specimens were successively removed from the furnace at varying time-intervals and allowed to cool under a graphite crucible.

The course of the reaction was followed by cutting the reacted cylinders in half, transversely, and measuring the diameters of the visible phase boundaries. In less than a minute after the cylinders were placed in the furnace, sulphur gas was liberated, which burned at the surface with its characteristic flame. As long as these flames were visible only two solid phases, CuS and Cu_2S, existed in the briquette in the relative positions as shown by Fig. 1. The interface between the two solids is, as Langmuir [4] has shown, the scene of the primary reaction, and it moves inward at a rate that is practically constant. Furnas,[5] Conley[6] and

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[3] Rivett, *The Phase Rule* (Oxford, at the Clarendon Press, 1923), p. 22.

[4] Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2263.

[5] Furnas, *Ind. Eng. Chem.*, 1931, **23**, 534.

[6] Conley, *Trans. Amer. Inst. Min. Met. Eng.*, 1942, **148**, 330.

Joseph[7] have found this to be the case in the calcination of calcium carbonate, which is also a case of simple decomposition.

Because the time for complete decomposition of CuS to Cu_2S was very short, less than 15 min. at temperatures above 550° c., and because it was too difficult to stop the reaction after a specimen had been removed from the furnace, extensive rate measurements were not made on the primary reaction. The subsequent reactions were investigated by heating the CuS compresses in air at 550° c. until they were completely converted to Cu_2S, after which the pieces were transferred to a second furnace set at the desired temperature. The briquettes were withdrawn at varying intervals of time and boundary measurements made. The sliced cylinders looked like Fig. 2 and 3. Identification of the phases was accomplished by taking X-ray photograms of powdered samples from each zone, using characteristic cobalt $K\alpha$ radiation in a Debye camera. The patterns of the unknowns were then compared with standards made of C.P. $CuSO_4$, Cu, Cu_2S, CuS, Cu_2O and CuO.

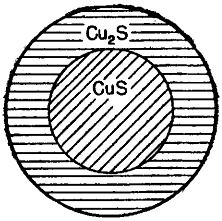

FIG. 1.—Partially roasted briquette of CuS.

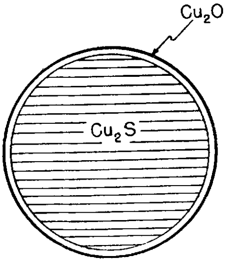

FIG. 2.—First stage in the roasting of Cu_2S.

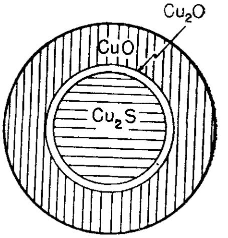

FIG. 3.—Second stage in the roasting of Cu_2S.

Results and Discussion

It could be concluded that under the conditions of the experiments at all temperatures from 430° to 965° c. the mechanism of the first stages in the roasting of cupric sulphide is represented by the following.

At the solid-solid interface,

$$2CuS(s) \rightleftharpoons Cu_2S\ (\beta) + \tfrac{1}{2}S_2(g) \quad . \quad . \quad . \quad (14)$$

$$S_2(g) \text{ at solid-solid interface, } \xrightarrow{\text{by diffusion}} S_2(g) \text{ at solid-gas interface} \quad . \quad (15)$$

and at the solid-gas interface,

$$\tfrac{1}{2}S_2(g) + O_2(g) = SO_2(g) \quad . \quad . \quad . \quad (2)$$

It is obvious that at the lower temperatures, where the rate of evolution and pressure of sulphur gas are low, reaction (2) may take place partly or wholly within the outer layer, and reaction (4) may also proceed.

TABLE I

THE RATE OF ADVANCE OF THE OXIDE LAYER IN THE ROASTING OF Cu_2S

Temperature ° C.	*Rate, in mm./min.*
430	0·0375
478	0·0385
525	0·0420
572	0·0480
663	0·0625
708	0·0690
787	0·080
873	0·0975
965	0·1065

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[7] Joseph, *Met. Tech.*, T. P. 1522, Dec., 1942.

For simplicity, we have considered in eqn. (14) that the sulphur gas is S_2. However, as shown by Kelley [8] in a critical survey, the gas resulting from (14) contains considerable quantities of S_8 and S_6. An extrapolation of semi-log plot of the work of Allen and Lombard,[9] giving the *total* sulphur pressure as a function of temperature, gives 495° C. as the temperature for which one atmosphere is the equilibrium sulphur pressure. As has been stated, the rate of sulphur evolution is relatively great, and, therefore, it seems unlikely that reactions (2) and (4) took place within the pores of the solid outer layer at temperatures greater than 495° C. Below this point the probability that these two reactions do occur in the aforementioned fashion increases inversely as some function of the temperature.

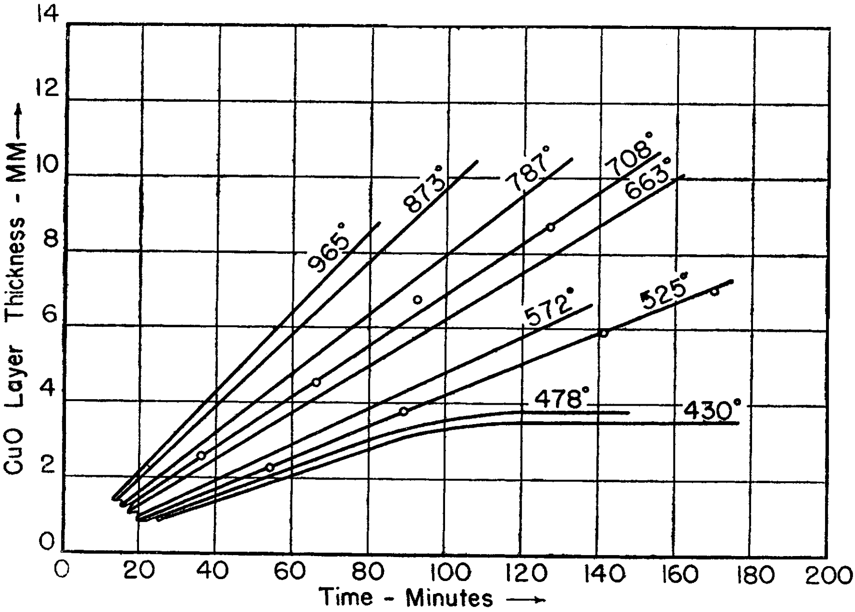

FIG. 4.—The thickness of the oxidised layer as a function of time at various temperatures.

The data for the second roasting stage, the oxidation of the Cu_2S, are summarised in Table I and Fig. 4 and 5. The rate of advance of the oxide layer was constant. In order not to confuse the drawing and to give a good idea of the conformity to lineality of the rate of advance of the phase boundary, experimental points have been inserted in Fig. 4 for only two of the temperatures—the best-fitting and the poorest.

Visual and X-ray examinations for all temperatures studied showed the solid phase in contact with the Cu_2S to be Cu_2O, as sketched in Fig. 2 and 3. The thickness of the cuprous oxide layer remained constant at a given temperature but varied with the temperature. At the lower temperatures it was about ½ mm. thick, and ¾–1 mm. at the higher temperatures. Fig. 6 shows prints made from the Debye patterns of this phase and that of C. P. cuprous oxide. This means, then, that the cuprous oxide is the first product resulting from the roasting of Cu_2S. This does not agree with Ashcroft,[10]

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[8] Kelley, *loc. cit.*, pp. 5–11 and 38.

[9] Allen and Lombard, *Amer. J. Sci.*, 1917, **43**, 175. Corrections to this article are given in *Econ. Geol.*, 1937, **32**, 253.

[10] Ashcroft, *Trans. Electrochem. Soc.*, 1933, **63**, 23.

who in a paper describing the roasting of copper ores states: "The theory formulated and afterward found to be correct is as follows: Reaction in roasting proceeds primarily and definitely to the formation of sulphates and not of oxides, the latter being a secondary formation, and SO_2 is likewise a secondary product, that is to say, a product of decomposition of the previously formed sulphates."

At temperatures above 663° c., CuO was the next and only solid phase to appear. Below 663° c., increasing amounts of sulphate were found intimately mixed with the cupric oxide. When the outer layer was wholly CuO, it was black, porous and easy to cut with a knife. The specimens containing sulphate became harder and less porous as the sulphate content increased until at 478° and 430° c. the pieces became so hard and dense as the time at temperature was made greater that the reaction practically ceased, as can be seen in Fig. 4.

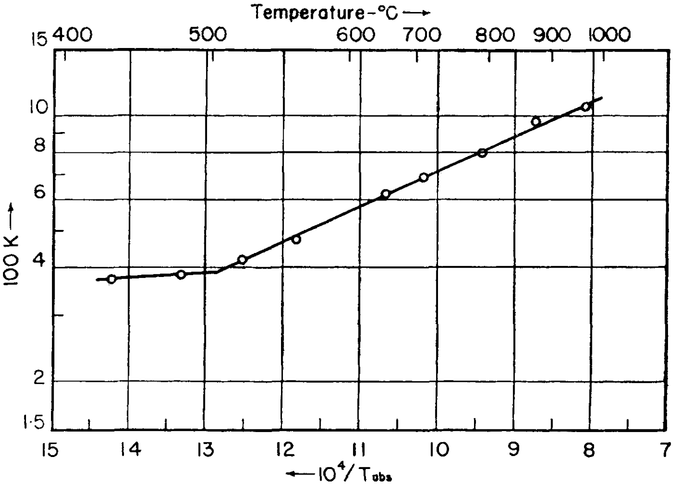

FIG. 5.—Log of the rate of advance of the oxidised layer as a function of the reciprocal absolute temperature.

From the data plotted in Fig. 5 an apparent activation energy of 4·19 kcal./mol. is obtained for temperatures above 525° c. It is possible that the mechanism here is the relatively slow process of the diffusion of the reacting gas to the scene of the reaction through a film of counter-diffusing reaction products. The temperature coefficient of the diffusion rate of a gas may be given approximately by the expression:

$$D_2 = D_1 (T_2/T_1)^n \quad . \quad . \quad . \quad . \quad (16)$$

where D is the diffusion coefficient, T is the absolute temperature, and the constant, n, varies from 1·5 for an ideal gas to about 2·0 for actual gases at high temperatures. Calculation of relative diffusion rates from eqn. (16) for temperatures between 525° and 950° c. yield for the activation energy a value of about 3·9 kcal./mol.

The roasting of Cu_2S as carried out in our experiments can then be represented as follows.

For temperatures greater than 663° c.,

$$O_2(g) \text{ in the atmosphere} \xrightarrow{\text{by diffusion}} O_2(g) \text{ at the } Cu_2O\text{–}Cu_2S \text{ interface} \quad . \quad (17)$$

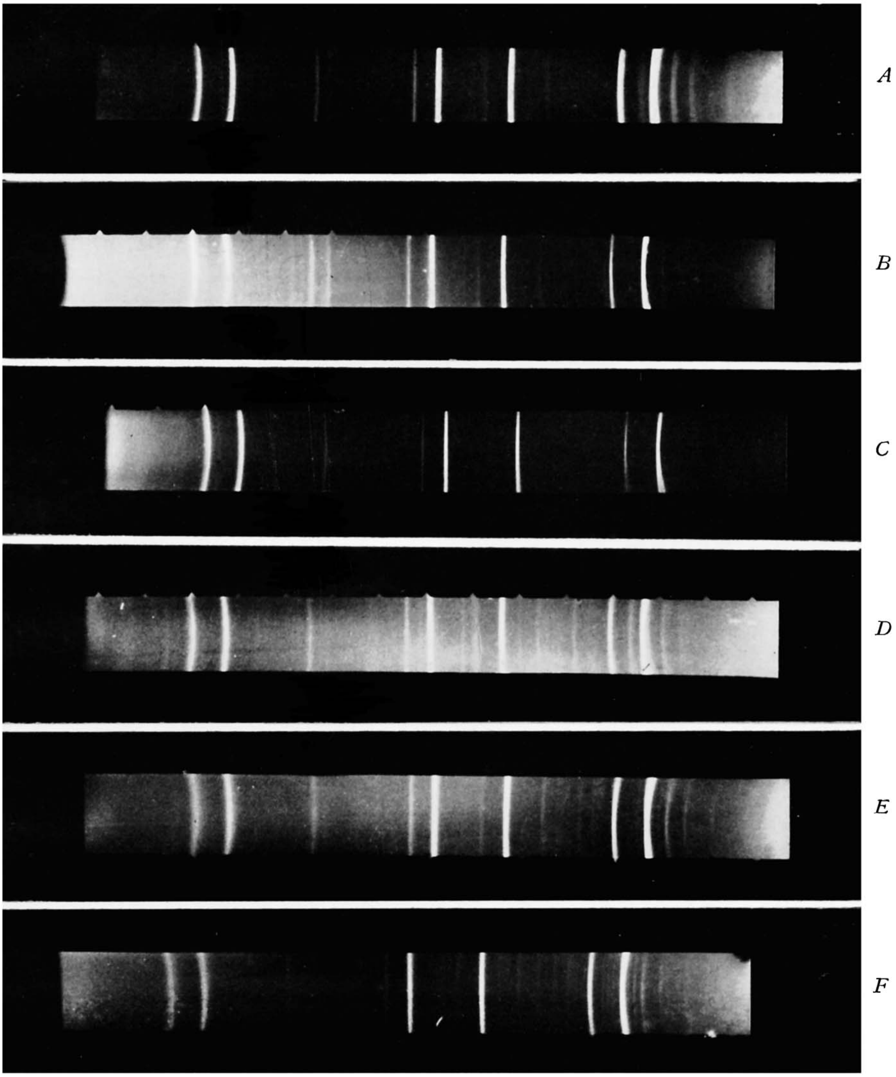

FIG. 6.—X-ray photograms of C.P. Cu_2O and primary solid phase formed during the roasting of Cu_2S at various temperatures. *A*—C.P. Cu_2O, *B*—965° C., *C*—787° C., *D*—663° C., *E*—572° C., *F*—525° C.

At the Cu_2O–Cu_2S interface,

$$Cu_2S(\beta) + 1\tfrac{1}{2}O_2(g) = Cu_2O(s) + SO_2(g) \qquad . \qquad . \qquad (18)$$

$$SO_2(g) \xrightarrow{\text{by diffusion}} SO_2(g) \text{ in the atmosphere} \qquad . \qquad . \qquad (19)$$

At the Cu_2O–CuO interface,

$$Cu_2O(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons CuO(s) \qquad . \qquad . \qquad . \qquad (20)$$

for temperatures below 663° c., (17), (18), (19) and (20) take place plus sulphatising reactions such as (4) and (5) occurring throughout the CuO layer.

The author is greatly indebted to Sam C. Carapella, Jr., Teaching Fellow in Metallurgy, University of Notre Dame, for helpful discussions and for aid in preparing the illustrations.

Summary

A new method for studying roasting reactions has been described. It has been shown by using the new procedure that the roasting of copper sulphides does not proceed primarily to the formation of sulphates, as has been previously reported, but rather to Cu_2S and Cu_2O in the case of CuS and Cu_2S respectively.

The mechanism of CuS roasting can be represented by the following sequence of reactions :

$$2CuS(s) \rightleftharpoons Cu_2S(\beta) + \tfrac{1}{2}S_2(g)$$
$$S_2(g) + \tfrac{1}{2}O_2(g) = SO_2(g)$$
$$Cu_2S(\beta) + 1\tfrac{1}{2}O_2(g) = Cu_2O(s) + SO_2(g)$$
$$Cu_2O(s) + \tfrac{1}{2}O_2(g) = CuO(s)$$

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