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Discussion Of "lime-enhanced Reduction Of Sulfide Concentrates: A Thermodynamic Discussion"

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Table I. Mass Spectrometric Measurements of $\text{Sb}_2(\text{g})$, $\text{S}_2(\text{g})$, and $\text{SbS}(\text{g})$ over Copper Saturated Molten Mattes Containing about 2.0 Mass Pct Sb at 1423 to 1523 K

Series	Temperature in K	Ion Intensity*			Equilibrium Constant for Reaction [1]	ΔH_{298}° by Third Law kJ/mol†
		Sb_2^+	S_2^+	SbS^+		
I	1423	12.26 ± 0.14	2.20 ± 0.11	28.82 ± 0.27	5.4 ± 0.2	171.2 ± 4.6
	1448	9.77 ± 0.10	1.87 ± 0.05	27.15 ± 0.24	6.1 ± 0.2	169.6 ± 4.6
	1473	14.86 ± 0.53	4.15 ± 0.89	40.58 ± 1.96	5.0 ± 0.9	171.6 ± 4.6
	1498	14.71 ± 0.05	4.68 ± 0.07	45.10 ± 0.70	5.3 ± 0.1	170.8 ± 4.6
	1523	20.31 ± 0.91	9.30 ± 1.33	68.93 ± 2.09	4.8 ± 0.6	172.1 ± 4.6
II	1423	5.37 ± 0.45	2.36 ± 0.51	11.79 ± 1.23	3.2 ± 0.7	177.5 ± 4.6
	1448	4.74 ± 0.16	2.46 ± 0.42	12.47 ± 0.24	3.5 ± 0.4	176.3 ± 4.6
	1473	7.15 ± 0.19	4.53 ± 0.12	21.37 ± 0.12	3.6 ± 0.1	175.8 ± 4.6
	1498	7.16 ± 0.18	5.90 ± 0.07	22.55 ± 0.30	3.4 ± 0.1	176.7 ± 4.6
	1523	7.56 ± 0.21	7.80 ± 0.22	25.03 ± 0.32	3.1 ± 0.1	177.5 ± 4.6

*Measured by applying 12 eV and expressed in arbitrary unit

†For the reaction: $\text{Sb}(\text{s}) + \text{S}(\text{rh}) = \text{SbS}(\text{g})$

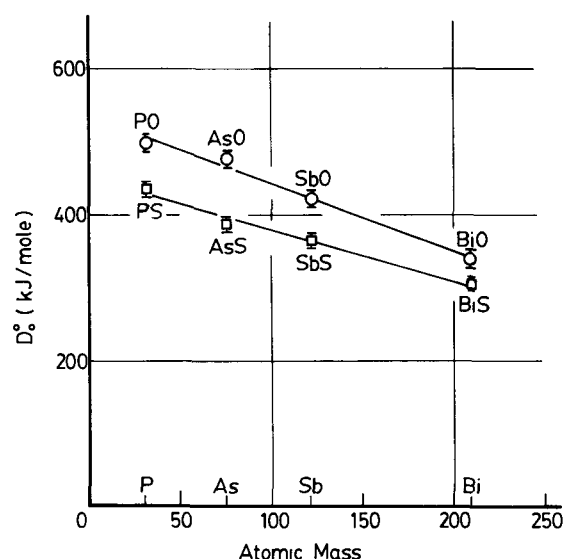


Fig. 1—Dissociation energies at 0 K, D° kJ/mol, for diatomic oxide and sulfide gases of the group V-a elements. The D° values for $\text{AsS}(\text{g})$ and $\text{SbS}(\text{g})$ are due to the present investigators.⁴

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Discussion of "Lime-Enhanced Reduction of Sulfide Concentrates: A Thermodynamic Discussion"

ARTHUR E. MORRIS and HARRY FLYNN

Udupa *et al.* report the results of an experimental and thermodynamic evaluation of the phases expected when various sulfide minerals are reduced in the presence of lime.¹ This subject has been studied by a number of investigators in an attempt to suggest process conditions for the selective or complete reduction of the minerals to metals without the evolution of significant SO_2 . A comprehensive

*A. R. UDUPA, K. A. SMITH, and J. J. MOORE: *Metall. Trans. B*, 1986, vol. 17B, pp. 185-96.

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assessment of the equilibrium phases expected during various reduction paths is therefore a timely and desirable goal. Unfortunately, the authors' calculations regarding the equilibrium phase assemblages and gas composition are incorrect for all reactions involving chalcopyrite, and for some lower temperature reactions involving pyrrhotite and chalcocite. The reason for the error is that the authors have used nonequilibrium condensed phase assemblages to calculate the composition of the gas. The purpose of this communication is to illustrate the correct method for making such calculations, and give examples of reaction paths for lime-enhanced reduction of chalcopyrite at 1100 K.

The best method for determining the equilibrium phases present in a multicomponent system is first to construct a thermodynamic stability diagram at each temperature of interest. Following this, specific reaction paths can be explored in detail to calculate the amounts of phases present, and the equilibrium gas composition. This method has already been ably demonstrated for lime-enhanced reduction of sulfide minerals by Yazawa² and Rosenqvist.³ The calculation of amounts of phases present along various reaction

paths is much easier once a stability diagram has been constructed, especially if done on a computer.

A temperature of 1100 K was chosen for use in illustrating the above method for the lime-enhanced reduction of chalcopyrite. The stability diagram for the Ca-Cu-Fe-S-O system is shown in Figure 1. The logarithms of the partial pressures of oxygen, sulfur, and sulfur dioxide are given in Table I. The diagram was constructed for conditions of equimolar amounts of copper and iron. The source of data was generally the same as that used by Udupa *et al.* except for the oxygen pressure at the wustite-magnetite phase boundary, which was taken from Giddings and Gordon,⁴ and the free energy of carbon oxysulfide and magnetite, which was taken from JANAF.⁵ Slight deviations from stoichiometry in the chalcopyrite, bornite, and pyrrhotite phases have been ignored. Following the suggestion of Rosenqvist,³ the formation of calcium and copper ferrites has also been ignored, although the diagram could easily be modified if desired to include these phases.

To aid in locating the gas composition along various reaction paths, two additional scales have been added to the

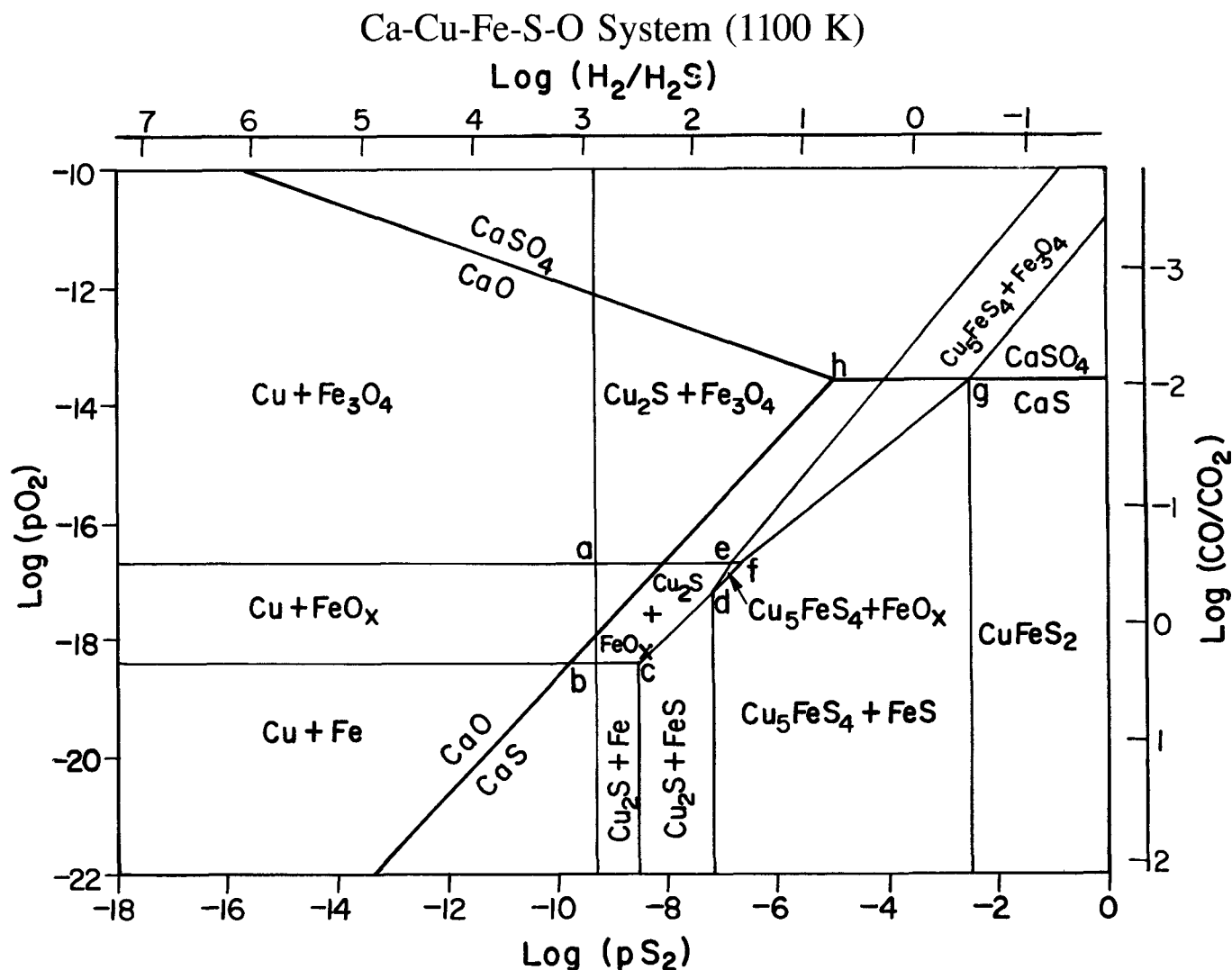


Fig. 1—Thermochemical stability diagram for the system Ca-Cu-Fe-S-O at 1100 K. The heavy lines represent the boundaries for the Ca-S-O system, while the light lines represent the boundaries for the Cu-Fe-S-O system. In the latter case, the copper-iron ratio has been fixed at 1. As discussed in the text, stability regions for the calcium and copper ferrites have been omitted.

Table I. Gas Composition at Invariant Points in the Ca-Cu-Fe-O-S System Diagram at 1100 K

Point	Condensed Phases	log p_{O_2}	log p_{S_2}	log p_{SO_2}
*a	Cu, Cu ₂ S, FeO _{1/2} , Fe ₃ O ₄	-16.71	-9.29	-7.98
b	Cu, Cu ₂ S, FeO _{1/5} , Fe	-18.33	-9.29	-9.60
c	Cu ₂ S, FeS, FeO _{1/5} , Fe	-18.33	-8.51	-9.21
**d	Cu ₂ S, FeS, Cu ₅ FeS ₄ , FeO _{1/10}	-17.18	-7.16	-7.39
e	Cu ₂ S, Cu ₅ FeS ₄ , FeO _{1/2} , Fe ₃ O ₄	-16.71	-6.82	-6.74
f	Cu ₅ FeS ₄ , FeS, FeO _{1/2} , Fe ₃ O ₄	-16.71	-6.64	-6.66
g	CuFeS ₂ , Cu ₅ FeS ₄ , FeS, Fe ₃ O ₄	-13.59	-2.48	-1.45
h	CaS, CaO, CaSO ₄	-13.58	-4.96	-2.68

*A ΔG_f° for FeO_{1/2} of -51680 cal was derived from log p_{O_2} data from Giddings and Gordon,⁴ together with ΔG_f° of Fe₃O₄ from JANAF.⁵

**The partial pressures of gases at point d are more uncertain than at other points, owing to the variation in ΔG_f° of wustite with composition.

ordinate and abscissa of the graph. However, the diagram as constructed does not show the stability ranges for any additional condensed phases that would be stable in the presence of carbon monoxide, carbon dioxide, hydrogen, hydrogen sulfide, or steam, as will be discussed later.

The first significant point to be noted from the diagram is that chalcopyrite is nowhere in equilibrium with copper, iron, or wustite, as indicated by the authors' reactions [2], [6], and [10], and therefore, gas compositions calculated by making such an assumption are in error. This means that the free energy change values from the authors' Figures 1, 9, and 15 are not for equilibrium phase assemblages, and the gas composition values from the authors' Figures 4 and 10 are not equilibrium compositions. Also, chalcopyrite is nowhere in equilibrium with both CaS and CaO as inferred from the six reactions written in the authors' Figure 1. The second significant point to be noted is that the lime-enhanced reduction of chalcopyrite can take place in stages which will depend on the amount of lime and reducing agent added. The presence of stable intermediate phases could be of considerable importance in attempting to elucidate the rate-controlling step(s).

Reaction path calculations were carried out for the admixture of various amounts of lime to 1 mol of chalcopyrite for two general situations—first, without any other added species, and second with carbon monoxide as a reducing agent. All reaction path calculations were carried out using the Solgasmix-PV computer program.⁶ The results show that 1.2 mols of lime are required to completely convert chalcopyrite to bornite and magnetite, with the formation of a gas phase whose composition can vary slightly depending on whether the phase assemblage is in equilibrium with chalcopyrite or chalcocite. If excess lime is added, 1.5 mols

of lime are consumed in completely converting chalcopyrite to chalcocite and magnetite. The amounts of phases and the log of the partial pressure of important gas species are shown in Table II for the sequence of reactions between lime and chalcopyrite, assuming negligible gas volume.

Reaction path calculations were also carried out for the reduction of 1 mol of chalcopyrite in the presence of excess lime, using various amounts of CO as a reducing gas. The calculations were designed to illustrate the equilibrium phases expected if lime, chalcopyrite, and CO were introduced into a continuous reaction furnace at 1100 K in the amounts indicated. The gas volume is large compared to the solids volume. The results are shown in Table III for four different amounts of CO added. One interesting result is obtained when 2 mols of CO are added: calcium carbonate is an equilibrium product of the reaction.* This result was

*Figure 1 does not show calcium carbonate because carbon was not chosen as a component in the system shown in Figure 1

apparently unanticipated by the authors, who did not consider it in any of their calculations. The formation of calcium carbonate as a reaction product tends to enhance carbon monoxide as a reducing agent in the presence of excess lime, especially at lower temperatures.

A thermodynamic assessment of reaction paths in complex systems requires careful consideration of all possible product phases. Construction of a thermochemical stability diagram is a good first step in assuring that stable species only will be included in equilibrium calculations. General-purpose computer software for calculating the equilibrium product phases is readily available, and gives reliable results.

Table II. Equilibrium Conditions during the Stages Reaction of One Mol of Chalcopyrite with Lime at 1100 K; Gas Volume Negligible

	Stage 1	Stage 2	Stage 3	Stage 4
Mols CaO added	1.2	1.2	1.5	1.5
Mols of phases present at equilibrium	0.2 Cu ₅ FeS ₄ 0.267 Fe ₃ O ₄ 1.167 CaS 0.33 CaSO ₄ trace CuFeS ₂	0.2 Cu ₅ FeS ₄ 0.267 Fe ₃ O ₄ 1.167 CaS 0.33 CaSO ₄ trace Cu ₂ S	0.5 Cu ₂ S 0.33 Fe ₃ O ₄ 1.458 CaS 0.042 CaSO ₄ trace Cu ₅ FeS ₄	0.5 Cu ₂ S 0.33 Fe ₃ O ₄ 1.458 CaS 0.042 CaSO ₄ trace CaO
Log p_{O_2}	-13.45	-13.45	-13.45	-13.45
Log p_{S_2}	- 2.36	- 3.92	- 3.92	- 5.10
Log p_{SO_2}	- 1.25	- 2.03	- 2.03	- 2.63

**Table III. Equilibrium Condition during the Stages Reduction of
One Mol of Chalcopyrite by CO in the Presence of Excess Lime at 1100 K**

	Mols CO Added			
	2	2.5	4	7
Mols CaO consumed	2.07	3.0	3.0	3.0
Mols of phases present at equilibrium	1.0 Cu	1.0 Cu	1.0 Cu	1.0 Cu
	2.0 CaS	2.0 CaS	2.0 CaS	2.0 CaS
	1.05 Fe _{0.95} O	1.05 Fe _{0.95} O	0.64 Fe _{0.95} O	1.0 Fe
	1.06 CO	1.56 CO	0.39 Fe	5.0 CO
	0.88 CO ₂	0.94 CO ₂	2.65 CO	2.0 CO ₂
	0.07 CaCO ₃		1.35 CO ₂	
Log p_{CO}	- 0.26	- 0.21	- 0.18	- 0.15
Log p_{CO_2}	- 0.34	- 0.42	- 0.47	- 0.54
Log p_{COS}	- 4.78	- 4.86	- 4.90	- 4.98
Log p_{O_2}	-17.92	-18.19	-18.33	-18.55
Log p_{S_2}	- 9.57	- 9.84	- 9.99	-10.20
Log p_{SO_2}	- 9.32	- 9.73	- 9.95	-10.27

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Authors' Reply

A. R. UDUPA, K. A. SMITH, and J. J. MOORE

Morris and Flynn suggest in their discussion of our paper¹ that a better way to elucidate the equilibrium phases formed during the reduction of chalcopyrite in the presence of lime is to construct a predominance area diagram, and they argue that equilibrium constants can be calculated only from reactions which have phases adjacent to each other on such a diagram.

We agree with the need to construct such a diagram and its usefulness in visualizing the reduction path. Indeed, we did construct a predominance area diagram early in our research program. However, the objective of our paper was to evaluate the overall reduction conditions and not to determine the reduction steps involved or to elucidate the rate controlling mechanisms. We have, therefore, reported only

the phases observed in the product of the reaction and related them to our experimental conditions. The phases mentioned were the phases we identified in the product of reaction at the end of the reduction process, carried out under predetermined experimental conditions. Hence, these may not represent any intermediate product phases. They are the products of the overall reaction, and the presence of these phases was supported by the thermodynamic discussion in the paper.

Morris and Flynn also expressed concern with the two-step representation of chalcopyrite reduction and the calculation of equilibrium constants for each step. They argue that equilibrium constants can be calculated only for those reactions which contain adjacent phases in the predominance area diagram and cite a paper by Yazawa² to that effect. However, they seem to have missed a point made by Yazawa in the same paper (page 311, item 4) where he states that the reactions involving phases not adjacent to each other on a predominance area diagram can be written and the corresponding equilibrium constants calculated. Yazawa gives the example of the formation of CuO from Cu₂S (note that they are not adjacent phases) and clearly states that the free energy of formation and hence equilibrium constants can be derived for such a reaction. Our two-step representation of chalcopyrite reduction does not depart from Yazawa's suggestion or the approach used by several other investigators. Our calculations are in agreement with the general approach found in the literature. The practice of writing reactions involving two non-adjacent phases found in the predominance area diagram and labeling the ratio of partial pressures of product gases and reactant gases as equilibrium constants is commonly used. Specific examples of the approach for chalcopyrite reduction can be found in papers by Prasad³ and Habashi *et al.*⁴ Additional examples for other reactions can be seen in oft-referenced thermodynamic data books such as the INCRA Series.⁵

Morris and Flynn have calculated equilibrium composition for chalcopyrite reduction at 1100 K using the SOLGASMIX-PV computer program. We agree with their observation that it is more convenient to use one of the software packages to calculate equilibrium composition and we have used SOLGASMIX-PV and F*A*C*T. If these software packages are not used cautiously, however, er-