Sir: McKenzie and Helgeson (1985) present activity diagrams that display equilibria among Cu-Fe sulfides, Fe oxides, and an aqueous phase at temperatures between 400° and 900°C. The authors claim that the phase relations presented "afford a comprehensive frame of reference for correlating field observations with mineral assemblages." Although the diagrams are valid thermodynamic representations for the stoichiometric phases considered, the application of the phase diagrams to natural systems is limited because many of the phases shown to be stable at high temperatures are in fact metastable with respect to their thermal decomposition products. In this discussion, I present modifications to the McKenzie and Helgeson diagrams that are dictated by experimental phase equilibrium studies.

At the outset, it is important to clarify the conventions and terminology related to activity diagrams. The conventions of McKenzie and Helgeson (also of Bowers et al., 1984), illustrated in Figure 1A, lead to the unfortunate results that: (1) both dashed and solid lines can represent stable or metastable equilibria, (2) only the metastable equilibria that lie at activity ratios higher than the "saturation limits" are shown in spite of the fact that a number of metastable equilibria lie within the "saturation limits," and (3) whether or not a particular phase represents a "saturation limit" depends only on the choice of phase composition and on the projection being used to display equilibria in two dimensions. Usage consistent with respect to stable and metastable equilibria (a convention that has historical and practical precedence) rather than with respect to "saturation limits" is preferred; this usage is shown in Figure 1B and is justified by Figure 2 and the paragraph that follows.

An important aspect of two-dimensional activity diagrams that display fluid-mineral equilibria written so as to conserve one or more components (in this case O₂) is that they represent projections of three or more dimensions (or variables). In the present case, the activity diagrams displayed in figures 1 to 4 of McKenzie and Helgeson are projections of the three-dimensional diagram that has either log \( f_{O_2} \) (with O₂ the balancing component) or log \( f_{S_2} \) (an alternate balancing component) as the third axis (Figs. 1C and 2A). The importance of Figure 2A is that it clarifies the meaning of the earlier diagrams by explicitly displaying the planar surfaces which define stable equilibrium between an aqueous phase and a solid phase of constant composition. Thus, all stable mineral fields and phase "saturation limits" of Figure 1A represent saturation surfaces, including pyrrhotite and chalcopyrite.

A critical step in the geochemical analysis of mineral stability relations is the consideration of all possible phases in the system. McKenzie and Helgeson merely list the phases that they are considering—without discussion; yet, many of the phases shown are not stable over the P-T range represented by the diagrams, i.e., they react to form new phases which the authors ignore. These reactions include: (1) chalcopyrite → digenite at 435°C, (2) covellite → digenite + liquid sulfur (\( S_0 \)) at 505°C, (3) chalcopyrite → "intermediate solid solution" (iss) + pyrite at 547°C, (4) α-iron + magnetite → FeO (wustite) at 560°C, and (5) pyrite → pyrrhotite + \( S_0 \) at 743°C (Barton and Skinner, 1979). Native copper and idaite round out the list of six additional stable phases in the system. Although the temperatures listed above are for low pressures (negligible to a few tens of bars), they are not affected greatly by increasing pressure to 2 kb; for example, \( dT/dP \) for the pyrite-terminal reaction is 14°C/kb (Kullerud and Yoder, 1959), which results in an upper thermal stability limit for pyrite of 770°C at 2 kb.

Consideration of all phases in the system leads to numerous changes in the activity diagrams of McKenzie and Helgeson. For example, on the basis of Figures 1C and 2A, a stability field for \( S_0 \) can be predicted at relatively low values of log \( (a_{Fe^2+/a_{H^+}}) \) and log \( (a_{Cu^+/a_{H^+}}) \) (see Figs. 1D and 2B). In addition to reducing significantly the size of the stability fields of pyrite, covellite, and hematite, the accounting for \( S_0 \) actually leads to disappearance of pyrite (at temperatures well below its thermal limit) at relatively low values of \( f_{H_2S} \) (400°C, pyrite is unstable at log \( f_{H_2S} \approx -0.7 \)). Thus, the presence of pyrite at a given temperature not only places lower bounds on the value of \( f_{H_2S} \) but also provides lower bounds on the value of \( a_{Fe^2+/a_{H^+}} \) in hydrothermal fluids if the value of \( f_{H_2S} \) can be estimated by other means.

Figure 3 presents activity diagrams that take into
FIG. 1. Two-dimensional logarithmic activity diagrams for the system Cu₂S-FeS-H₂S-O₂-H₂O-HCl at 2 kb, 400°C, $f_{\text{H_2O}} = 1$, $n_{\text{O_2}} = 1$, balanced on O₂ or S₂, drawn with the aid of computer program SUPCRT (written by D. H. Kirkham, J. V. Walther, and G. C. Flowers) with data from Helgeson and Kirkham (1974, 1976) and Helgeson et al. (1978, 1981). 1A, B, and C are drawn on the assumption that the only stable condensed phases are pure solids and consist of pyrrhotite (PO), magnetite (MT), pyrite (PY), covellite (CV), chalcopyrite (CP), bornite (BN), and chalcocite (CC). D includes liquid sulfur ($S_\text{O}$) in addition to the above phases. A. Activity diagram using conventions of McKenzie and Helgeson (1985). Solid lines represent "equilibrium among the stoichiometric minerals shown in adjoining fields and a coexisting aqueous solution" (p. 1966), whereas the dashed lines represent "saturation of the fluid phase with respect to the designated phase" (p. 1967) and are termed "saturation limits" (p. 1970). "Metastable equilibria are thus portrayed at values of log ($a_{\text{Cu}^+/a_{\text{H}^+}}$) and log ($a_{\text{Cu}^+/a_{\text{H}^+}}$) greater than those corresponding to the dashed lines" (p. 1970). B. Activity diagram using the conventions that stable equilibria are denoted by solid lines and metastable equilibria by dashed lines; not all possible metastable equilibria are illustrated. C. Activity diagram displaying only stable phase equilibria and contoured for $f_{\text{H_2S}}$, one of the many possible descriptive variables that can be used to represent the balancing component and to illustrate the third dimension. D. Activity diagram for stable equilibria illustrating the saturation surface for $S_\text{O}$. Dotted lines, representing the reaction $S_\text{O} = 2 S_{\text{O}_2}$ calculated from data in table 7-2 of Barton and Skinner (1979) and applied to the $f_{\text{H_2S}}$ contours from SUPCRT data base (1C), would indicate that $S_\text{O} + BN$ is stable relative to $PY + CV$. However, this result is incompatible with experimental data, which indicate that $PY + CV$ is stable at 400°C, a location of the $S_\text{O}$ stability field that satisfies the experimental data on phase compatibilities is shown by the dashed lines.
FIG. 2. Three-dimensional logarithmic activity-fugacity diagrams for the system Cu₂S·FeS·H₂S·O₂·H₂O·HCl, at 2 kb, 400°C, f₂s = 1, a₂o = 1, constructed with the same data as Figure 1, and illustrating stable equilibria according to the assumptions of Figure 1. Planes labeled with mineral abbreviations represent equilibrium between the designated condensed phase and an aqueous phase; these are saturation surfaces. An aqueous phase inside the volume described by these saturation surfaces is undersaturated with respect to all condensed phases; an aqueous phase outside the volume is supersaturated with respect to one or more condensed phases (but may be in metastable equilibrium with one or more other condensed phases). A. Three-dimensional diagram contoured for gas fugacities (compare with Fig. 1C). Note that log f₂s and log f₂o have a direct linear relation; dashed lines indicate the increase in fugacity of both O₂ and S₂ from PO→CC to PY→CV. B. Three-dimensional diagram showing the approximate location of the S(0) saturation surface (compare with Fig. 1D).

of approximations from experimental studies (e.g., fig. 7.17, Barton and Skinner, 1979). Scales have been left off because of uncertainties in those equilibria involving solids that are not in their standard states. In addition, uncertainties in equilibrium constants for reactions involving bornite, solid solution and intermediate solid solution may be as high as ±1.0 kcal, which translates into uncertainties of ±0.3 log units in f₂s. An educated guess is that the scales of Figures 1 and 2 apply to Figure 3 to within ±0.5 log units of the activity ratios. New phase fields that appear on the two-dimensional projection (Fig. 3A) of the three-dimensional diagram (Fig. 3B) include S(0), idaite and intermediate solid solution. Consideration of the actual compositions of pyrrhotite and chalcocite which occur in mineral deposits results in the appearance of saturation fields (rather than saturation lines) for these phases as well (Fig. 3A). “Saturation limits” for the activity diagram include six different assemblages of two solids, including both native copper and native iron. These relations are more easily seen in the three-dimensional diagram (Fig. 3B).

In the application of phase relations, McKenzie and Helgeson state that “close estimates of prevailing temperatures and values of f₂s, a₂o/a₁₂, and a₁₂/a₁₁ during ore deposition can be assessed from the presence or absence of chalcopyrite in hydrothermal mineral assemblages” (p. 1970). However, even if one were to qualify the “hydrothermal mineral assemblages” as those containing other Cu-Fe-S-O phases, and even if one were to accept standard state calculations as accurate with respect to stable equilibria involving naturally occurring minerals, this statement and the ensuing discussion would be misleading. For example, the authors conclude (p. 1972) that the presence of the assemblage magnetite-pyrite-chalcopyrite in pre-Main Stage ores at Butte implies maximum temperatures of ≈600°C. However, this conclusion is neither supported by their discussion nor consistent with their standard state calculations. Such calculations would indicate (Fig. 4) that magnetite-pyrite-chalcopyrite is a stable assemblage in the range from <400° to >900°C. Hence, the thermodynamic analysis of sulfide-oxide assemblages by McKenzie and Helgeson yields no new insights into the temperature of formation of the ores; none would be expected, because the thermal limits of the assemblages that they discuss have been known for over two decades (e.g., Kullerud and Yoder, 1959; Yund and Kullerud, 1966). The lack of thermal constraints on the sulfide assemblage translates into very large uncertainties in the chemical parameters of the hydrothermal fluid, contrary to what is implied by McKenzie and Helgeson. For example, if one accepts 650° ± 100°C as the temperature of early hydrothermal fluids at Butte (Brimhall, 1977), then the presence of magnetite-py-
rile-chalcopyrite can be used in conjunction with standard state thermodynamic data to calculate the corresponding range of log ($a_{\text{FeS}^+/a_{\text{CuS}}^+}$): the maximum value is $\approx 7.2$ (at 550°C, $f_{\text{H}_2}\text{S} = 1.2$; Fig. 4) and the minimum is $\approx 1.6$ (at 750°C, $f_{\text{H}_2}\text{S} = 1.5$), a range of over five orders of magnitude. Even this calculation has questionable application: over the range of temperature and $f_{\text{H}_2}\text{S}$ given above, intermediate solid solution rather than chalcopyrite is stable with pyrite and magnetite (Fig. 4). Because intermediate solid solution was the likely Cu-Fe sulfide deposited in pre-Main Stage veinlets at Butte, the computation yields activity ratios that are too low.

In conclusion, we are faced with a dilemma in the application of thermodynamic relations to understanding high-temperature geological processes. On the one hand, high temperatures in sulfide systems result in extensive solid solutions that cannot be treated at present in a quantitative manner. In spite of this, the extension of thermodynamic relations in aqueous systems to high temperatures by McKenzie and Helgeson is to be applauded because it represents a step toward a future goal. The diagrams that they present are accurate representations given present limitations, but they are the bare skeletons of the actual phase relations in the system and contain large areas of metastability; in those areas the diagrams yield incorrect results with respect to stable phase equilibria. The diagrams presented in this discussion have some flesh on them—they represent stable phase equilibria, but they lack a quantitative thermodynamic model to back them up. Until all of the phases in the system and the partitioning of elements between these phases can be
FIG. 4. Polythermal log \( \log (a_{Fe}^+/a_{H}^+) \) versus log \( \log (a_{Cu}^+/a_{H}^+) \) diagram at 2 kbar illustrating the stability field of the assemblage MT-PY-CP contoured for \( \log f_{H_2S} \), based on SUPCRT data. The stability field is limited by solid lines representing the four-phase assemblages MT-HM-PY-CP and MT-PO-PY-CP. With intermediate solid solution and \( S_0 \) taken into account, the assemblage MT-PY-CP is limited to the black area; at lower activity ratios and higher \( f_{H_2S} \) than the black area, MT-PY-CP is metastable with respect to several other stable phase assemblages.

DEALED WITH IN A RIGOROUS FASHION, I SEE NO ALTERNATIVE BUT TO ACCEPT THE FORMER AS A PROGRESS REPORT AND THE LATTER AS AN INDICATION OF FUTURE GOALS.

SEPTEMBER 25, 1986

REFERENCES


