Thermodynamic Properties of (Zn,Fe)S Solid Solutions at 850°C

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Abstract

The activity of ZnS and FeS in sphalerite at 850°C has been calculated from published data on the compositions of equilibrated pyrrhotite and sphalerite using the Gibbs-Duhem equation. Although ZnS behaves more non-ideally than FeS, the mixing is approximately symmetrical about $x^{sp}_{ZnS} = 0.5$. The excess free energy of mixing at this composition is +0.344 kcal/mole. There is a good correlation between the reduction in stability on substitution of Zn by Fe and bond strain, the non-ideal behavior appearing to result from the difference in atomic size of Zn^{II} and Fe^{II}. The mean value of the ratio of the Lewis and Randall activity of FeS in coexisting pyrrhotite and sphalerite is 1.62.

Introduction

The compositions of coexisting sphalerite and pyrrhotite solid solutions in the Fe–Zn–S system have been investigated in detail in the temperature range 580 to 850°C at low pressure (Barton and Toulmin, 1966). These authors, as well as Scott and Barnes (1971) and Scott (1973), have estimated the activity coefficient of FeS in sphalerite (γ^{sp}_{FeS}) from the relationship between the activity of FeS in pyrrhotite (a^{po}_{FeS}) and mole percent FeS in sphalerite. This is equivalent to considering (Zn,Fe)S as a solution of sphalerite (ZnS) and troilite (FeS). However, the mixing behavior of ZnS and FeS in sphalerite can be determined more conveniently from data referred to the metastable FeS end-member isostructural with sphalerite. The present study shows how this may be accomplished. The Gibbs-Duhem equation is used to calculate the activity of FeS (a^{sp}_{FeS}) and ZnS (a^{sp}_{ZnS}) in sphalerite from data in the Barton and Toulmin study, and this allows a discussion of the mixing properties of (Zn,Fe)S solid solutions.

Theory

Definition of Activity

This study uses the activity system defined by the relationship, $\mu_{AX} = \mu^{\circ}_{AX} + RT \ln a_{AX}$ (Lewis and Randall, 1961, p. 243), where a_{AX} is the activity of AX, μ_{AX} is the chemical potential of AX, and μ°_{AX} is its standard chemical potential. For a molecular component, μ° is equal to the standard free energy of formation at the reference temperature and pressure. For ideal solid solutions, $a_{AX} = x_{AX}$, where x_{AX} is the mole fraction of AX, and for non-ideal solid solutions, $a_{AX} = \gamma_{AX} \cdot x_{AX}$, where γ_{AX} is the activity coefficient. γ_{AX} is a function only of the non-ideality of the solution; for example, the excess free energy of mixing (ΔG_E) of $(A,B)X$ is given by, $\Delta G_E = RT (x_{AX} \ln \gamma_{AX} + x_{BX} \ln \gamma_{BX})$. In applying this system to sphalerite, (Zn,Fe)S is regarded as a mixture of ZnS (sphalerite) and FeS (metastable end-member isostructural with sphalerite).

The activity system used by Barton and Toulmin (1966), which has been adopted by many sulfide mineral investigators, may be regarded as a hybrid between that of Lewis and Randall and the absolute activity system of Guggenheim (1959, p. 220) which is defined by $\mu = RT \ln \lambda$, where λ is the absolute activity. The values used for the activity of FeS in pyrrhotite (a^{po}_{FeS}) are consistent with the Lewis and Randall system. Hence γ^{po}_{FeS} directly reflects the non-ideality of the mixing of FeS in pyrrhotite. However, the activity of FeS in sphalerite ("a"$^{sp}_{FeS}$) is determined in the manner of the equality of the absolute activities of Guggenheim, that is, "a"$^{sp}_{FeS} = a^{po}_{FeS}$, and the activity coefficient ("a"$^{sp}_{FeS}/x^{sp}_{FeS}$) is a function of both the non-ideality of the solid solution and the standard chemical potential difference ($\mu^{\circ,po}_{FeS} - \mu^{\circ,sp}_{FeS}$). It is for an analogous reason that Guggenheim (1959, Chap. 5) reverts to the Lewis and Randall activity and activity coefficient to discuss many of the properties of mixtures.

Gibbs-Duhem Equation

In what have become classical studies, the Gibbs-Duhem equation has been applied to the calculation

of a_{FeO} in wüstite (Fe$_{1-x}$O; Darken and Gurry, 1945) and a_{FeS} in pyrrhotite (Fe$_{1-x}$S; Toulmin and Barton, 1964). Both studies used the equality, d log a_X^{solid} = d log f_X^{vapor}, where X is O or S_2. In the present case the solid phase being investigated is equilibrated with a second solid phase. This is a slightly different situation and the underlying theory will be stated explicitly to minimize any misunderstanding.

For (Zn, Fe)S at constant temperature and pressure the Gibbs-Duhem equation may be written in the following form,

$$x^{sp}_{ZnS} \, d \log a^{sp}_{ZnS} = -x^{sp}_{FeS} \, d \log a^{sp}_{FeS},$$

where x^{sp}_{ZnS} is the mole fraction of ZnS in sphalerite, and so on. This reduces to,

$$d \log a^{sp}_{ZnS} = -r \, d \log a^{sp}_{FeS}, \qquad (1)$$

where $r = x^{sp}_{FeS}/x^{sp}_{ZnS}$.

Now, from the necessary equality of chemical potentials of FeS in the coexisting phases,

$$\mu^{o,sp}_{FeS} + RT \ln a^{sp}_{FeS} = \mu^{o,po}_{FeS} + RT \ln a^{po}_{FeS},$$

and,

$$d \log a^{sp}_{FeS} = d \log a^{po}_{FeS} \qquad (2)$$

By substitution of Equation (2) in Equation (1),

$$\log a^{sp}_{ZnS} = -\int_0^{r'} r \, d \log a^{po}_{FeS} \qquad (3)$$

Since the relationship between a^{po}_{FeS} and sphalerite composition at constant temperature has been determined experimentally, a^{sp}_{ZnS} may be calculated directly and used, in turn, to calculate a^{sp}_{FeS} from,

$$\log a^{sp}_{FeS} = -\int_0^{1/r'} \frac{1}{r} \, d \log a^{sp}_{ZnS} \qquad (4)$$

Calculation of a^{sp}_{ZnS} and a^{sp}_{FeS}

The data used in this study were taken from Barton and Toulmin (1966, Table 3). Initially, an attempt was made to integrate the right hand side of Equation (3) by an analytical method through fitting polynomial expressions to the values of log a^{po}_{FeS} and r for each of the six temperatures most extensively investigated by these authors. However, the resulting values of a^{sp}_{ZnS} were higher than expected at low values of r (x^{sp}_{ZnS} near unity). This is because the experimental data cover only the range in x^{sp}_{FeS} from about 0.16 to 0.56, and the polynomial expressions did not describe properly the asymptotic nature of the log a vs r distributions as r approaches zero. Other attempts at variations on the analytical method

(expressing log a as a function of x^{sp}_{ZnS} and extrapolating the a^{po}_{FeS} vs x^{sp}_{FeS} distributions toward $x^{sp}_{FeS} = 0$) did not improve the situation. For this reason the integration was done graphically.

Using the data for 850°C, a smoothed curve was fitted through the plot of a^{po}_{FeS} against x^{sp}_{FeS} and extrapolated to cover the range in x^{sp}_{FeS} from 0 to 1. The data were plotted from $r = 0.01$, and the abscissa scale was adjusted for different ranges of r to optimize the precision of the area measurements at low values of r. The resulting data for a^{sp}_{ZnS} were smoothed by plotting them against x^{sp}_{ZnS}; representative data for 0.1 intervals of x^{sp}_{ZnS} are given in Table 1. Data for a^{sp}_{FeS} were obtained in a similar way by graphical integration of Equation (4) (Table 1).

Barton and Toulmin (1966) have shown that the a^{po}_{FeS} vs x^{sp}_{FeS} distributions are almost independent of temperature above 580°C, and Scott and Barnes (1971) have shown that this condition appears to continue down to at least 340°C. For this reason, and in view of the time-consuming nature of the graphical integration method, the calculation of activities for the five other temperatures for which data were available was not attempted. The iron content of sphalerite coexisting with troilite *does* decrease slightly with decrease in temperature (Barton and Toulmin, 1966, Fig. 10). However, the scatter in the data for less iron-rich compositions tends to obscure this correlation in the a^{po}_{FeS} vs x^{sp}_{FeS} distributions (Barton and Toulmin, 1966, Fig. 14), and a comparison of the mixing properties of sphalerite solid solutions with temperature calculated from these data would not be too meaningful.

The error in the activity values in Table 1 is a combination of (1) the uncertainty in the a^{po}_{FeS} data, calculated to be not greater than ± 0.03 of log a_{FeS} (Toulmin and Barton, 1964); (2) the uncertainty in the observed a^{po}_{FeS} vs x^{sp}_{FeS} distribution for 850°C,

TABLE 1. Thermodynamic Parameters for (Zn,Fe)S Solutions at 850°C

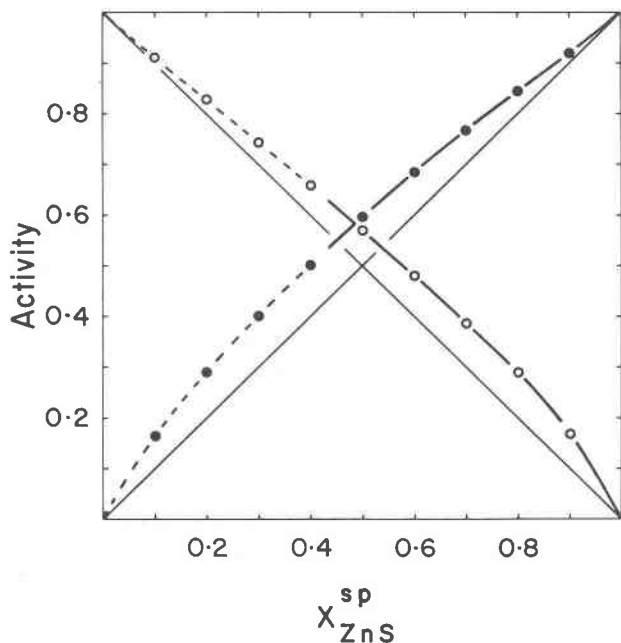| x^{sp}_{ZnS}	a^{sp}_{ZnS}	γ^{sp}_{ZnS}	a^{sp}_{FeS}	γ^{sp}_{FeS}	$\dfrac{\ln \gamma^{sp}_{ZnS}}{(x^{sp}_{FeS})^2}$	$\dfrac{\ln \gamma^{sp}_{FeS}}{(x^{sp}_{ZnS})^2}$
0.1	0.165	1.65	0.912	1.01	0.618	0.995
0.2	0.290	1.45	0.828	1.04	0.581	0.981
0.3	0.400	1.33	0.744	1.06	0.582	0.647
0.4	0.501	1.25	0.660	1.10	0.620	0.596
0.5	0.597	1.19	0.570	1.14	0.696	0.524
0.6	0.685	1.14	0.480	1.20	0.819	0.506
0.7	0.767	1.10	0.387	1.29	1.059	0.520
0.8	0.844	1.06	0.290	1.45	1.457	0.581
0.9	0.920	1.02	0.169	1.69	1.980	0.648

FIG. 1. Activity *versus* composition in mole fractions for ZnS and FeS in (Zn,Fe)S at 850°C: solid circles, ZnS; open circles, FeS; broken curves, metastable compositions.
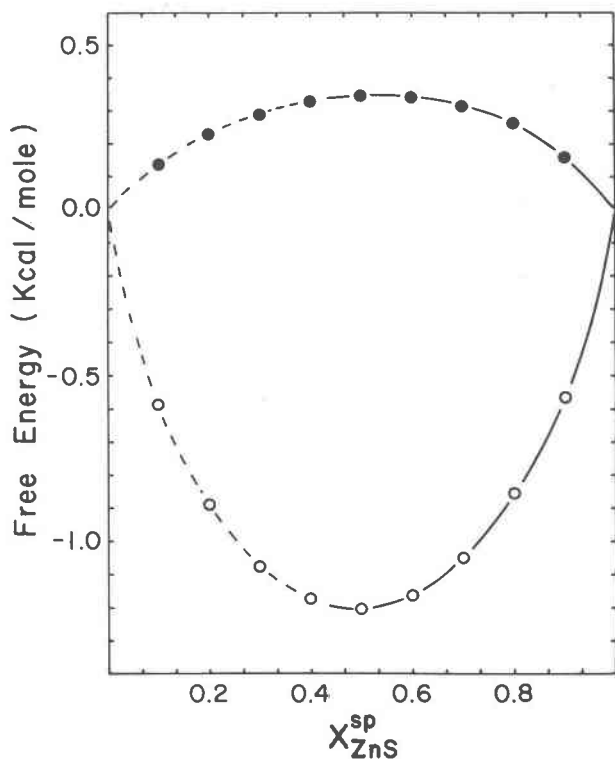

FIG. 2. Variation of the excess free energy of mixing (ΔG_E) and total free energy of mixing (ΔG_M) of ZnS and FeS with mole fraction of ZnS (x^{sp}_{ZnS}) at 850°C: solid circles, ΔG_E; open circles, ΔG_M; broken curves, metastable compositions.

estimated from Barton and Toulmin (1966, Fig. 12) to be less than the uncertainty in a^{po}_{FeS} except at low values of a^{po}_{FeS}; and (3) the error introduced in making the present calculations. An estimate of the precision of the extrapolation to low concentrations of the activity-*vs*-mole-fraction distributions and of the graphical integration of Equations (3) and (4) may be obtained by recalculating a^{sp}_{ZnS} using the calculated data for a^{sp}_{FeS}. The discrepancies in a^{sp}_{ZnS} at x^{sp}_{ZnS} values of 0.5, 0.7, and 0.9 are −1.17, −0.59 and −0.27 percent, respectively. These discrepancies are relatively small compared to the uncertainty in a^{po}_{FeS}. The error resulting from the extrapolation of a^{po}_{FeS} in the x^{sp}_{FeS} range 0.56 to 1.00 is difficult to estimate. However, if a^{po}_{FeS} is a smoothly varying function of x^{sp}_{FeS}, this error must be relatively small also. Thus the uncertainty in the activity data in Table 1 is not expected to be appreciably greater than that of the corresponding a^{po}_{FeS} data.

Discussion

The calculated activity coefficients (Table 1) and the plots of a against x (Fig. 1) indicate that the departures of ZnS and FeS from ideal solution in sphalerite are not very great. Although ZnS departs slightly more from ideality, both a vs x distributions are generally similar and symmetrical to each other. Nearly symmetrical distributions are indicated also in plots against composition of the excess free energy of mixing [$\Delta G_E = RT(x^{sp}_{FeS} \ln \gamma^{sp}_{FeS} + x^{sp}_{ZnS} \ln \gamma^{sp}_{ZnS})$] and the total free energy of mixing [$\Delta G_M = RT(x^{sp}_{FeS} \ln a^{sp}_{FeS} + x^{sp}_{ZnS} \ln a^{sp}_{ZnS})$] (Fig. 2).

It follows that the mixing behavior of ZnS and FeS might be approximated by a regular solution model. Following the procedure for non-electrolyte liquid solutions (for example, Lewis and Randall, 1961, p. 284), a regular solution model would imply the following relations, $\ln \gamma^{sp}_{FeS} = w/RT (x^{sp}_{ZnS})^2$ and $\ln \gamma^{sp}_{ZnS} = w/RT (x^{sp}_{FeS})^2$, where w is the interaction parameter. In view of the estimated uncertainty in the activity data, the calculated ratios $\ln \gamma^{sp}_{FeS}/(x^{sp}_{ZnS})^2$ and $\ln \gamma^{sp}_{ZnS}/(x^{sp}_{FeS})^2$ (Table 1) are not inconsistent with this model. Significant departures from constant ratios occur only for high values of x^{sp}_{ZnS} and x^{sp}_{FeS} and actually represent quite small discrepancies in the calculated values of the activities.

The activity coefficients are greater than unity at all compositions. Thus, ΔG_E is always positive and the substitution of Zn by Fe causes a reduction in the stability of the mixture relative to ideal solution. However, ΔG_M remains negative at all compositions

(Fig. 2) and there is only one minimum in the ΔG_M *vs* x^{sp}_{ZnS} distribution.

Barton and Toulmin (1966) have shown that for sphalerite the variation with composition of the unit cell edge is non-linear and that the data may be represented by the equation, a (Å) $= 5.4093 + 0.0005637X - 0.000004107X^2$, where X is the mole percent FeS in sphalerite. For ideal solution the variation of the unit cell volume with composition should be linear. A crude estimate of the excess molar volume of mixing may be obtained by extrapolating the Barton and Toulmin expression to 100 mole percent FeS. The resulting data are compared with ΔG_E in Figure 3. The validity of this extrapolation may be questioned because it involves a large range of x^{sp}_{FeS} and was made from the point where the distribution unit-cell parameter *vs* x^{sp}_{FeS} appears to change slope. However, the calculated value of the unit cell parameter of the FeS end-member (5.425 Å) compares favorably with observed data for the metastable sphalerite modification of FeS prepared in the presence of excess iron (5.423 Å, de Médicis, 1970; 5.426 Å, Skinner and Berner, 1970; 5.417 Å, Takeno, Zôka, and Niihara, 1970), and the excess
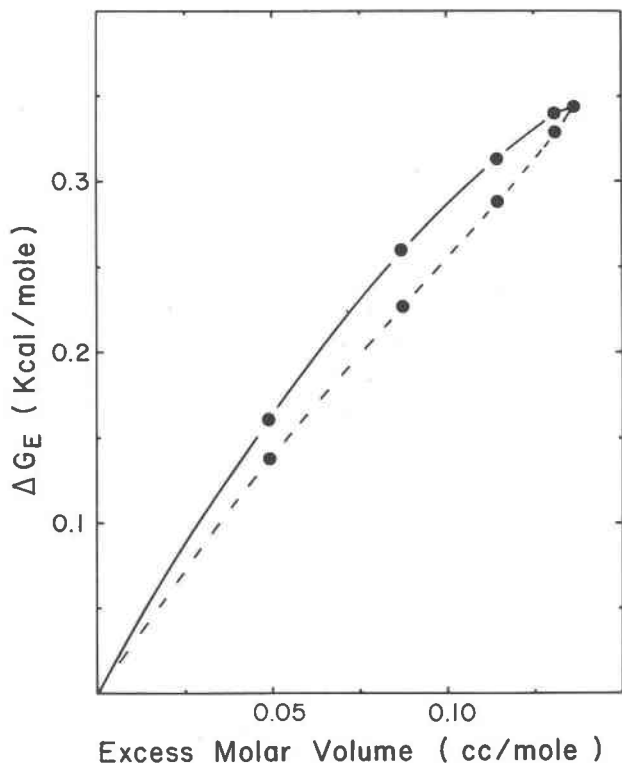

FIG. 4. Plot of the activity of FeS in pyrrhotite (a^{po}_{FeS}) against the activity of FeS in sphalerite (a^{sp}_{FeS}) at 850°C: straight line represents the mean value of $a^{po}_{FeS}/a^{sp}_{FeS}$ (1.62₃).

molar volume of mixing does have a nearly symmetrical distribution with x^{sp}_{ZnS}. On the other hand, Barton (personal communication, 1974) suggests that the synthetic metastable FeS may be nonstoichiometric ($Fe_{1+x}S$), equivalent to sphalerite equilibrated with troilite and excess iron (Barton and Toulmin, 1966). However, the present data do show a good correlation between ΔG_E and the excess molar volume of mixing, and this correlation would persist within the limits of uncertainty of the activity data over a considerable variation in the estimated unit cell parameter of metastable FeS. Thus the reduction in stability on substitution of Zn by Fe appears to be a direct result of bond strain.

This relative destabilization is most probably associated with the structural accommodations required by the difference in effective atomic size of Zn^{II} and Fe^{II}. In covalent minerals and compounds in which it is not substituted by another metal, Fe^{II} generally prefers six-fold coordinated sites whereas Zn^{II} has a distinct preference for the smaller, tetrahedral sites. As discussed earlier, the activities of ZnS and FeS in sphalerite are expected to be almost independent of temperature, at least above 340°C. This suggests that the temperatures investigated ex-

FIG. 3. Variation of the excess free energy of mixing (ΔG_E) with the excess molar volume of mixing in (Zn,Fe)S at 850°C: broken curve, metastable compositions.
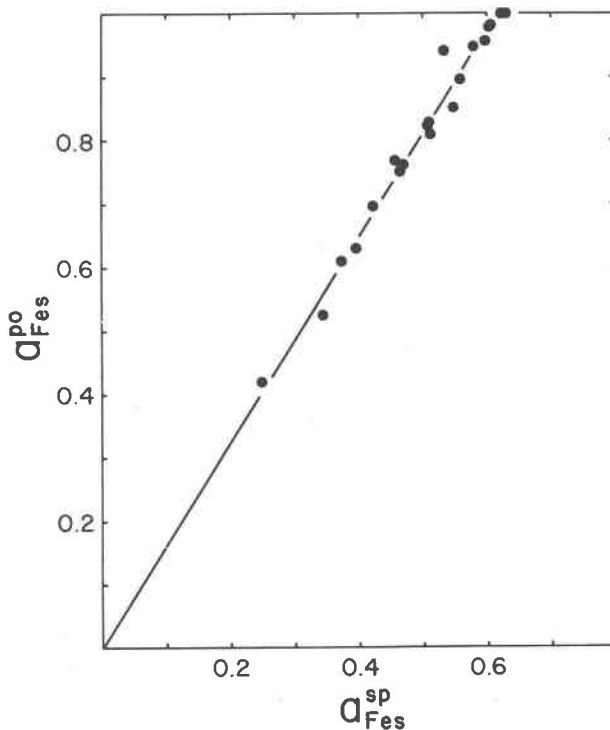
perimentally have been below the threshold temperature at which the thermal energy may compensate for the size differential of Zn^{II} and Fe^{II}.

a^{po}_{FeS} is compared with a^{sp}_{FeS} in Figure 4. As expected there is a good linear relationship between them. Because of the requirement for equality of the chemical potential of FeS in the coexisting pyrrhotite and sphalerite, the slope of the correlation line (k) is defined by the following expression,

$$k = a^{po}_{FeS}/a^{sp}_{FeS} = e\left(\frac{\mu^{o,sp}_{FeS} - \mu^{o,po}_{FeS}}{RT}\right) = 1.62_3$$

Hence, k is related to the difference in free energy between the sphalerite modification of FeS and troilite at 850°C.

The data for a^{sp}_{ZnS} in Table 1 and Figure 1 disagree with those of Barton and Skinner (1967, Fig. 7.2), the associated activity coefficients for which are less than unity. However, Barton and Skinner have recognized that an arithmetic error was made in their calculations and this will be corrected in the revised version of their work (Barton, personal communication, 1974).

Acknowledgments

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