American Mineralogist, Volume 65, pages 1063–1064, 1980

Calculated phase relations for pyrite–pyrrhotite–sphalerite: correction

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Hutcheon (1978) published a calculated phase diagram for sphalerite–pyrite–pyrrhotite. In that paper it was stated that thermal expansion and isothermal compressibility data were not needed to calculate sphalerite compositions which were in agreement with experimental values given by Scott (1973). Contrary to this statement, this agreement is fortuitous because the wrong molar volume for pyrite (15.962 cm^3) was used in final calculations for the published manuscript. Using the correct volume (23.940 cm^3) results in a marked discrepancy with the experimental data. Calculations have been repeated using expansion and compressibility data.

Because of the error in the published calculations

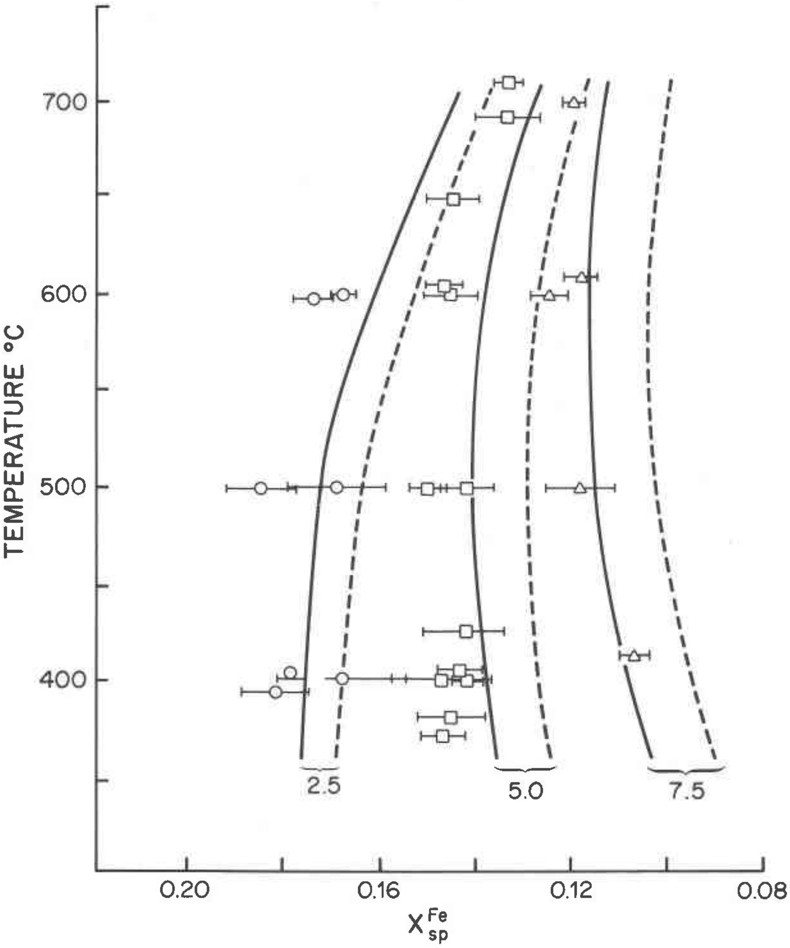

Fig. 1. Calculated phase relationships for pyrite, pyrrhotite, and sphalerite are in reasonable agreement with the experimental data of Scott (1973) if thermal expansion and isothermal compressibility data are used (solid lines). Calculated isobars which do not include expansion and compressibility data (dashed lines) do not agree with the experimental data. The curves shown are for 2.5, 5, and 7.5 kbar. The brackets represent the experimental points determined by Scott at 2.5 (circles), 5 (squares), and 7.5 (triangles) kbar.

0003–004X/80/0910–1063$02.00

the procedure is given here in more detail for 400°C and 5kbar. The composition of pyrrhotite coexisting with pyrite at any temperature between 400 and 750°C at 1 atm is obtained from a polynomial, fitted to the data of Toulmin and Barton (1964):

$$N^{po}_{FeS} = 0.9545099 + 1.019706 \times 10^{-5}(T) - 1.132749 \times 10^{7}(T^{2})$$

where T = Celsius temperature.

The expressions in Toulmin and Barton are then used to calculate log fS_2 (−7.3686) and log a^{po}_{FeS} (−0.2678). From the isothermal compressibility and isobaric thermal expansion data given by Scott (1973), the volumes of pyrite (24.167 cm³), pyrrhotite (18.874 cm³), FeS sphalerite (24.092 cm³, from data for ZnS sphalerite) and sulfur with the pyrrhotite structure (15.129 cm³) are calculated at 400°C and 5kbar. If it is assumed that a^{po}_{FeS} is not pressure dependent, the equilibria:

$$\underset{\text{pyrrhotite}}{FeS + 1/2S_2} \quad \leftrightarrows \quad \underset{\text{pyrite}}{FeS_2} \qquad (1)$$

and:

$$\underset{\text{(in pyrrhotite)}}{S} \quad \leftrightarrows \quad \underset{\text{(in vapor)}}{1/2S_2} \qquad (2)$$

may be used to obtain log fS_2(−7.061) and a^{po}_{FeS} (0.608) at 400°C and 5kbar, using the volumes calculated above. This procedure is described in more detail in Hutcheon (1978) and is not repeated here.

Table 1. The molar volumes of phases used in calculations

Phase	Volume (cc)	Source
Pyrite	23.94	Kullerud and Yoder (1959)
Troilite	18.20	Scott (1973)
Sphalerite (FeS)	24.033	Hutcheon (1978)
Sulfur (pyrrhotite structure)	14.456	Froese and Gunter (1976)

Having obtained a^{po}_{FeS}, at the pressure and temperature of interest, the free energy change for the equilibrium:

$$\underset{\text{pyrrhotite}}{FeS} \quad \leftrightarrows \quad \underset{\text{sphalerite}}{FeS} \qquad (3)$$

may be calculated from:

$$G^{\circ}_{(3)} = 239 + 0.840\,T$$

The expression in Hutcheon (1978, p. 88) contains a minus (−) sign which is a typographical error. Using the molar volumes, corrected by isothermal compressibility and isobaric thermal expansion data, the procedure outlined in Hutcheon (p. 91) is then used to calculate a^{sp}_{FeS}(0.209) by iterating for X^{sp}_{FeS} (0.138) at 400°C and 5kbar. The value of γ^{sp}_{FeS} would be 1.514, using the relationship $a = \gamma \cdot X$.

On Figure 1 the results of these calculations with the expansion and compressibility data (solid lines) and without these data (dashed lines) are shown. The molar volumes at 25°C and 1 atm are shown in Table 1. As pointed out by Scott (1973), the isobaric thermal expansion data and isothermal compressibility data are necessary to obtain a reasonable fit to the published experimental values. A Fortran IV program was written to perform these calculations and copies can be obtained from the author.

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Manuscript received, April 29, 1980;
accepted for publication, May 9, 1980.