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POINT DEFECTS IN PYRRHOTITE

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ABSTRACT

The nature of point defects in pyrrhotite can be determined from measurements of composition and the corresponding fugacity of S_2 by examining reaction equilibria written to involve perfectly ordered FeS, species deduced from point defects, and S_2. This approach is illustrated using the experimental data of Rau (1976) at 1257 K. In S-rich pyrrhotite, the predominant defect is produced by vacancies on Fe sites, supporting previous knowledge from density measurements. In Fe-rich pyrrhotite, the predominant defect consists of Fe atoms on S sites. Rau's (1976) fitted thermodynamic parameters in the temperature range from 820 to 1374 K can be expressed in terms of the change in standard free energy of the reaction giving rise to vacancies on Fe sites, the excess partial molar free energy at infinite dilution of □S and FeS in the binary solution FeS – □S, and the change in standard free energy of the reaction giving rise to Fe on S sites:

½ S_2 (gas) = □S $\Delta G^o = 49\,229 + 113.695\,T$ J mol^{-1}
Solution FeS – □S $\overline{G}^{ex\,\infty}{}_{\square S} = \overline{G}^{ex\,\infty}{}_{FeS} = -185\,151 - 26.273\,T$ J mol^{-1}
FeS = FeFe + S_2 (gas) $\Delta G^o = 514\,457 - 226.773\,T$ J mol^{-1}

On the basis of the thermodynamic data derived, it is possible to calculate, for a given composition of pyrrhotite, the fugacity of S_2 and the activity of FeS in pyrrhotite at any temperature.

Keywords: pyrrhotite, point defects, thermodynamic properties.

SOMMAIRE

On peut déterminer la nature des défauts ponctuels dans la pyrrhotite à partir des mesures de composition et de la fugacité du soufre correspondante en examinant les équilibres des réactions proposées impliquant le FeS parfaitement ordonné, les espèces hypothétiques conçues pour exprimer les défauts ponctuels, et le soufre, S_2. Il est possible d'illustrer cette démarche avec les données expérimentales de Rau (1976) à 1257 K. Dans la pyrrhotite enrichie en soufre, le défaut prédominant implique des lacunes sur le site Fe, ce qui concorde avec les mesures antérieures de la densité de la solution solide. Dans la pyrrhotite enrichie en fer, le défaut prédominant impliquerait des atomes de Fe logés sur le site S. On peut exprimer les paramètres thermodynamiques de Rau (1976) sur l'intervalle de température entre 820 et 1374 K en termes du changement dans l'énergie libre standard de la réaction menant à la formation des lacunes sur les sites Fe, l'excès en énergie libre molaire partielle à dilution infinie de □S et de FeS dans la solution solide binaire FeS – □S, et le changement en énergie libre standard de la réaction menant à l'incorporation des atomes de Fe sur les sites S:

½ S_2 (gaz) = □S $\Delta G^o = 49\,229 + 113.695\,T$ J mol^{-1}
Solution FeS – □S $\overline{G}^{ex\,\infty}{}_{\square S} = \overline{G}^{ex\,\infty}{}_{FeS} = -185\,151 - 26.273\,T$ J mol^{-1}
FeS = FeFe + S_2 (gaz) $\Delta G^o = 514\,457 - 226.773\,T$ J mol^{-1}

À la lumière des données thermodynamiques dérivées, il est possible de calculer, pour une composition donnée de pyrrhotite, la fugacité de S_2 et l'activité de FeS dans cet échantillon de pyrrhotite, quelle que soit la température envisagée.

(Traduit par la Rédaction)

Mots-clés: pyrrhotite, défauts pontuels, propriétés thermodynamiques.

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INTRODUCTION

Compounds of the transition elements and intermetallic compounds exhibit a considerable range of solid solution. The physical chemistry of these nonstoichiometric compounds has been discussed by Libowitz (1965, 1969), Libowitz & Lightstone (1967) and Lightstone & Libowitz (1969); the following summary is based on these reviews.

In covalent binary compounds, the deviations from stoichiometry can be produced by means of six possible types of point defects: 1) vacancies on metal sites, 2) vacancies on nonmetal sites, 3) substitution of metal atoms on nonmetal sites, 4) substitution of nonmetal atoms on metal sites, 5) incorporation of metal atoms on interstitial sites, and 6) incorporation of nonmetal atoms on interstitial sites.

In intermetallic compounds, a second distinctive site also is occupied by a metal atom. Compounds commonly incorporate only two point defects, one accounting for positive, and the other for negative deviation from stoichiometry. At the stoichiometric composition, the effects of the two defects balance. As a compound deviates from stoichiometry, the concentration of one defect decreases sharply, so that the mechanism of solid solution is represented essentially by one defect. Five pairs of defects, known as intrinsic defects, have been observed; most of these have been given names, as indicated in Figure 1.

It is possible to deduce the type of defect from fugacity measurements of one of the elements over a range of compositions. The required relationship between fugacity, composition, and the type of defect can be derived from statistical mechanics or, alternatively, equilibria can be considered that involve the defects as species (Libowitz 1965, Libowitz & Lightstone 1967). The second approach is used here to discuss point defects in pyrrhotite. The method is illustrated using Rau's (1976) experimental data at 1257 K.

Rau's (1976) results extend over a temperature range from 820 to 1374 K. They were found to be compatible with intrinsic defects in pyrrhotite involving vacancies on Fe sites and incorporation of Fe on S sites. He fitted his data to parameters that appear in formulas deduced from general relationships given by Libowitz (1969). These parameters can be expressed in terms of changes in standard free energy of specific reactions and by a measure of the nonideality of the $\mathrm{FeS} - \square\mathrm{S}$ solution. The thermodynamic data derived can be used to calculate the fugacity of S_2 and the activity of FeS in pyrrhotite at any temperature and composition of pyrrhotite.

METHODOLOGY

Bonds in sulfides are highly covalent (Prewitt & Rajamani 1974), and pyrrhotite exhibits metallic conductivity (Kaplan & Worrell 1970). For these reasons, defects in pyrrhotite have been treated in terms of uncharged species by Ward (1971), Libowitz (1972), Rau (1976), and Powell (1983). Fictive compounds, deduced from possible combinations of point defects, will be used as species in chemical reactions. In perfectly ordered pyrrhotite, $\mathrm{FeS}(\square)_2$, S atoms form a framework of hexagonal close-packing, and the Fe atoms occupy octahedral sites (Ward 1970). There are twice as many tetrahedral sites as octahedral sites (Wuensch 1974); the

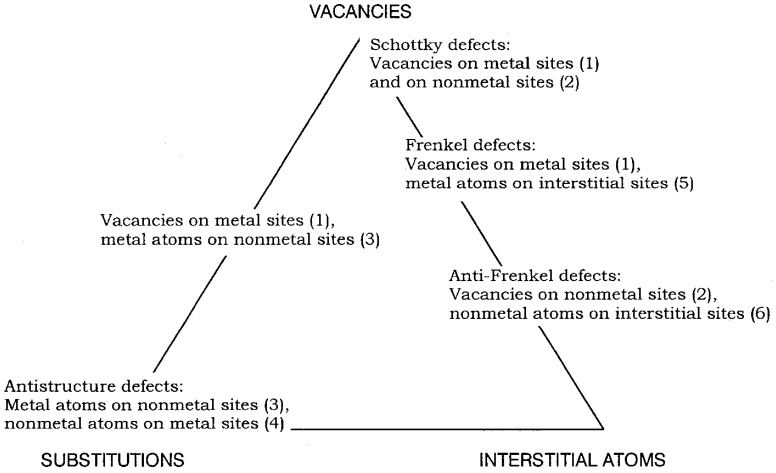

FIG. 1. Intrinsic defects (pairs of point defects) in binary compounds.

tetrahedral sites are vacant in perfectly ordered pyrrhotite, but could provide sites for interstitial atoms. The following species are considered:

Vacancies on Fe sites	$\square S(\square)_2$
S on Fe sites	$SS(\square)_2$
S on interstitial sites	$FeS(S)_2$
Vacancies on S sites	$Fe\square(\square)_2$
Fe on S sites	$FeFe(\square)_2$
Fe on interstitial sites	$FeS(Fe)_2$

In order to examine possible arrangements of point defects, it is convenient to write the reaction of formation for each defect species and to express the standard free energy of formation (ΔG^o) in terms of the fugacity of S_2 and the activities of species. The standard state of S_2 is the perfect gas at 1 atm at any temperature. The standard state of $FeS(\square)_2$ and all defect species is the perfectly ordered species at any temperature and 1 atm. At 1 atm, the unit activity state is equal to the standard state. In the simplest nonideal binary solution model, the activity coefficient γ of a species is related to the mole fraction N as follows (Guggenheim 1967):

$$RT \ln \gamma = w(1 - N)^2$$

where w is a coefficient depending on pressure and temperature. As $RT \ln \gamma$ is the excess partial molar free energy (Denbigh 1981), w is equal to the excess partial molar free energy at infinite dilution $G^{ex\,\infty}$ (Froese 1976), which is a measure of nonideality. The numerical value of $G^{ex\,\infty}$ is the same for both species. The letters X, Y, and Z will be used to designate mole fractions of a binary solution produced by mixing vacancies and atoms on the Fe, S, and interstitial sites, respectively. The equations involving ΔG^o have been rearranged, so that $G^{ex\,\infty}$ appears as the slope and ΔG^o as the intercept in a linear equation.

POINT DEFECTS IN S-RICH PYRRHOTITE

Three point defects are considered that could produce S-rich pyrrhotite.

Vacancies on Fe sites, producing the solid solution $FeS(\square)_2 - \square S(\square)_2$

$$\tfrac{1}{2} S_2\ (gas) = \square S(\square)_2 \qquad (1)$$

$$\Delta G^o_{(1)} = \tfrac{1}{2} RT \ln f_{S2} - RT \ln X_{\square S(\square)2} - G^{ex\,\infty}_{(1)} (1 - X_{\square S(\square)2})^2$$

$$RT\,(\tfrac{1}{2} \ln f_{S2} - \ln X_{\square S(\square)2}) = \Delta G^o_{(1)} + G^{ex\,\infty}_{(1)} (1 - X_{\square S(\square)2})^2$$

S on Fe sites, producing the solid solution $FeS(\square)_2 - SS(\square)_2$

$$S_2\ (gas) = SS(\square)_2 \qquad (2)$$

$$\Delta G^o_{(2)} = RT \ln f_{S2} - RT \ln X_{SS(\square)2} - G^{ex\,\infty}_{(2)} (1 - X_{SS(\square)2})^2$$

$$RT(\ln f_{S2} - \ln X_{SS(\square)2}) = \Delta G^o + G^{ex\,\infty}_{(2)} (1 - X_{SS(\square)2})^2$$

S on interstitial sites, producing the solid solution $FeS(\square)_2 - FeS(S)_2$

$$FeS(\square)_2 + S_2\ (gas) = FeS(S)_2 \qquad (3)$$

$$\Delta G^o_{(3)} = RT \ln f_{S2} + 2\,RT \ln Z_{FeS(\square)2} + 2G^{ex\,\infty}_{(3)} (1 - Z_{FeS(\square)2})^2 - 2\,RT \ln Z_{FeS(S)2} - 2G^{ex\,\infty}_{(3)} (1 - Z_{FeS(S)2})^2$$

$$RT(\tfrac{1}{2} \ln f_{S2} + \ln Z_{FeS(\square)2} - \ln Z_{FeS(S)2}) = \tfrac{1}{2}\Delta G_{(3)} + G^{ex\,\infty}_{(3)} [(1 - Z_{FeS(S)2})^2 - (1 - Z_{FeS(\square)2})^2]$$

A given composition of pyrrhotite, *e.g.*, S/Fe = 1.05168, can be expressed in terms of three possible mole fractions:

Vacancies on Fe sites:
$(Fe_{0.95086}\square_{0.04914})S(\square)_2$, $X_{\square S(\square)2} = 0.04914$

S on Fe sites:
$(Fe_{0.97481}S_{0.02519})S(\square)_2$, $X_{SS(\square)2} = 0.02519$

S on interstitial sites:
$FeS(\square_{0.97416}S_{0.02584})_{\Sigma 2}$, $Z_{FeS(S)2} = 0.02584$

Rau (1976) measured f_{S2} for pyrrhotite samples of known composition over a wide range of temperatures. To illustrate the deduced relationships, his values, at 1257 K, were used to solve equations (1), (2), and (3) for $G^{ex\,\infty}$ and ΔG^o. From a fit to all data points (Rau 1976), these values, in the case of vacancies on Fe sites, are:

Vacancies on Fe sites: $FeS(\square)_2 - \square S(\square)_2$

$$\overline{G}^{ex\,\infty}_{(1)} = -218\ 176\ \mathrm{J\ mol^{-1}}$$

$$\Delta G^o_{(1)} = 192\ 074\ \mathrm{J\ mol^{-1}}$$

This relationship has been shown graphically by Powell (1983) by plotting $RT(\tfrac{1}{2} \ln f_{S2} - \ln X_{\square S(\square)2})$ against $(1 - X_{\square S(\square)2})^2$. In the other two cases, approximate values were obtained from two data points (S/Fe = 1.05168 and 1.01239) with the following results:

S on Fe sites: $FeS(\square)_2 - SS(\square)_2$

$$\overline{G}^{\mathrm{ex}\,\infty}{}_{(2)} = -1\ 215\ 000\ \mathrm{J\ mol^{-1}}$$

S on interstitial sites: $\mathrm{FeS}(\square)_2 - \mathrm{FeS(S)}_2$

$$\overline{G}^{\mathrm{ex}\,\infty}{}_{(3)} = -453\ 000\ \mathrm{J\ mol^{-1}}$$

It is apparent that vacancies on Fe sites result in the least nonideal solution. Deviations from ideality are produced by choosing the wrong mixing species and by interaction between species. It is here assumed that the least nonideal solution represents the correct choice of mixing species, *i.e.*, in this case, vacancies on Fe sites. This conclusion is supported by density measurements (Hägg & Sucksdorff 1933).

POINT DEFECTS IN FE-RICH PYRRHOTITE

The method discussed for S-rich pyrrhotite can be used for Fe-rich pyrrhotite as well.

Vacancies on S sites, producing the solid solution $\mathrm{FeS}(\square)_2 - \mathrm{Fe}\square(\square)_2$

$$\mathrm{FeS}(\square)_2 = \mathrm{Fe}\square(\square)_2 + \tfrac{1}{2}\,\mathrm{S}_2\ (\mathrm{gas}) \qquad (4)$$

$$\Delta G^{\mathrm{o}}{}_{(4)} = RT \ln Y_{\mathrm{FeS}(\square)2} + \overline{G}^{\mathrm{ex}\,\infty}{}_{(4)}\,(1 - Y_{\mathrm{FeS}\,(\square)2})^2 - RT \ln Y_{\mathrm{Fe}\square(\square)2} - G^{\mathrm{ex}\,\infty}{}_{(4)}\,(1 - Y_{\mathrm{Fe}\square(\square)2})$$

$$-\tfrac{1}{2}\,RT \ln f_{\mathrm{S2}}$$

$$RT\,(\ln Y_{\mathrm{FeS}(\_)2} - Y_{\mathrm{Fe}\square(\square)2} - \tfrac{1}{2} \ln f_{\mathrm{S2}}) = \Delta G^{\mathrm{o}}{}_{(4)} + G^{\mathrm{ex}\,\infty}{}_{(4)}\,[(1 - Y_{\mathrm{Fe}\square(\square)2})^2 - (1 - Y_{\mathrm{FeS}(\square)2})^2)$$

Fe on S sites, producing the solid solution $\mathrm{FeS}(\square)_2 - \mathrm{FeFe}(\square)_2$

$$2\ \mathrm{FeS}(\square)_2 = \mathrm{FeFe}(\square)_2 + \mathrm{S}_2\ (\mathrm{gas}) \qquad (5)$$

$$\Delta G^{\mathrm{o}}{}_{(5)} = 2\,RT \ln Y_{\mathrm{FeS}(\square)2} + 2\,\overline{G}^{\mathrm{ex}\,\infty}{}_{(5)}\,(1 - Y_{\mathrm{FeS}(\square)2})^2 - RT \ln Y_{\mathrm{FeFe}(\square)2} - G^{\mathrm{ex}\,\infty}{}_{(5)}\,(1 - Y_{\mathrm{FeFe}(\square)2}) - RT \ln f_{\mathrm{S2}}$$

$$RT\,(2 \ln Y_{\mathrm{FeS}(\square)2} - \ln Y_{\mathrm{FeFe}(\square)2} - \ln f_{\mathrm{S2}}) = \Delta G^{\mathrm{o}}{}_{(5)} + G^{\mathrm{ex}\,\infty}{}_{(5)}\,[(1 - Y_{\mathrm{FeFe}(\square)2})^2 - 2(1 - Y_{\mathrm{FeS}(\square)2})^2]$$

Fe on interstitial sites, producing the solid solution $\mathrm{FeS}(\square)_2 - \mathrm{FeS(Fe)}_2$

$$3\ \mathrm{FeS}(\square)_2 = \mathrm{FeS(Fe)}_2 + \mathrm{S}_2\ (\mathrm{gas}) \qquad (6)$$

$$\Delta G^{\mathrm{o}}{}_{(6)} = 6\ \mathrm{RT} \ln Z_{\mathrm{FeS}(\square)2} + 6\,\overline{G}^{\mathrm{ex}\,\infty}{}_{(6)}\,(1 - Z_{\mathrm{FeS}(\square)2})^2 - 2\,RT \ln Z_{\mathrm{FeS(Fe)2}} - 2\,\overline{G}^{\mathrm{ex}\,\infty}{}_{(6)}\,(1 - Z_{\mathrm{FeS(Fe)2}}) - RT \ln f_{\mathrm{S2}}$$

$$RT\,(3 \ln Z_{\mathrm{FeS}(\square)2} - \ln Z_{\mathrm{FeS(Fe)2}} - \tfrac{1}{2} \ln f_{\mathrm{S2}}) = \tfrac{1}{2}\,\Delta G^{\mathrm{o}}{}_{(6)} + G^{\mathrm{ex}\,\infty}{}_{(6)}\,[(1 - Z_{\mathrm{FeS(Fe)2}})^2 - 3(1 - Z_{\mathrm{FeS}(\square)2})^2]$$

If measurements of f_{S2} and composition were available for Fe-enriched pyrrhotite, the same procedure to compare $G^{\mathrm{ex}\,\infty}$ for each solid solution could be used to determine the point defect that is dominant in Fe-rich pyrrhotite. This is not the case, and it is necessary to resort to a more complicated procedure. In S-rich pyrrhotite, for any given value of ln f_{S2}, the derived values of $\Delta G^{\mathrm{o}}{}_{(1)}$ and $G^{\mathrm{ex}\,\infty}{}_{(1)}$ can be used to calculated $X_{\square\mathrm{S}}$, which corresponds closely to the measured composition. However, as the stoichiometric composition is approached, the measured composition diverges from $X_{\square\mathrm{S}}$ owing to the presence of a second point defect. For example, at log $f_{\mathrm{S2}} = -6.727$, $X_{\square\mathrm{S}} = 0.00438$ (Rau 1976). This gives a composition of S/Fe = 1.00440, whereas the measured composition is 1.00126. Retaining $X_{\square\mathrm{S}} = 0.00438$, one of three possible defects can be introduced to account for the measured composition:

Vacancies on S sites
$(\mathrm{Fe}_{0.99562}\square_{0.00438})(\mathrm{S}_{0.99687}\square_{0.00313})(\square)_2$,
$Y_{\mathrm{Fe}\square(\square)2} = 0.00313$

Fe on S sites
$(\mathrm{Fe}_{0.99562}\square_{0.00438})(\mathrm{S}_{0.99844}\mathrm{Fe}_{0.00156})(\square)_2$,
$Y_{\mathrm{FeFe}(\square)2} = 0.00156$

Fe on interstitial sites
$(\mathrm{Fe}_{0.99562}\square_{0.00438})\mathrm{S}(\square_{0.99844}\mathrm{Fe}_{0.00156})_2$,
$Z_{\mathrm{FeS(Fe)2}} = 0.00156$

By regarding the Fe site as completely filled with Fe, mixing either on the S site or on the interstitial site can be treated as a binary solution. Solving the rearranged equation expressing the equilibrium constant for two data points (S/Fe = 1.00880 and 1.00126) gives the following results:

Vacancies on S sites
$\mathrm{FeS}(\square)_2 - \mathrm{Fe}\square(\square)_2$, $\overline{G}^{\mathrm{ex}\,\infty}{}_{(4)} = 1\ 922\ 000\ \mathrm{J\ mol^{-1}}$

Fe on S sites
$\mathrm{FeS}(\square)_2 - \mathrm{FeFe}(\square)_2$, $\overline{G}^{\mathrm{ex}\,\infty}{}_{(5)} = 147\ 000\ \mathrm{J\ mol^{-1}}$

Fe on interstitial sites
$\mathrm{FeS}(\square)_2 - \mathrm{FeS(Fe)}_2$, $\overline{G}^{\mathrm{ex}\,\infty}{}_{(6)} = 3\ 940\ 000\ \mathrm{J\ mol^{-1}}$

The values of $\overline{G}^{\mathrm{ex}\,\infty}$ are very sensitive to variations in composition; changing the composition from S/Fe = 1.00880 to 1.00878 produces the following results:

$$\overline{G}^{\mathrm{ex}\,\infty}{}_{(4)} = 1\ 852\ 000\ \mathrm{J\ mol^{-1}}$$

$$\overline{G}^{\mathrm{ex}\,\infty}{}_{(5)} = -9\ 000\ \mathrm{J\ mol^{-1}}$$

$$\overline{G}^{\mathrm{ex}\,\infty}{}_{(6)} = 3\ 711\ 000\ \mathrm{J\ mol^{-1}}$$

However, $FeS(\square)_2 - FeFe(\square)_2$ remains the least nonideal solution, which suggests that Fe on S sites is the most likely defect.

THERMODYNAMIC DATA

To illustrate the relationship between the fugacity of S_2 and the type of point defects present in a nonstoichiometric compound, the two defects in pyrrhotite have been deduced separately at an example temperature of 1257 K. On the other hand, Rau (1976) fitted simultaneously all his experimental data in the temperature range from 820 to 1374 K (listed in his Table 1) to equations involving f_{S2}, the composition of pyrrhotite, and various energy parameters deduced from general relationships given by Libowitz (1969). Assuming the solution $FeS(\square)_2 - FeFe(\square)_2$ to be ideal, he obtained three parameters A, B, and C related to $\Delta G^o_{(1)}$, $G^{ex\,\infty}_{(1)}$, and $\Delta G^o_{(5)}$ as follows:

$$A = -135\,922 + 87.367\,T = \Delta G^o_{(1)} + \bar{G}^{ex\,\infty}_{(1)} \text{ J mol}^{-1}$$

$$B = 185\,151 + 26.273\,T = -\bar{G}^{ex\,\infty}_{(1)} \text{ J mol}^{-1}$$

$$C = -514\,456 + 226.664\,T = -\Delta G^o_{(5)} \text{ J mol}^{-1}$$

Thus

$$\Delta G^o_{(1)} = \text{A} + \text{B} = 49\,229 + 113.640\,T \text{ J mol}^{-1}$$

The relationship between parameters A and B, on the one hand, and $\Delta G^o_{(1)}$ and $\bar{G}^{ex\,\infty}_{(1)}$, on the other, is best illustrated on a plot of G (chemical potential) *versus* ln X (Fig. 2), as suggested by Powell (1978) and used by Froese (1981).

Rau (1976) used a standard state of 1 atm for S_2. To convert to a 1 bar standard state:

$$\Delta G^o\text{ (1 bar)} = \Delta G^o\text{ (1 atm)} + nRT\int_{1.01325}^{1.0}(1/P)\mathrm{d}P$$

$$= \Delta G^o\text{ (1 atm)} - nT(0.109)$$

where n is the number of moles of gas produced in the reaction. Thus:

$$\Delta G^o_{(1)}\text{ (1 bar)} = 49\,229 + 113.695\,T \text{ J mol}^{-1}$$

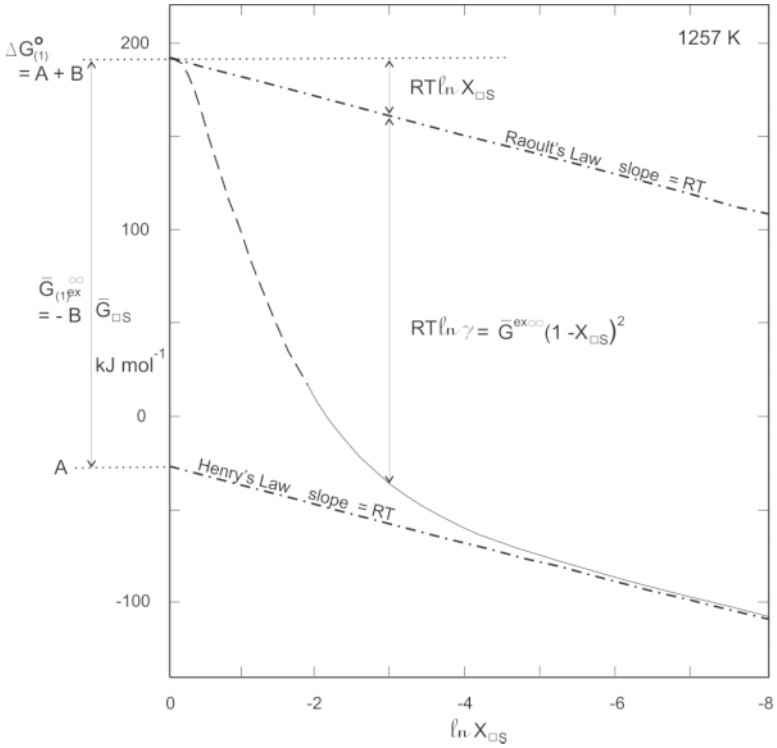

FIG. 2. The standard free energy of formation of □S ($\Delta G^o_{(1)}$) and the chemical potential of □S ($G_{\square S}$).

and

$$\Delta G^{o}_{(5)}\ (1\ \text{bar}) = 514\,457 - 226.773\ T\ \text{J mol}^{-1}$$

In S-rich pyrrhotite, knowing $\Delta G^{o}_{(1)}$ and $\overline{G}^{\text{ex}\,\infty}_{(1)}$, it is possible to calculate ln f_{S2} for any composition from the relationship

$$\tfrac{1}{2}\ S_2\ (\text{gas}) = \square S \qquad (1)$$

$$\Delta G^{o}_{(1)} = \tfrac{1}{2}\ RT \ln f_{S2} - RT \ln X_{\square S} - \overline{G}^{\text{ex}\,\infty}_{(1)}\ (1 - X_{\square S})^2$$

The corresponding activity of FeS in pyrrhotite follows from

$$RT \ln a_{FeS} = RT \ln X_{FeS} + \overline{G}^{\text{ex}\,\infty}_{(1)}\ (1 - X_{FeS})^2.$$

In Fe-rich pyrrhotite, ln f_{S2}, for any composition, is obtained from the relationship

$$2\ FeS = FeFe + S_2\ (\text{gas}) \qquad (5)$$

$$\Delta G^{o}_{(5)} = 2\ RT \ln Y_{FeS} - RT \ln Y_{FeFe} - RT \ln f_{S2}$$

and the corresponding activity of FeS is given by $a_{FeS} = X_{FeS}$ because the solution FeS – FeFe has been assumed to be ideal.

Near the stoichiometric composition, both point defects are present. For a given composition of pyrrhotite, those values of $X_{\square S}$ and Y_{FeFe} must be found which give the same log f_{S2} according to the equilibria of reactions (1) and (5). Thus at 1257 K, pyrrhotite of stoichiometric composition and with the following point defects $(Fe_{0.99606}\square_{0.00394})(S_{0.99803}Fe_{0.00197})$ gives nearly the same values of log f_{S2} (with f_{S2} in bars) of –6.830 and –6.829, according to reactions (1) and (5), respectively. In these calculations, the stoichiometric composition has been approximated as $(Fe_{0.99606}\square_{0.00394})S$ in the case of reaction (1) and $Fe(S_{0.99803}Fe_{0.00197})$ in the case of reaction (5), in order to apply the activity relationship for binary solutions.

In order to calculate the activity of FeS in the vicinity of the stoichiometric composition, it is necessary to abandon the binary solution model and consider the effect of mixing on both lattice sites by treating pyrrhotite as a reciprocal solution (Wood & Nicholls 1978). By neglecting any interaction between the two lattice sites, the activity FeS in pyrrhotite is given by

$$RT \ln a_{FeS} = RT \ln [Fe/(Fe + \square)] + RT \ln [S/(S + Fe)]$$

At 1257 K, the activity of FeS at the stoichiometric composition is 0.9941. For practical purposes, it can be taken as 1.0, and S-rich pyrrhotite can be regarded as a binary solution FeS – $\square$S with perfectly ordered end-members (Froese & Berman 1994). The difference in G between perfectly ordered FeS and real FeS, given by $RT \ln a$, is merely –62 J mol^{-1}. Calculated values of log f_{S2} and a_{FeS}, at 1257 K, as functions of composition are shown in Figure 3.

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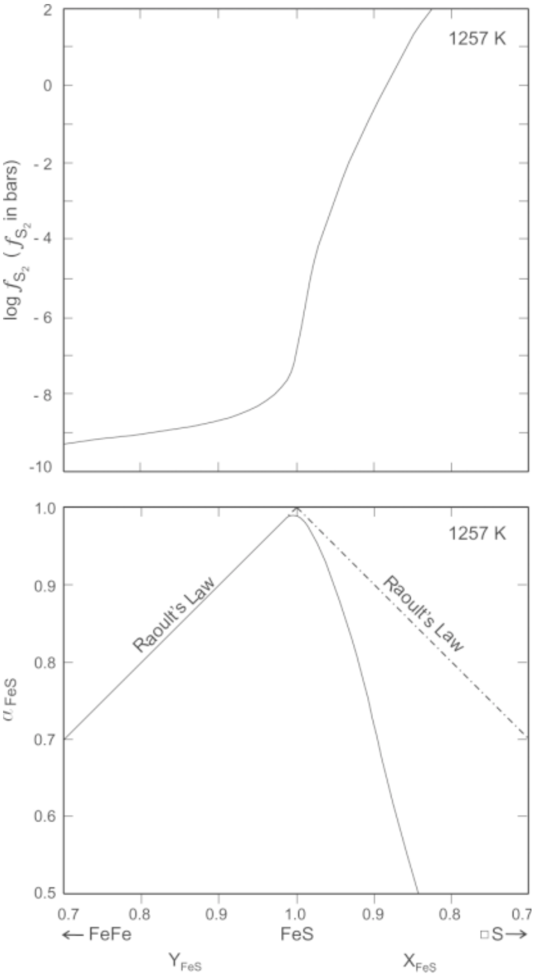

FIG. 3. Calculated thermodynamic properties of pyrrhotite.

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