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Thermodynamic mixing properties of pyrrhotine, $Fe_{1-X}S$

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ABSTRACT. Published data from pyrrhotine–vapour equilibrium experiments are used to make inferences concerning the high-temperature thermodynamic mixing properties of pyrrhotine. Darken's quadratic formalism provides the justification for plotting activity of sulphur data against $(1-X)^2$, where X is used in $Fe_{1-X}S$ to express the composition of non-stoichiometric pyrrhotine. Such plots show that the thermodynamic behaviour of pyrrhotine appears to be different on either side of $X = 0.125$, the Fe_7S_8 composition.

PYRRHOTINE occurs widely in rocks. Early hopes that the composition of pyrrhotine in the common assemblage pyrrhotine + pyrite might be used geothermometrically foundered when it was discovered that pyrrhotine re-equilibrated extremely readily on cooling (e.g. Barton and Skinner, 1979). Nevertheless, the thermodynamic properties of high-temperature, hexagonal pyrrhotine are of interest because they are required for the description of phase relations in several important systems, notably Fe–Zn–S and Fe–Ni–S. The thermodynamics of pyrrhotine is also of intrinsic interest because it involves understanding the formation of, and interactions between defects in a crystal structure. Pyrrhotine is a good phase in which to study defect equilibria because there is a considerable amount of published experimental data on the dependence of the activity of sulphur on the non-stoichiometry of pyrrhotine (Burgmann *et al.*, 1968; Rau, 1976; following the classic work of Toulmin and Barton, 1964).

The phase relationships in Fe–S are summarized by Craig and Scott (1974) and Vaughan and Craig (1978). Pyrrhotine is non-stoichiometric having excess sulphur compared with FeS. The non-stoichiometry in pyrrhotine in the assemblage pyrrhotine + pyrite ranges from $X \sim 0.099$ at 300 °C to $X \sim 0.179$ at 730 °C, the upper stability limit of pyrite at low pressure (e.g. Toulmin and Barton, 1964). Pyrrhotine which is in equilibrium with metallic iron is stoichiometric FeS within experimental error in this temperature range (e.g. Burgmann *et al.*, 1968). This asymmetry in the non-stoichiometry with respect to the composition FeS must reflect the radically different energetics involved in producing the defects to make Fe-excess and S-excess pyrrhotine. There is little doubt that the defects responsible for the non-stoichiometry in pyrrhotine are vacancies on the Fe site. As the stoichiometric composition is approached, a compensating defect having the potential to produce Fe-excess pyrrhotines becomes important. It has been suggested that these defects are interstitial Fe atoms (Libowitz, 1972), as in wüstite, or Fe atoms on the S site (Rau, 1976).

At temperatures above about 300 °C, the only stable pyrrhotine has a hexagonal NiAs structure in which the vacancies and Fe atoms on the Fe site are more or less randomly distributed. Nevertheless it might be expected that vacancies would show a preference for avoiding vacancy nearest neighbours. Below 300 °C various pyrrhotine superstructures appear (Kissin and Scott, 1982). These superstructures involve various optimal orderings of the vacancies, avoiding vacancy near neighbours. For example, 4*C* (monoclinic) pyrrhotine occurs at or near the Fe_7S_8 composition, and the vacancy ordering is well-understood for this composition, (e.g. Vaughan and Craig, 1978, 46–7).

Thermodynamics of pyrrhotine

Equilibrium between pyrrhotine and a vapour can be described using:

$$\tfrac{1}{2}\,\mu_{S_2,V} = \mu_{S,po} \qquad (1)$$

where μ_{ij} is the chemical potential of end-member i in phase j. Thus the first requirement is to formulate the chemical potential of sulphur in pyrrhotine for different models of the energetics of the phase.

Compositions away from stoichiometric FeS (say $X > 0.025$). Given that the defects in pyrrhotine with compositions away from stoichiometric FeS are Fe site vacancies, the formulation of the thermodynamics requires a decision on whether the species

mixing on the Fe site are considered to be charged or not. The natural choice is to consider mixing of Fe^{2+}, Fe^{3+} and variously ionized vacancies. However, it is relevant to note that pyrrhotine shows metallic conduction. The implication is that the excess negative charge involved in defect formation is delocalized and not trapped on the cations. Furthermore, the metallic electrons may effectively screen the charged vacancies, weakening the Coulombic interaction considerably. In this situation, the major interactions may well be due to local deformation of the structure produced by defect formation. Thus the thermodynamics is considered first in terms of mixing of effectively uncharged iron atoms and vacancies on the Fe site.

The interactions between the Fe atoms and the vacancies are likely to be very strong, vacancies preferring Fe rather than vacancy nearest neighbours. The simplest formulation incorporating this non-ideality is the regular model (e.g. Powell, 1977). The regular model involves non-zero interaction energies yet assumes random mixing. This logical inconsistency can be at least partly avoided by using the quasi-chemical model (e.g. Powell, 1983). However, numerical experiments (Church and Powell, unpubl.) show that for strong non-ideality, the quasi-chemical model seriously under-estimates short-range order. The unavoidable conclusion is that there is no realistic way of expressing the activity–composition relations in this case. Darken (1967), considering similarly complex thermodynamic data for alloy and other systems, showed that binary activity coefficient data plotted against $(1-x)^2$, where x is a bulk composition term, exhibited straight-line segments which are connected across transition regions whose composition ranges usually include the compositions of compounds which are stable at lower temperatures. This essentially empirical approach he calls the quadratic formalism.

A naïve justification for the form of plot advocated by Darken comes in fact from the regular model. Writing non-stoichiometric pyrrhotine as $Fe_{1-X}S$, the proportion of vacant iron sites

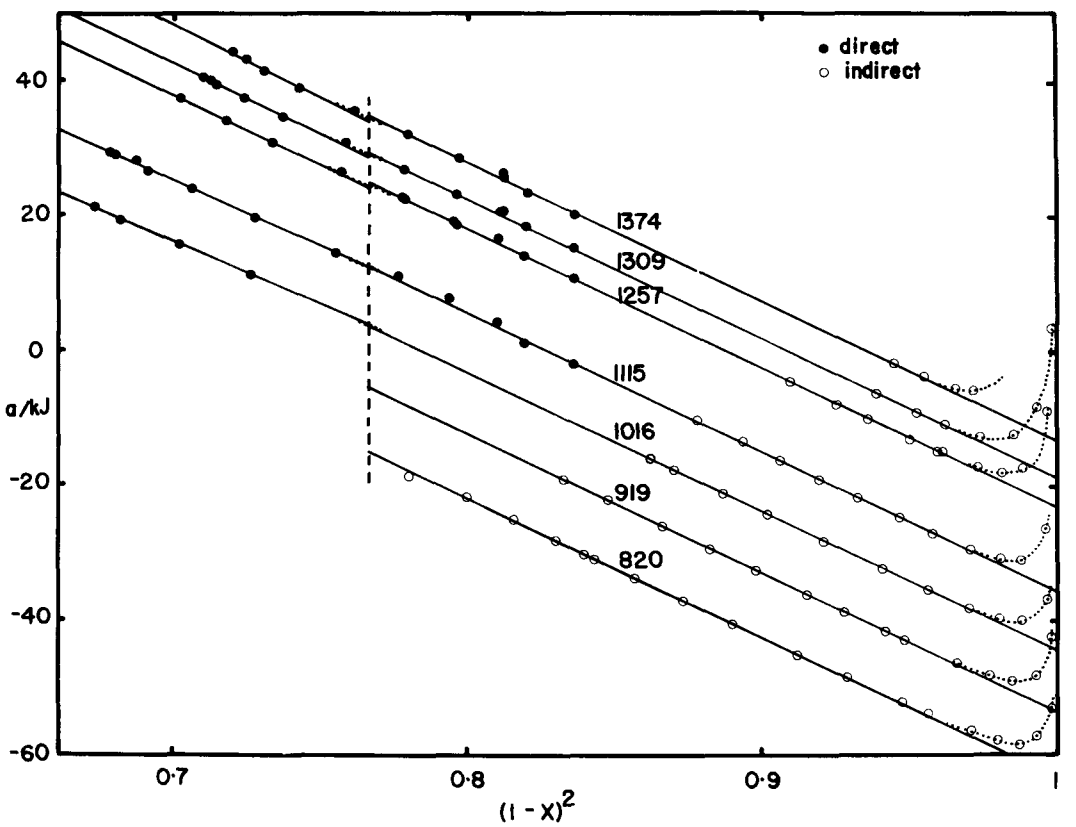

FIG. 1. The experimental data of Rau (1976) plotted as discussed in the text. a is defined by (3). The temperatures are in K. Note the transition in properties across $(1-X)^2 = 0.766$, ie. $X = 0.125$.

is simply X, and the proportion of filled sites is $(1-X)$. Then, for the regular model:

$$\mu_{S,po} = \mu_{\square S} = \mu^{\circ}_{\square S} + RT \ln X + w(1-X)^2 \quad (2)$$

where $w = 2\varepsilon_{Fe\square} - \varepsilon_{FeFe} - \varepsilon_{\square\square}$, and ε_{ij} is the energy of ij nearest neighbour pairs. Clearly w should be dominated by $\varepsilon_{\square\square}$, and thus we would expect w to be large and negative. Substituting (2) into (1) gives:

$$a = c + w(1-X)^2 \quad (3)$$

where: $$a = \tfrac{1}{2}RT \ln a_{S_2,V} - RT \ln X$$

$$c = \mu^{\circ}_{\square S} - \tfrac{1}{2}\mu^{\circ}_{S_2,V}$$

Plotting the data on a graph of a against $(1-X)^2$ conforms to Darken's quadratic formalism, so that linear segments might be expected at each temperature.

The data of Rau (1976), which are considerably more precise than those of Burgmann *et al.* (1968), are plotted in fig. 1. Rau's measurements involve direct and indirect sulphur activity measurements. Following Rau, the indirect data are not only extremely precise but also form an internally consistent data set, each data point being in error by the same value of X. The direct data, though less precise, are assumed to be accurate. Therefore the direct data provide a means of establishing the inaccuracy of the indirect data. Rau did this using all the direct data with a model which reduces to (2) for $X > 0.025$. However, careful perusal of the data reveals a change of behaviour across $X = 0.125$. This is discussed below. One consequence is that Rau's adjusted indirect measurements were readjusted fractionally (by $-0.003(1-X)$) to be consistent with only those direct measurements with $X < 0.125$.

Least squares regression of the data for $X > 0.125$ and $X < 0.125$ was undertaken to ascertain that a change in behaviour occurs across $X = 0.125$. The regression corresponds to using (3) empirically, so that the slope of each line in fig. 1 is w and the intercept is c. The compositions nearer stoichiometric FeS give a well-constrained temperature-independent w of -206 kJ, which is incidentally large and negative as predicted. The more non-stoichiometric compositions give a poorly constrained w, but which, nevertheless, is strongly temperature dependent. The two trends on fig. 2 appear to be statistically different. Having obtained w for the two composition ranges, the data were refitted to obtain the intercept c, fig. 3. Both trends are well-constrained. The data of Burgmann *et al.* (1968) are also included in fig. 3. Least squares of their data at each temperature gave 95% confidence bands which included the line for that temperature predicted from the Rau data. Thus, it appears that

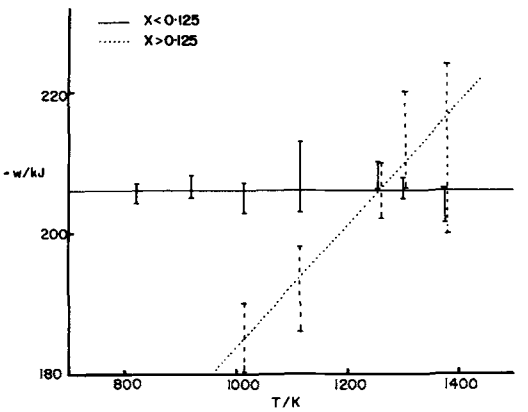

FIG. 2. The slope of the lines (w) in fig. 1 plotted against temperature. The brackets are two standard deviations from the linear least-squares regression of the data in fig. 1.

the data form two separate linear segments with a transition across $X = 0.125$ at each temperature, fig. 1. More data are required to confirm this conclusion, particularly at lower temperatures where the difference between the slopes of the two segments are larger. However, if this conclusion is correct, Darken (1967) provides an interesting explanation for the position of the transition between the segments. He suggests that smooth transitions in thermodynamic properties across particular compositions, revealed readily on plots of $RT \ln \gamma_1$ against $(1-x_1)^2$ for binary data, reflect

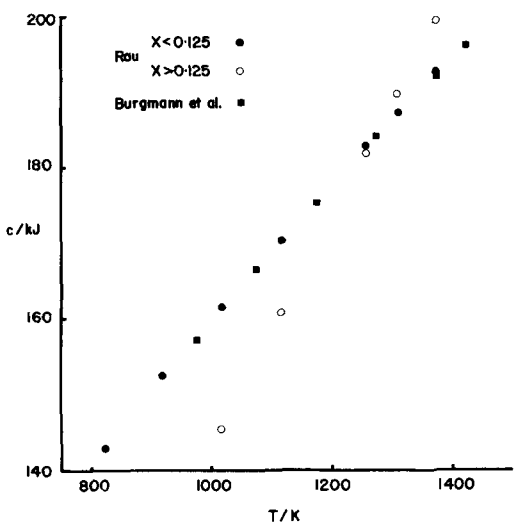

FIG. 3. The intercept of the lines (c) in fig. 1 plotted against temperature. The uncertainties on the points are less than the size of the symbols.

optimal ordering in the structure, which, enhanced by decreasing temperature, leads to compound formation at low temperature. In this case, the compositon $X \sim 0.125$, corresponds to the important low temperature pyrrhotine structure, 4*C* pyrrhotine, or rather to a composition with a particularly favourable ordering of vacancies. It does seem reasonable that the favourable nature of this ordering should be reflected in the higher temperature thermodynamic properties given the large negative interaction energies implied by fig. 2.

The alternative formulation of the thermodynamics involves charged ions and vacancies. Again using the regular model and assuming un-ionized vacancies, the chemical potential of sulphur is:

$$\mu_{S,po} = \mu^{\circ}_{\square S} + RT \ln X \left(\frac{2X}{1-3X}\right)^2 + \\ + \text{terms quadratic in } X$$

Appropriate plots do not show the required form, even with the extra adjustable parameter. This approach does not appear to be useful.

Compositions near stoichiometric FeS. It would be pleasing to account for the departure from the linear trends in fig. 1 near stoichiometry and thus to predict the compensating defect accounting for the intrinsic disorder in stoichiometric FeS. Rau (1976) did this and predicted that the defect involved is Fe atoms on S sites. However there is a serious problem here because small adjustments to the indirect data have a profound effect on those measurements with small X, precisely those data being considered. The fractional readjustment of Rau's indirect data justified above makes a Schottky defect model more appropriate than the iron on sulphur site model of Rau. Note, however, that this attempt at distinguishing between defect models involves serious assumptions about the appropriateness of simplistic thermodynamic models; even if the treatment of Rau's indirect data is appropriate, the conclusion that Schottky defects are involved may not be correct.

Discussion

The main conclusion of this study is that the mixing properties of pyrrhotine are more complex than previously suggested. The different thermodynamic behaviour of pyrrhotine in the two composition ranges (figs. 1–3) is important because it means that measurements of, for example, volume or phase boundary relationships for one composition range cannot be extrapolated into the other composition range.

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