Thermodynamic data for Fe-bearing phases obtained using noble metal alloys as redox sensors

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Abstract—The technique of using noble metal alloys as redox sensors has been adapted for use in hydrothermal experiments in the piston-cylinder apparatus at the reduced conditions of the iron-wüstite (IW) buffer. The required high f'O₂ was maintained for several days using thick-walled (0.5 mm) Ag outer capsules. Such conditions permit the Gibbs free energy of Fe²⁺-bearing phases to be obtained from the composition of the co-existing alloy. The Ir-Fe system is more amenable than either Pt-Fe or Pd-Fe since only one phase (γ-fcc) is stable in this system over a large temperature range, and the solubility of Ag (capsule material) in Ir is negligible.

Experiments with the assemblage fayalite-quartz-Fe (in alloy) (QFI) were used as a test of the method by comparison with the electrochemical measurements of O'Neill (1987a). The resulting agreement demonstrates the utility of the method between 700 and 1000°C at ~10 kbar. Further experiments with FeSiO₃-bearing assemblages (ferrosilite-quartz-iron, PYQI, and ferrosilite-fayalite-iron, PYFAI) indicate the method is viable up to 20 kbar and between 700°C and 1000°C. However, small systematic deviations of about 1–2 kJ per mole of O₂ in the quartz-saturated experiments are interpreted to indicate that the high solubility of SiO₂ at high pressures may result in a lowering of the H₂O activity in the co-existing supercritical fluid phase.

1. INTRODUCTION

The thermodynamic properties of oxides and silicates containing transition metals or other easily reducible elements are commonly obtained from the study of reduction reactions of the type:

\[ \text{MO}_x(\Omega O) = M + x/2 \text{O}_2 \]  

where x is the valence state of the metal, M, and (\(\Omega O\)) refers to silicate or aluminosilicate, etc. At equilibrium, the Gibbs free energy of such reactions is related to the oxygen fugacity \(f_{O_2}\), by the relation:

\[ -\Delta G^\circ = RT \ln \left[ \frac{a(M)a(\Omega O)}{a_{\text{MO}_x(\Omega O)}} \right] + x/2 RT \ln f_{O_2} \]  

Hence, when the phases are pure, determination of the equilibrium \(f_{O_2}\) suffices to define the free energy of the reaction. Oxygen fugacity is a parameter that can be measured or continuously varied by several well established means. For example, O’Neill (1987a) determined the free energy of formation of fayalite by electrochemically measuring the equilibrium \(f_{O_2}\) between fayalite, quartz, and iron metal (QFI)

\[ \text{Fe}_2\text{SiO}_4 = 2 \text{Fe} + \text{SiO}_2 + \text{O}_2 \]  

Combining these data with previously well-determined thermodynamic data for Fe metal and quartz yielded precise values for the \(\Delta G^\circ\) for fayalite. This method has been applied to a number of other phases such as hercynite spinel (Chau et al., 1973), ilmenite (O’Neill et al., 1988), Ni₂SiO₄ (O’Neill, 1987b), Co₂SiO₄ (O’Neill, 1987b), almandine garnet (Woodland and Wood, 1989) as well as simple oxides (e.g., Holmes et al., 1986). However, the electrochemical method is currently limited to phases that are stable at atmospheric pressure and, most importantly, that display favourable reaction kinetics (e.g., O’Neill and Pownceby, 1993).

An alternative approach for studying redox reactions is to impose an accurately known fixed \(f_{O_2}\), and to vary the activity of M (\(a(M)\)) by alloying M with an otherwise inert noble metal. Thus, for the above QFI equilibrium with a noble metal alloy substituted for the pure Fe metal, we have, at constant temperature and pressure and pure fayalite and quartz:

\[ \log K_1 = 2 \log a_{\text{Fe}}^{\text{all}} + \log f_{O_2} \]  

By externally fixing the \(f_{O_2}\) at the iron-wüstite (IW) buffer, for example, the activity of Fe is then fixed in this divariant assemblage. Measuring the activity of Fe from the alloy composition then allows the equilibrium constant, \(K_1\), to be determined for each temperature and pressure. With this value and appropriate data for Fe metal and quartz, the \(\Delta G^\circ\) for fayalite can then be derived. There are a number of advantages to this approach. The experiments can be performed theoretically at any pressure and temperature conditions below the melting point of the binary alloy. Second, the experiments can be performed in the presence of H₂O using the double capsule technique to control the \(f_{O_2}\) (Eugster, 1957). Thus, hydrous as well as anhydrous phases can be studied. The presence of H₂O also acts to enhance reaction rates. Potentially, this method can yield very precise results.
down to the ±100 J/mol range. Taylor et al. (1992) have described the use of several simple metal-metal oxide assemblages as potential monitors of the redox state in experiments. Their method is based upon displacing the Ni-NiO or Co-CoO oxygen buffer assemblages either by equilibrating the pure metal with a binary oxide solid solution or by equilibrating the pure oxide with a binary alloy containing Pd. The NiO-Ni,Pd, assemblage was successfully employed by Pownceby and O’Neill (1994) to measure and calibrate the position of the Re-ReO2 oxygen buffer in T-f space.

Iron is the most important transition element from a geological point of view. Therefore, it would be of great interest to be able to apply the noble alloy redox sensor method to extract the thermodynamic properties of Fe-bearing phases. Applying the method to Fe-bearing assemblages, however, requires a number of special experimental conditions which are not easily attained in many experimental apparatuses (see section 2). In this work, we describe a method for determining the properties of Fe-bearing phases by using noble metal alloys in piston-cylinder experiments. After outlining the experimental technique, we proceed with examples of the QF1 equilibria and ferrosilite-bearing equilibria as tests of the method. Previously, Jamieson et al. (1992) and Gudmundsson and Wood (1995) used somewhat similar methods to monitor the fo2 imposed by graphite capsules in piston-cylinder experiments. After outlining the experimental technique, we proceed with examples of the QF1 equilibria and ferrosilite-bearing equilibria as tests of the method. Previously, Jamieson et al. (1992) and Gudmundsson and Wood (1995) used somewhat similar methods to monitor the fo2 imposed by graphite capsules in piston-cylinder experiments.

Adapting the redox sensor approach, for example as outlined by Taylor et al. (1992) for Ni and Co equilibria, to Fe-bearing assemblages involves several important modifications. First, the method loses accuracy as the activity of Fe decreases, leading to unacceptable large errors when AT is less than about 0.1. Consequently, the imposed fo2 should not be much more than about two log-bar units above that of the target univariant equilibrium. It is also desirable to work under reducing conditions in order to minimize the possibility of formation of Fe2+ during the experiment and to be certain, therefore, that the correct phase stoichiometry is maintained. These considerations make the IW buffer the logical choice for the imposed fo2. However, such reduced conditions are not readily attainable in cold seal bombs. This is because the bombs are made of a Ni-bearing alloy which imparts an intrinsic fo2 close to Ni-NiO. The result is that even the Co-CoO buffer (Δlogfo2 CoCoO – IW = 2.15 at 800°C; O’Neill and Pownceby, 1993) is difficult to maintain for the necessary length of time to achieve equilibrium in an experiment (M. Pownceby, pers. commun.). Reaching and maintaining the reducing conditions of the IW buffer are also problematic in internally heated pressure vessels, even when employing a Shaw membrane to control the fo2. These experimental difficulties are directly attributable to the high fo2 of an O-H fluid in equilibrium with the IW buffer. We are able to achieve such high fo2 in the piston-cylinder apparatus and maintain them for long periods up to at least 5 days.

2.1. The Capsule Arrangement

In order to impose a particular fo2 on the sample assemblage during the experiment, we have employed the traditional double-capsule technique (Eugster, 1957). The outer capsule that contains the solid buffer assemblage + H2O along with the sample capsule must be relatively impermeable to H2. Otherwise, the correct fo2 will not be imposed upon the inner sample capsule long enough for equilibrium to be assured in the sample assemblage. Our outer capsules are made of very thick-walled (0.5 mm) Ag obtained by drilling a 4 mm hole in 5 mm diameter rods of 99.95% Ag (Goodfellow GmbH). The choice of Ag as capsule material was based upon three factors: (1) Ag is relatively impermeable to H2 with a performance similar to that of Au (Chou, 1986), (2) there is virtually no alloying between Ag and Fe, which could be a problem with Au at such reduced conditions (Massalski, 1986), and (3) Ag is relatively inexpensive, often costing less than high purity Fe. In addition to the intrinsic behaviour of Ag, we have relied on the 0.5 mm thick capsule walls to inhibit H2 escape during the experiment. A sketch of the capsule arrangement is presented in Fig. 1. The base of the capsule is ~1 mm thick. The capsule is sealed by hammering a 1 mm thick Ag friction-fitting lid in place and introducing a further 1 mm thick Ag disc on top. We find that during the initial stages of compression and heating in the piston-cylinder, a cold weld is formed between the capsule and the two discs (see Fig. 1), thereby rendering the capsule watertight. After the experiment, it is virtually impossible to separate the Ag disc from the rest of the capsule. The only major drawback to using Ag is its relatively low melting point which restricts the maximum temperature of the experiment. However, the melting point of Ag does increase with increasing pressure (Mirwald and Kennedy, 1979), and from our experience, experiments up to 975°C can be reliably made at 10–12 kbar. When the melting point is too closely approached, the Ag loses its strength and water can escape from the capsule. On the other hand, when the temperature is too low, the Ag is not malleable enough to form a cold weld and water can also escape. By slightly modifying the experimental procedures (see section 2.4.), a temperature range of 700°C–1000°C can readily be achieved between 10 and 20 kbar.

The inner capsule must be relatively permeable to H2 so that the oxygen buffer can impose the correct fo2 on the sample assemblage. Taylor et al. (1992) and Pownceby and O’Neill (1994) used Pt as an inner capsule material with an inner ZrO2 sleeve to prevent reaction between the sample and the capsule. However, their experiments were performed at much lower pressures in the Ni-O and Co-O systems. This arrangement proved ineffective for sample assemblages containing Fe, Ti, and/or Si at the conditions of the piston-cylinder experiments. In experiments involving silicates, Si in solution reacted with the ZrO2 sleeve, producing euhedral zircon and thereby altering the bulk composition of the sample. Reaction was also observed between the sleeve and Ti-bearing phases. Furthermore, Fe was freely transported in solution alloying extensive alloying with the Pt capsule, despite the physical barrier of the ZrO2 sleeve. In one experiment with ilmenite and rutile in the sample assemblage, all the ilmenite was eliminated due to Fe loss to the
The activity-composition relations of T-IX-Fe alloys only one stable form, fcc γ-Ir-Fe, between 650°C and 1400°C across bearing experiments and up to ~0.2 mol% in the Pt alloys. A correction for the activity coefficient, γ_yFe, is provided in Table I along with the corresponding 1σ uncertainties in the fit parameters, which are 1.5–2.0 kJ mol⁻¹ in magnitude.

2.3. Sample Preparation
Sample mixes were prepared by gently grinding under ethanol, high purity, fine powdered powders of Ir metal (nominally <60 μm, 99.9% purity) and Fe metal (99.9% purity). In practice, most of the Ir metal grains were found to be <10 μm across. Use of powders rather than a piece of wire was deemed advantageous on the grounds that (1) equilibration times for <60 μm grains would be much faster, (2) less mass of Ir and Fe could be used, and (3) the Ir would be more evenly distributed throughout the sample. The relative proportions of Ir and Fe were set from the anticipated final composition of the alloy. This Ir-Fe powder mixture was then used as a feedstock for a series of experiments. In essence, we used mechanical mixtures of Ir and Fe metal in our experiments. A drawback to our method is that it is not feasible to produce Fe-bearing Ir powders, as presintering results in a large slag of alloys. Obtaining fine-grained powder from such a metallic slug is difficult without introducing unacceptable contamination. This precludes the possibility of approaching the equilibrium alloy composition from the direction of relatively Fe-rich compositions, which would correspond to approaching equilibrium from relatively reducing conditions. It is possible, however, to conduct experiments at different pressures or with different imposed f₀₂ buffers. Although the direction of approach to equilibrium is the same, different alloy compositions would be obtained at constant temperature and would provide further confidence that equilibrium was reached.

The sample assemblage was produced by gently grinding together, under ethanol, the desired silicate and/or oxide phases with 6–8 wt% of the Ir-Fe powder mixture. When working with SiO₂-bearing assemblages, care must be made to assure that enough quartz is added to account for the high solubilities of SiO₂ in supercritical solutions (i.e., Walther and Helgeson, 1977). The sample mixture was packed into 2 mm diameter thin-walled Ag capsules, which were then welded shut after the addition of ~2 drops of distilled H₂O from a microliter pipette. Once they are carefully flattened, up to three sample capsules can conveniently fit into the outer capsule along with ~0.2 g of the IW buffer assemblage. The f₀₂ buffer is an 80–20% by weight mixture of Fe metal and wüstite to which 30–35 mg of distilled H₂O are added. The capsule is then closed by hammering a friction-fitting lid in place (Fig. 1).

2.4. Experimental Procedure and an Initial Test
The experiments were performed between 700°C and 1000°C in a piston-cylinder apparatus using talc-Pyrex pressure cells 1.905 cm in diameter with a tapered graphite heater. The temperature was controlled by means of a Pt-PtRh₀.₅ thermocouple with no correction for the effect of pressure on the emf. The thermocouple bead was positioned ~1 mm above the capsule by means of a crushable alumina spacer to prevent contamination from the Ag capsule. Thermal gradients were considered to be minimal across the sample capsules in light of (1) the large mass of Ag in the outer capsule which is a very efficient thermal conductor, (2) the presence of >160 mg of Fe metal in the buffer assemblage surrounding the sample capsules, and (3) the presence of a fluid phase inside the outer capsule which would be free to circulate and further reduce any temperature differences. In an effort to better seal the outer capsule at the outset of the experiment, the piston-out technique was used. The oil pressure was reduced to the desired value after ~1 h.

Due to the problematic nature of calibrating the pressure in piston-out experiments, the pressure correction was taken to be half of that determined from piston-in experiments. Details of the piston-in calibration are given in Woodland and O’Neill (1993). The uncertainty in the pressure is estimated to be ±1 kbar. The effect of this pressure uncertainty on the resulting thermodynamic properties of a particular phase is directly related to the difference between the ΔV of the sample reaction and the ΔV of the IW equilibrium. For
example, a difference in $\Delta V$ for the two reactions of 0.1 J bar$^{-1}$ results in an uncertainty in the $\Delta G$ of the sample reaction of $\pm 100$ J per mole of O$_2$. The duration of the experiments varied with temperature: 1 day for experiments at $>900^\circ$C, 1–2 days for experiments at 850°C and 900°C, 2–4 days at 800°C, and 4–5 days for experiments $>800^\circ$C. The experiments were terminated by turning off the power. The initial quench rate was on the order of 30–40°C s$^{-1}$ so that the thermocouple temperature always read below 200°C after 20 s, independent of the initial run temperature.

Upon retrieval from the pressure cell, the outer capsule was pierced with a small drillbit under a binocular microscope. After warming the capsule, it was dried at 150°C and weighed again to determine the amount of H$_2$O remaining in the buffer assemblage. When desired, it was possible to open the sample capsules and remove some of the material for XRD analysis. This allowed the unit cell parameters of the oxide and/or silicate phases to be checked to detect any shift in composition during the experiment. The sample capsules were then mounted in epoxy and prepared for microprobe analysis. Impregnation of the soft sample material was necessary. The alloy grains were analysed using Cameca SX50 (Bayreuth) and Cameca SX51 (Heidelberg) electron microprobes operating at 15 kV and a sample current of 20 nA in wavelength dispersive mode. Pure metals were used as standards (same mount for both microprobes) with counting times on both the peak and background of 20 s. The raw counts were recalculated using the PAP correction program supplied by Cameca.

Although the presence of H$_2$O in the outer Ag capsule after an experiment readily demonstrates that the capsule was effectively sealed, it was apparent that some H$_2$O was always lost at the onset of the experiment during the initial compression. Upon heating, the Ag disc, lid, and body of the capsule (Fig. 1) rapidly formed a cold weld which then sealed the remaining H$_2$O inside the capsule for the remainder of the experiment. The sealing behaviour of the outer Ag capsule was found to be very good above 800°C. However, below this temperature, the Ag was apparently not malleable enough to reliably form a cold weld before all H$_2$O had escaped. To mitigate this problem, we found it sufficient to initially heat the experiment at 900°C for 12 min and then ramp down to the desired temperature at a rate of 10°C min$^{-1}$. Thus, within 32 min (for the 700°C experiments) or less, the sample was brought to the desired temperature and the outer capsule was effectively sealed. With this technique, we can perform experiments reliably down to 700°C and maintain about 1/3 or more of the initial amount of H$_2$O (8–19 mg for experiments at 700°C) in the outer capsule. We did not attempt experiments at temperatures below 700°C.

To demonstrate that a reduced $f_{0_2}$ and, therefore, a high $f_{0_2}$ corresponding to the IW buffer could be produced and maintained in our experimental arrangement, we performed an experiment with dry hematite in the sample capsule at 1000°C and 18.7 kbar for 45.5 h (with piston-in mode). The resulting black powder in the sample capsule was identified by optical observation and XRD analysis as wüstite with a trace of Fe metal. Therefore, we concluded that our capsule arrangement could not only maintain the IW buffer for nearly 2 days at 1000°C, but that the correct $f_{0_2}$ was imposed inside the sample capsule. Imposition of the correct $f_{0_2}$ inside the sample capsules at lower temperatures, where H$_2$O diffusion is slower, is demonstrated by the results of the experiments with the quartz-fayalite-alloy assemblage described below.

### 3. TREATMENT OF DATA

Derivation of the standard thermodynamic properties of Fe-bearing phases from the experimental technique described above involves three steps: (1) calculation of the $\Delta G^o$ of the equilibrium of interest at the pressure and temperature of the experiments via a mass action equation, (2) extrapolation of these results to 1 bar, and (3) extraction of the standard free energy of formation of the desired phase by application of available thermodynamic data for the other co-existing phases. As is conventional, a mixed standard state was used in the thermodynamic calculations, with the solid phases referenced to the pure phase at the pressure and temperature of the experiment, while for O$_2$ the standard state was 1 bar and the temperature of the experiment. Because the $\alpha$–$\gamma$ transition in Fe occurs within the temperature and pressure range of our experiments and the Ir-Fe alloy has the fcc ($\gamma$) structure, we chose to reference all our calculations relative to $\gamma$-Fe and then make the necessary small correction to those experiments in the $\alpha$-Fe field at the end of the computation. The $\Delta G^o_{\gamma \rightarrow \alpha}$ transition in Fe was described by equation (1) of Kaufman et al. (1963), and is given in Table 1. The molar volume of $\gamma$-Fe alloys was estimated by fitting the molar volume data for $\gamma$-Ir-Fe alloys from Raub et al. (1964) and Schwertfeger and Zwell (1968), which yielded $V_{\gamma \rightarrow \alpha} = 0.6922 (12) $ J bar$^{-1}$ (Table 1). Combining this result with the thermal expansion of $\gamma$-Fe derived from the data of Basinski et al. (1955) and Kohlhaas et al. (1967) and assuming the compressibility of $\gamma$-Fe is similar to that of $\alpha$-Fe (6.01 $\times$ 10$^{-7}$ bar$^{-1}$; Guinian and Beshers, 1968), we obtain the expression for $V_{\gamma \rightarrow \alpha}^o$ given in Table 1. Likewise, the partial molar volume of $\gamma$-Fe in $\gamma$-Ir-Fe alloy as a function of composition was obtained from the data of Raub et al. (1964) and Schwertfeger and Zwell (1968). By assuming the same thermal expansion and compressibility constants as for pure $\gamma$-Fe, an expression for the partial molar volume of $\gamma$-Fe in the $\gamma$-Ir-Fe alloys can be derived as a function of temperature and pressure (Table 1).

<table>
<thead>
<tr>
<th>Table 1. Some thermodynamic properties of $\gamma$-Fe-Ir alloys, $\gamma$-Fe and the iron-wüstite (IW) equilibrium.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\gamma \rightarrow \alpha}$ = 0.6922 (12) $\times$ 10$^{-7}$ (T - 298) - (6.01 $\times$ 10$^{-7}$ P)</td>
</tr>
<tr>
<td>$V_{\alpha \rightarrow \gamma}$ = 0.6922 (12) + 0.0736 (12) X$_{Fe}$</td>
</tr>
<tr>
<td>$\Delta G^o_{\gamma \rightarrow \alpha}$ = -17.361 + 115.424 $\times$ 14.1112 $\times$ T</td>
</tr>
<tr>
<td>$\Delta G^o_{\alpha \rightarrow \gamma}$ = -545964 + 217.4937 - 0.81937 $\times$ T - 0.002557 $\times$ T</td>
</tr>
<tr>
<td>$RT$ ln $\gamma$-Fe$^o$ = $X_2$ $\times$ [57305 - 5491 (3 $X_2$ - $X_{Ir}$)]</td>
</tr>
</tbody>
</table>

References: 1, Raub et al. (1964); 2, Schwertfeger and Zwell (1968); 3, Basinski et al. (1955); 4, Kohlhaas et al. (1967); 5, Kaufman et al. (1963); 6, IW equilibrium. O’Neill and Pownceby (1993) corrected for 3'-Fe, valid from 960 K-1644 K; 7, Swartzendruber (1984); quoted 1σ uncertainties are ±57305(2000) and ±5491(1500) J mol$^{-1}$.
Thermodynamic properties of Fe-bearing phases

Table 2. Results from QFI experiments employing γ-Ir-Fe alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Pressure (kbar)</th>
<th>Time (hr)</th>
<th>2RT log ( a_{Fe}^{\text{eq}} )</th>
<th>( \Delta G_{\text{T, eq}}(\text{QFI})^* )</th>
<th>( \Delta G_{\text{T, eq}}(\text{QFI})^{**} )</th>
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<tbody>
<tr>
<td>aw72</td>
<td>700</td>
<td>10.5</td>
<td>23.0</td>
<td>0.6256 (31)</td>
<td>25.97 (37)</td>
<td>416.97</td>
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<tr>
<td>aw74</td>
<td>700</td>
<td>10.2</td>
<td>67.0</td>
<td>0.6247 (45)</td>
<td>26.07 (53)</td>
<td>414.71</td>
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<tr>
<td>aw76</td>
<td>700</td>
<td>10.2</td>
<td>69.0</td>
<td>0.6338 (51)</td>
<td>25.01 (59)</td>
<td>416.34</td>
</tr>
<tr>
<td>aw92</td>
<td>700</td>
<td>11.0</td>
<td>93.0</td>
<td>0.6558 (66)</td>
<td>22.52 (73)</td>
<td>422.98</td>
</tr>
<tr>
<td>aw119</td>
<td>700</td>
<td>10.9</td>
<td>98.5</td>
<td>0.6313 (75)</td>
<td>25.26 (88)</td>
<td>415.83</td>
</tr>
<tr>
<td>aw103</td>
<td>700</td>
<td>10.5</td>
<td>95.0</td>
<td>0.6572 (86)</td>
<td>23.22 (75)</td>
<td>417.28</td>
</tr>
<tr>
<td>aw88</td>
<td>800</td>
<td>10.5</td>
<td>23.0</td>
<td>0.6612 (79)</td>
<td>22.61 (88)</td>
<td>410.17</td>
</tr>
<tr>
<td>aw75a</td>
<td>900</td>
<td>10.0</td>
<td>43.0</td>
<td>0.6789 (41)</td>
<td>21.31 (45)</td>
<td>386.11</td>
</tr>
<tr>
<td>aw75b</td>
<td>900</td>
<td>10.0</td>
<td>43.0</td>
<td>0.6732 (46)</td>
<td>21.79 (51)</td>
<td>386.74</td>
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<tr>
<td>aw70</td>
<td>950</td>
<td>10.6</td>
<td>20.5</td>
<td>0.6732 (43)</td>
<td>22.27 (50)</td>
<td>379.81</td>
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<tr>
<td>aw71</td>
<td>950</td>
<td>10.4</td>
<td>19.0</td>
<td>0.6934 (42)</td>
<td>20.05 (48)</td>
<td>377.80</td>
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<tr>
<td>aw114</td>
<td>950</td>
<td>10.3</td>
<td>29.0</td>
<td>0.6713 (51)</td>
<td>22.49 (58)</td>
<td>380.35</td>
</tr>
<tr>
<td>aw90</td>
<td>1000</td>
<td>10.5</td>
<td>24.0</td>
<td>0.6886 (29)</td>
<td>20.88 (32)</td>
<td>371.95</td>
</tr>
<tr>
<td>aw105</td>
<td>1000</td>
<td>10.4</td>
<td>28.0</td>
<td>0.6939 (56)</td>
<td>20.30 (61)</td>
<td>371.48</td>
</tr>
</tbody>
</table>

Short duration experiment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Pressure (kbar)</th>
<th>Time (hr)</th>
<th>2RT log ( a_{Fe}^{\text{eq}} )</th>
<th>( \Delta G_{\text{T, eq}}(\text{QFI})^* )</th>
<th>( \Delta G_{\text{T, eq}}(\text{QFI})^{**} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>aw88coarse</td>
<td>800</td>
<td>11.0</td>
<td>2.5</td>
<td>0.6240 (74)</td>
<td>25.32 (89)</td>
<td>402.35</td>
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<td>aw88hiFe</td>
<td>800</td>
<td>11.0</td>
<td>2.5</td>
<td>0.6398 (53)</td>
<td>23.77 (62)</td>
<td>400.78</td>
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<tr>
<td>aw88hiFe</td>
<td>800</td>
<td>11.0</td>
<td>2.5</td>
<td>0.6469 (73)</td>
<td>22.94 (84)</td>
<td>399.96</td>
</tr>
</tbody>
</table>

* All values referenced to γ-Fe.
** Extrapolated to 1 bar using data of Holland and Powell (1990, vers. 2.3, data: 11.06.94). At \( T < 910°C \), values referenced to α-Fe.

stable γ-Fe-wüstite equilibrium at temperatures <1163 K (Table 1). Extrapolation to the conditions of the experiments was performed by using the data in Table 1 for γ-Fe and the respective values of \( 3.6 \times 10^{-4} \) K\(^{-1} \) and \( 6.452 \times 10^{-3} \) bar\(^{-1} \) for the thermal expansion and compressibility of wüstite with the reference composition Fe\(_{0.9470}\)O (Jackson et al., 1990). The activity of Fe in the experimental assemblage was derived from the analysed Ir-Fe alloy compositions. \( \Delta G_{\text{T, eq}}^{\gamma}(\text{QFI}) \) was corrected to 1 bar using the molar volume thermal expansion and compressibility data of Holland and Powell (1990, vers. 2.3, data: 11.06.94) for the various silicate phases in the assemblage. Final extraction of the \( \Delta G_{\text{T, eq}}^{\alpha}(1 \text{ bar}) \) for the phase of interest was achieved using thermodynamic data of Holland and Powell (1990, vers. 2.3, data: 11.06.94) for the co-existing phases.

4. THE QFI EQUILIBRIUM: A TEST OF THE METHOD

The QFI equilibrium was considered to be a good test of the method since precise thermodynamic data for this equilibrium are available (O’Neill, 1987a) with which we can compare our experimental results. Over the last 40 yr, a number of measurements of the QFI equilibrium have been made using various methods, with most of these studies lying within ±4.0 kJ mol\(^{-1} \) of the calibration of O’Neill (1987a). In light of this general agreement and the fact that the results of O’Neill (1987a) also agree with published calorimetric data for the participating phases, we have chosen the data of O’Neill (1987a) as our reference for the QFI equilibrium at 1 bar total pressure. The interested reader is referred to the discussion in O’Neill (1987a) for a comparison with the other published studies. A series of experiments were performed at a pressure of ~10 kbar. The alloy composition under these conditions ranged from \( X_{\text{Fe}}^{\text{eq}} = 0.62 \) to 0.69 (Table 2). The resulting free energy of the QFI equilibrium extrapolated to 1 bar pressure is given in Table 2 and compared with the data of O’Neill (1987a) in Fig. 3. Agreement is very good over the entire temperature range, with most experiments yielding values within ±1 kJ per mole of the determination by O’Neill (1987). The error bars shown in Fig. 3 only consider the uncertainty due to the alloy composition. The uncertainty in the pressure determination of each experiment contributes relatively little to the overall uncertainty in the \( \Delta G_{\text{T}}^{\gamma}(\text{QFI}) \) of the QFI equilibrium; an uncertainty of 1 kbar pressure yields an additional uncertainty of...
<100 J per mole O₂. The reproducibility of our hydrothermal method can also be considered to be good as judged by the results of repeated experiments at the same temperature which generally agree with each other within their uncertainties (Fig. 3). At 700°C, a maximum variation of \(X_{\text{Fe}_{2}SiO_{4}}\) \(= 0.03\) in the alloy composition between five experiments leads to a range in \(\Delta G_{\text{F}; \text{bar}}\) of about 3.5 kJ mol\(^{-1}\) (Table 1).

As a test of the kinetics of equilibration in our hydrothermal experiments, we performed an experiment at 800°C with three separate sample capsules containing different quartz-fayalite-Ir-Fe mixtures and terminated the run after 2.5 h. Capsule A contained a mechanical mixture of <60 μm Ir metal and Fe metal powders in the proportions 0.25 Ir:0.75 Fe. Extremely fine grained iodridium black was combined with Fe metal in capsules B and C in the proportions 0.5 Ir:0.5 Fe and 0.25 Ir:0.75 Fe, respectively. The resulting \(\Delta G\) computed for each of these three samples lies within 2.5 kJ/mol of the value of O’Neill (1987a), indicating that the approach to equilibrium is rapid under hydrothermal conditions (Table 2, Fig. 3). The availability of reduced Fe and the grain size of the Ir are important in determining the rate of equilibration. As a result of this test, we employed mixtures that were relatively Fe-rich in our further experiments. However, due to analytical difficulties with the very fine grained iridium black starting material, we opted to continue using the coarser form of Ir. We considered that since the composition of the coarser alloy was already within a few mole% of the equilibrium composition after only 2.5 h, equilibrium would be readily achieved in the 48 h duration of a normal experiment at this temperature.

The apparent rapid approach to equilibrium and the consistent results compared with literature data for the QFI equilibrium leads us to conclude that (1) the relatively reduced IW reference oxygen buffer can be maintained for long periods, up to 5 days at 700°C; (2) Ir-Fe alloys can be used as redox sensors (or as monitors of \(a_{\text{O}}\)) in hydrothermal experiments; and (3) precise thermodynamic data (+1 kJ per mole O₂) can be retrieved from experiments over a temperature range of 700°C–1000°C.

### 5. Experiments with Ferrosilite: A Further Test of the Method

To assess the applicability of our experimental method to higher pressures, we investigated two equilibria involving orthoferrosilite:

\[
2 \text{FeSiO}_3 = 2 \text{Fe} + 2 \text{SiO}_2 + \text{O}_2 \quad (\text{PYQI})
\]

and

\[
2 \text{Fe}_2\text{SiO}_4 = 2 \text{Fe}_2\text{SiO}_3 + 2 \text{Fe} + \text{O}_2 \quad (\text{PYFAI})
\]

The advantage in investigating these two equilibria is that (1) the properties of all phases are well known and (2) the combination of the results from the PYQI and PYFAI equilibria yields a further measure of the QFI equilibrium, and comparison with the lower pressure QFI experiments described above permits us to rigorously investigate the effects of pressure in our hydrothermal experiments. In addition, this ‘cross-referencing’ allows us to build up an internally consistent set of thermodynamic data for Fe-bearing phases.

Experiments involving the PYQI and PYFAI equilibria were performed at ~17 kbar and the results are summarized in Table 3. By adding \(\Delta G_{\text{QFI}\text{1 bar}}\) (PYQI) to \(\Delta G_{\text{QFI}\text{1 bar}}\) (PYFAI) and dividing by two, we arrive at the \(\Delta G_{\text{QFI}\text{1 bar}}\) for the QFI equilibrium. The results of this calculation are compared with those from the previously described QFI experiments and with the data from O’Neill (1987a) in Fig. 4. Agreement is generally very good; however, there is a systematic difference of about 1–2 kJ per mole O₂ between the ferrosilite-bearing experiments and the determination of O’Neill (1987a). Although the difference is only slightly larger than the combined uncertainties from the PYQI and PYFAI equilibria, its systematic nature suggests a minor problem exists with the experiments involving one or the other of the pyroxene-bearing equilibria. Resolution of this discrepancy can be addressed by modifying the above procedure and considering each of the ferrosilite-bearing equilibria separately in combination with the QFI equilibrium. Subtraction of \(\Delta G_{\text{QFI}}\) from \(\Delta G_{\text{PYFAI}}\) yields the \(\Delta G\) of ferrosilite from fayalite and quartz:

\[
2 \text{FeSiO}_3 = \text{Fe}_2\text{SiO}_3 + \text{SiO}_2 \quad (\text{PYFAQ})
\]

Likewise, subtraction of \(\Delta G_{\text{PYFAI}}\) from \(\Delta G_{\text{QFI}}\) yields the \(\Delta G\) of the PYFAQ equilibrium. For the most part, the results derived from the PYFAI experiments agree with those computed from Holland and Powell (1990, vers. 2.3, data: 11.06.94), within their mutual uncertainties (Fig. 5). The uncertainty in the Holland and Powell (1990) data shown in Fig. 5 was derived from the correlation matrix computed by their program for the PYFAQ equilibrium. On the other hand, results from the PYQI experiments tend to lie just outside the band of acceptable values from Holland and Powell (1990, vers. 2.3, data: 11.06.94), suggesting it is the PYQI experiments that are responsible for the small systematic deviation observed in Fig. 4 between the ferrosilite-bearing experiments and the QFI experiments. The deviations in the PYQI experiments and the agreement of the PYFAI experiments are even more apparent when compared with a newer version of the Holland and Powell data set (\(\Delta G_{\text{PYFAQ}}\) is shifted to more negative values on the order of 0.5 kJ mol\(^{-1}\) relative to the curve shown in Fig. 5; T. Holland, pers. commun.). The same behaviour is also observed when the data set of Wood (1987) is used as a comparison instead of Holland and Powell (1990): \(\Delta G\) values of the PYFAQ equilibrium derived from the PYFAI experiments agree with those calculated from Wood (1987) while the PYQI experiments yield \(\Delta G\) values that are less negative by 1–2 kJ. A possible explanation for the deviation of the PYQI experiments is that since the assemblage is quartz saturated, the high solubility of SiO₂ under supercritical conditions could act to lower the activity of H₂O in the fluid phase. This, in turn, would slightly shift the \(f_0\) in the inner sample capsule at constant \(f_{0\text{H}}\), which is externally buffered by the IW assemblage in the outer capsule. The end result is that the \(\Delta G_{\text{PYFAQ}}\) calculated from the alloy composition is slightly less negative by about 1–2 kJ per mole O₂ than it should be. For example, at 800°C this difference would
Thermodynamic properties of Fe-bearing phases

Table 3. Results from ferrosilite-bearing experiments employing γ-Fe alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Pressure (kbar)</th>
<th>Time hr</th>
<th>2 ( RT \log a^{\text{Fe}}_{\text{Fe}} ) kJ</th>
<th>( \Delta G_{f}^{\text{ref}} ) kJ</th>
<th>( \Delta G_{f}^{\text{bar}} ) kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>aw131</td>
<td>700</td>
<td>17.3</td>
<td>118.0</td>
<td>0.6082 (99)</td>
<td>−28.05 (1.20)</td>
<td>411.71</td>
</tr>
<tr>
<td>aw118</td>
<td>750</td>
<td>16.6</td>
<td>98.0</td>
<td>0.6291 (46)</td>
<td>−25.94 (55)</td>
<td>403.61</td>
</tr>
<tr>
<td>aw122</td>
<td>800</td>
<td>16.5</td>
<td>92.0</td>
<td>0.6324 (63)</td>
<td>−25.93 (75)</td>
<td>396.99</td>
</tr>
<tr>
<td>aw125</td>
<td>850</td>
<td>17.2</td>
<td>26.3</td>
<td>0.6400 (53)</td>
<td>−25.41 (63)</td>
<td>389.04</td>
</tr>
<tr>
<td>aw112</td>
<td>900</td>
<td>17.3</td>
<td>98.5</td>
<td>0.6558 (49)</td>
<td>−23.92 (57)</td>
<td>381.03</td>
</tr>
<tr>
<td>aw116</td>
<td>900</td>
<td>17.2</td>
<td>28.0</td>
<td>0.6509 (60)</td>
<td>−24.49 (70)</td>
<td>381.5249</td>
</tr>
<tr>
<td>aw115</td>
<td>950</td>
<td>17.3</td>
<td>27.3</td>
<td>0.6620 (54)</td>
<td>−23.55 (63)</td>
<td>373.83</td>
</tr>
</tbody>
</table>

PYFAI experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Pressure (kbar)</th>
<th>Time hr</th>
<th>2 ( RT \log a^{\text{Fe}}_{\text{Fe}} ) kJ</th>
<th>( \Delta G_{f}^{\text{ref}} ) kJ</th>
<th>( \Delta G_{f}^{\text{bar}} ) kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>aw131</td>
<td>700</td>
<td>17.3</td>
<td>118.0</td>
<td>0.6487 (49)</td>
<td>−23.31 (55)</td>
<td>406.97</td>
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<tr>
<td>aw118</td>
<td>750</td>
<td>16.6</td>
<td>98.0</td>
<td>0.6416 (68)</td>
<td>−24.39 (67)</td>
<td>402.05</td>
</tr>
<tr>
<td>aw122</td>
<td>800</td>
<td>16.5</td>
<td>92.0</td>
<td>0.6613 (43)</td>
<td>−22.60 (48)</td>
<td>393.67</td>
</tr>
<tr>
<td>aw124</td>
<td>850</td>
<td>17.2</td>
<td>46.0</td>
<td>0.6565 (61)</td>
<td>−23.49 (70)</td>
<td>387.13</td>
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<tr>
<td>aw116</td>
<td>900</td>
<td>17.2</td>
<td>28.0</td>
<td>0.6747 (65)</td>
<td>−21.78 (70)</td>
<td>378.77</td>
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<tr>
<td>aw115</td>
<td>950</td>
<td>17.3</td>
<td>27.3</td>
<td>0.6821 (53)</td>
<td>−21.28 (59)</td>
<td>371.56</td>
</tr>
</tbody>
</table>

* All values referenced to γ-Fe.
** Extrapolated to 1 bar using data of Holland and Powell (1990, vers. 2.3, data: 11.06.94).

At \( T < 910°C \), values are referenced to α-Fe.

The observed larger discrepancy at higher temperature is consistent with the expectation that the solubility of SiO2 will increase with increasing temperature as well as pressure (e.g., Walther and Helgeson, 1977; Manning, 1994).

In summary, the results of the ferrosilite-bearing experiments involving the PYQI and PYFAI equilibria demonstrate that the IW oxygen buffer can be maintained even at pressures approaching 20 kb at 700–950°C. Thermodynamic analysis of these two equilibria suggests that at such high pressures and under quartz saturation, the high solubility of SiO2 in the supercritical fluid can effectively lower the activity of H2O, thereby causing measurable changes in the thermodynamic properties derived for a particular phase or phase assemblage. This effect can be minimized by choosing a sample assemblage that is not quartz saturated. On the other hand, a further implication of these observations is that this type of redox experiment, using noble metal alloys, could be applied to the determination of the thermodynamic properties of complex supercritical fluids, particularly at high pressures and temperatures.

Fig. 4. Free energy of the QFI equilibrium determined by combination of the results of the pyroxene-bearing, PYQI and PYFAI, experiments as a function of temperature, extrapolated to 1 bar. The results from our QFI experiments (this study) and data from O’Neill (1987a) are shown for reference as open diamonds and open squares, respectively.

Fig. 5. Plot of \( \Delta G^o \) for the reaction ferrosilite = fayalite + quartz (PYFAQ) as a function of temperature at 1 bar. Circles denote results obtained from the PYQI experiments in combination with the data for QFI from O’Neill (1987a). Squares denote results obtained from the PYFAI experiments also in combination with the same QFI data. The errors shown include the uncertainty related to the alloy composition and that due to an uncertainty of ±1 kbar in the pressure of the experiments (≈±200 J and ≈±100 J for the PYQI and PYFAI equilibria, respectively, per mole O2). The position of the PYFAQ reaction, along with the propagated uncertainty dashed lines, calculated from the data of Holland and Powell (1990, vers. 2.3, data: 11.06.94), is shown for comparison.
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