Thermodynamic properties of the Pt-Fe system

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ABSTRACT

We determined activity-composition relationships for the Pt-Fe system by equilibrating Fe-oxides with Pt-Fe alloys at temperatures in the range of 1200–1400 °C and oxygen fugacities from 1.6 to 7.7 log units above the iron-wüstite (IW) buffer. The system is characterized by strong negative deviations from ideality throughout the investigated temperature range (e.g., $\gamma^{alloy}_{Fe} > 0.02$ for $X^{alloy}_{Fe} < 0.3$). Our data are consistent with an asymmetric regular solution of the form:

$$RT \ln \gamma^{alloy}_{Fe} = [W_{Fe} + 2(W_{Fe} - W_{Si})X^{alloy}_{Fe}](X^{alloy}_{Fe})^{-1}$$

where $W_{Fe} = -138.0 \pm 3.3$ kJ/mol and $W_{Si} = -90.8 \pm 24.0$ kJ/mol (1σ). Based on experiments at 1200–1400 °C, variations in the activity coefficients at a given composition are consistent with $\ln \gamma^{alloy}_{Fe}(T)/\ln \gamma^{alloy}_{Fe}(T) = T_f/T_f$.

The Pt-Fe alloy composition in equilibrium with a FeO-bearing silicate liquid can be obtained from:

$$\log f_O^{alloy} = \log \{\exp [\ln a_{FeO}^{alloy} - \ln a_{SiO_2}^{alloy} - 2\ln a_{FeO}^{alloy} - (\Delta G_f^{alloy})/RT]\}$$

where $\Delta G_f^{alloy}$ is the standard state free energy for the reaction $2Fe^{alloy} + O_2^{alloy} + SiO_2^{alloy} = Fe_2SiO_4^{alloy}$. We obtained values of $a_{FeO}^{alloy}$ from our model and used the program MELTS together with the thermodynamic properties of these elements to evaluate activities of SiO$_2$ and Fe$_2$SiO$_4$ components in the liquid and $\Delta G_f^{alloy}$. We provide sample calculations showing how to predict the optimum Fe concentrations for pre-saturation of Pt-bearing containers to reduce Fe loss from the charge during experiments on magmatic liquids at high temperatures and pressures from 1 atm to 40 kbar.

INTRODUCTION

Among the primary goals of experimental petrology is the simulation of processes within the Earth and other terrestrial planets and the determination of physical and thermodynamic properties of relevant solid and liquid phases. Iron is an ubiquitous element in these systems and there continues to be a search for suitable container materials for experimentation involving Fe-bearing samples. Some prospective materials are limited by their low melting points (e.g., Ag, Au) and/or their tendency to interact with the sample (e.g., SiO$_2$, Al$_2$O$_3$, Mo), whereas others can only be used under relatively reducing conditions (e.g., Mo, graphite). In many respects, Pt is an ideal container material: it can be used at high temperatures (e.g., 1600 °C); it is stable over a wide range of $f_O$; and, in many systems, it is essentially inert. Unfortunately, the use of Pt for Fe-bearing systems is complicated by a complete solid solution that stretches across the Pt-Fe join between 1350 and 1500 °C, and by the occurrence of solid solutions and stable intermetallic compounds at lower temperatures (Hultgren et al. 1973). This can lead to serious problems as Fe-loss from a sample in contact with Pt can significantly change the phase equilibria (e.g., Bowen and Schairer 1932; Presnall and Brenner 1974). In addition, for experiments in sealed capsules, loss of Fe to a Pt capsule leads to the release of O$_2$ and a change in the oxidation state of the sample (Merrill and Wyllie 1973; Stern and Wyllie 1975). A less widely recognized potential problem in gas-mixing furnaces is the possible contamination of thermocouples and of electrodes for oxygen sensors because of Fe vaporizing from samples, which could lead to errors in the measurement of temperature and $f_O$.

The problems associated with loss of Fe to a Pt sample container can be minimized by using a pre-saturated Pt-Fe alloy that, at the oxygen fugacity of the experiment, has a Fe content close to that of an alloy in equilibrium with the experimental charge. Grove (1981) showed through characterization of Fe partitioning between Pt-Fe alloys and coexisting phases how the alloy composition can be customized such that Fe gain or loss from the charge is minimized. Pt-Fe alloys can also be used to determine the thermodynamic properties of coexisting Fe-bearing phases if the activity-composition relations of the alloy are known. Moreover, if the oxygen fugacity is known, Pt-Fe alloys can also be used to determine the activities of Fe-oxide components (e.g., FeO, Fe$_2$O$_3$) in coexisting oxide and silicate phases (e.g., Nolan 1977; Gudmundsson and Holloway...