Thermodynamic properties of alloys of gold-74/palladium-26 with variable amounts of iron and the use of Au-Pd-Fe alloys as containers for experimental petrology

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ABSTRACT

Iron oxide-alloy equilibration experiments were conducted in H\textsubscript{2}-CO\textsubscript{2} gas mixtures at 1 atm and 1125–1240 °C using strips of Au\textsubscript{97}Pd\textsubscript{3} (wt%) and produced Au-Pd-Fe alloys with 0.03–13 wt% iron. A thermodynamic calibration for the mixing of Au\textsubscript{97}Pd\textsubscript{3} with iron using an asymmetric regular solution leads to $W_{\text{G-Fe}} = -45.0 \pm 1.8$ kJ/mol and $W_{\text{G-AuPd}} = +19.5 \pm 7.7$ kJ/mol (1σ). Internal oxidation of iron was observed in a reversal experiment, suggesting that oxygen can be transferred across capsule boundaries during high-temperature experiments. This thermodynamic calibration is applicable to a wide range of oxygen fugacities and iron activities relevant to petrological and metallurgical applications at 1 atm and, as previous studies suggest excess volumes in this system are small, it can also be used to predict Fe activities in experiments at elevated pressure (up to 3 GPa). By pre-doping Au-Pd capsules to match Fe activities expected for the sample during an experiment, it is possible to maintain samples with little to no loss of iron. Pre-saturation of the capsule also provides a method for controlling the oxygen fugacity of samples if no formal oxygen buffer is available.

Keywords: Gold-palladium, capsules, iron, internal oxidation

INTRODUCTION

Understanding rock-forming processes in planetary bodies requires production of equilibrated samples covering a considerable range of temperatures, pressures, and compositions. Investigation of high-temperature and high-pressure metamorphism or melting of rocks presents special challenges because of the potential for interactions between the sample and its surroundings. Often, an experimental charge is encapsulated in a precious metal with a high melting point, such as Pt, Au, or Ag (e.g., Chou 1986; Kawamoto and Hirose 1994), but under conditions of geologic interest, these materials can interact with the sample and provide a conduit for interactions between the sample and the external medium.

For volatile-bearing experiments at low temperatures, gold capsules are commonly used, as this metal has a low diffusivity for hydrogen and other volatile elements (e.g., Wyllie and Tuttle 1961; Chou 1986; Truckenbrodt and Johannes 1999), but the relatively low melting point of Au makes it inappropriate for many problems relevant to the Earth’s interior. Au-Pd alloys melt at higher temperatures than pure Au (Okamoto and Massalski 1985), but retain the desirable property of slow hydrogen diffusion (e.g., Mas and Flanagan 1973). Unfortunately, Au-Pd alloys can also dissolve large amounts of Fe from a sample while at high temperature, making it difficult to establish equilibrium or to interpret the observed phase chemistry (e.g., Hall et al. 2004). The use of Au-Pd alloys to enclose Fe-bearing samples therefore requires understanding the issue of Fe solubility.

Iron solubility in Pt, a commonly used container material in experimental petrology, has long been a problem, and approaches similar to those used to mitigate Fe-loss to Pt capsules may also be applicable to Au-Pd capsules. Commonly applied techniques include graphite capsule liners to separate the sample from the container (e.g., Arndt 1976; Harrison 1981; Médard et al. 2008), restricting experiments to highly oxidizing conditions where the Fe solubility is low (e.g., Hall et al. 2004), and pre-doping of the container with Fe before use (e.g., Grove 1981; Aubaud et al. 2008). In principle, Fe-doping is the most flexible of these mitigation methods. Graphite liners or highly oxidizing environments limit the redox conditions that can be explored (and may contaminate the sample with carbon), whereas Fe contents of pre-doped containers can, in principle, be prepared to match a wide variety of conditions. In practice, however, pre-saturation is a Goldilocks problem. Just the right amount of Fe must be introduced; if too much Fe is introduced, the sample will gain Fe from the container; if too little Fe is introduced there will be Fe loss to the container. Furthermore, oxygen fugacity changes can be imposed on capsules from elsewhere in the assembly, such as from the heating element, making control even more difficult. Previous approaches to this problem for Au-Pd alloys have been largely ad hoc. For example, several authors, including Gaetani and Grove (1998), Kägi et al. (2005), Aubaud et al. (2008), and Botcharnikov et al. (2008) prepared Au-Pd capsules by first pre-saturating them in a gas mixing furnace at 1 atm using liquids similar to the ones expected at high pressure. This step adds Fe to the capsule material, but locating the conditions at 1 atm needed to saturate Au-Pd with the proper amount of Fe for a high-pressure experiment is an empirical and arduous process. Moreover, even after the correct 1 atm pre-doping conditions are determined for one high-pressure experiment, these conditions will differ from those needed for the next experiment in...