

A METHOD FOR THE EXTRACTION OF THERMODYNAMIC PROPERTIES OF ALLOYS WHICH ARE SPARINGLY SOLUBLE IN SILICATE MELTS AT HIGH TEMPERATURE.
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Introduction: Thermodynamic solution properties for alloys at high temperature may be obtained by two classes of methods. There are direct methods including vapor pressure measurement techniques (such as the Knudsen cell effusion method) and high temperature calorimetric techniques. Indirect methods can also be used by a judicious choice of phase equilibria experiments. It is usually the case that the direct measurements are technically difficult to perform, while many of the indirect methods suffer from the requirement that they depend on values of thermodynamic parameters of other phases participating in the equilibria. For temperatures where many alloys are liquid most direct measurements are not feasible, and knowledge of the thermodynamic behavior for the solid alloys in the liquidus regime will often depend on long extrapolations through temperature space. Outlined below is an indirect method for obtaining alloy properties which does not rely on values of thermodynamic properties for any of the other participating phases.

We use silicate melts in equilibrium with alloys to record the alloy component activities at high temperature and then quench the melt to a glass to measure the concentrations of dissolved alloy. It is essential only that both alloy components be in the Henry's Law concentration regime in the silicate melt. The equilibration of each alloy must then be made under the same conditions because the Henry's Law constants are functions of bulk melt composition, temperature and pressure. If these requirements are satisfied it is possible to devise experiments to extract the thermodynamic behavior of alloys under extreme conditions where direct thermodynamic measurements would be impossible. For instance, equilibration of metals (molten or solid) with silicate melts in piston cylinder apparatus or other currently available high pressure equipment would allow the extraction of the thermodynamic properties of alloys relevant to core formation. In this latter case, low solubilities for Fe components in the melt could be obtained by fixing an appropriately low oxygen fugacity for equilibration. **Method:** Capobianco *et al.* (1990) report solubility experiments for noble metal alloys in a silicate system. Consider the equilibration of Au-Pd alloys at 1450°C with a silicate melt in air to derive the required expression. With the assumption of Henrian behavior in the silicate melt for the alloy components,

$$\mu_{\text{Au}}^{\text{sil}} = \mu_{\text{Au}}^{\text{sil}} + RT \ln h_{\text{Au}} + RT \ln X_{\text{Au}}^{\text{sil}} \quad (1)$$

where h_{Au} is the Henry's Law constant for Au in

the silicate melt (sil), $X_{\text{Au}}^{\text{sil}}$ is the mole fraction of Au in (sil) and $\mu_{\text{Au}}^{\text{sil}}$ is the standard state chemical potential for Au in the silicate. At equilibrium the chemical potential for Au in the alloy equals the Au chemical potential in the silicate melt. We parameterize the mixing behavior in the alloy using a simple one parameter regular solution model as in equation (2).

$$\mu_{\text{Au}}^{\text{alloy}} = \mu_{\text{Au}}^{\text{alloy}} + \Omega(1 - X_{\text{Au}}^{\text{alloy}})^2 + RT \ln X_{\text{Au}}^{\text{alloy}} \quad (2)$$

In this equation Ω is the parameter we wish to determine for the alloy. By equating (1) to (2) and combining constant terms into K_{Au} one obtains equation (3).

$$K_{\text{Au}} + RT \ln X_{\text{Au}}^{\text{sil}} = \Omega(1 - X_{\text{Au}}^{\text{alloy}})^2 + RT \ln X_{\text{Au}}^{\text{alloy}} \quad (3)$$

A similar equation can be written for the Pd component yielding equation (4a).

$$K_{\text{Pd}} + RT \ln X_{\text{Pd}}^{\text{sil}} = RT \ln X_{\text{Pd}}^{\text{alloy}} + \Omega(1 - X_{\text{Pd}}^{\text{alloy}})^2 \quad (4a)$$

By making the substitution $X_{\text{Au}}^{\text{alloy}} = 1 - X_{\text{Pd}}^{\text{alloy}}$ in equation (4a) we get (4b).

$$K_{\text{Pd}} + RT \ln X_{\text{Pd}}^{\text{sil}} = RT \ln (1 - X_{\text{Au}}^{\text{alloy}}) + \Omega(X_{\text{Au}}^{\text{alloy}})^2 \quad (4b)$$

Now, subtracting (4b) from (3) produces equation (5).

$$\Delta K + \ln \left[\left(\frac{X_{\text{Au}}}{X_{\text{Pd}}} \right)_{\text{sil}} \left(\frac{1 - X_{\text{Au}}}{X_{\text{Au}}} \right)_{\text{alloy}} \right] = \Omega'(1 - 2X_{\text{Au}}^{\text{alloy}}) \quad (5)$$

Equation (5) may now be used to advantage to determine $\Omega' = \Omega/RT$ for the alloys equilibrated because equation (5) is linear on a plot of the right-hand side against the logarithmic term. The slope on such a plot gives directly the interaction parameter. Due to the logarithmic ordinate the method is not sensitive to systematic errors in the values of the solubilities in the silicate melt. If, for instance, all of the solubility measurements for one component were systematically too high by a constant factor that factor would change the intercept of the plot but not the slope. In fact, both components may be off by different constant factors and it still would not make a difference to the determination of Ω . Note also that the only thermodynamic data required are phase compositions, and temperature of equilibration.

An added advantage comes from the fact that both components must be sparingly soluble in the silicate melt because this allows a further simplification in the calculation of X_i^{sil} 's.

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$$X_{Au}^{sil} = \left[\frac{Au \text{ ppm}}{M.W._{Au}} \right] + \left[\frac{Au \text{ ppm}}{M.W._{Au}} + \sum_i \frac{i \text{ ppm}}{M.W._i} \right] \quad (6)$$

In equation (6) $M.W._{Au}$ is the molecular weight of Au, (Au ppm) is the concentration of Au in the silicate melt in parts per million and the summation term includes all other components of the silicate melt. When the summation term is large compared to (Au ppm/ $M.W._{Au}$) as must be the case, we may neglect the (Au ppm/ $M.W._{Au}$) term in the denominator without significant error. Then the summation terms cancel when the ratio of X_{Au}^{sil} to X_{Pd}^{sil} is formed. The ratio of molecular weights for Pd and Au is subsumed into the ΔK term and does not affect the determination of Ω . Hence, we may use the ppm values directly in equation (5).

An Example: To illustrate the method, consider the data shown in Figure 1, a plot of Pd and Au solubilities in isocompositional silicate melts equilibrated at 1450°C (melt composition in wt. %: CaO=9.99; MgO=9.14; Al₂O₃=34.86; SiO₂=45.04). The noble metal measurements were made using the PIXE microprobe at Los Alamos National Laboratory. One can easily see the break in slope on this plot showing the difference in behavior for liquid and solid alloys in the Au:Pd system. It is also of note that the two line segments, three point lines, are very nearly linear. This indicates that both liquid and solid metallic solutions have ratios of activity coefficients which do not change much and therefore the solutions must have small excess free energies. We parameterize the deviations from ideality with the method outlined above by calculating the slope of the line segments on Figure 2. The Ω value for the liquid is -0.7 kcal/mol and for the solid it is -0.4 kcal/mol indicating slight negative deviations for the two phases under consideration; however these small magnitudes are probably not distinguishable without further solubility data to constrain the slope. Note that the Ω 's for each phase are strictly pertinent to the alloy compositional range where the solubility measurements have been made.

Okamoto and Massalski (1985) have reviewed existing data for the Au-Pd system to calculate the liquidus phase diagram. There are no thermodynamic data available for the liquid phase, but tin solution calorimetric data for 298K for the solid alloy have been measured (Darby, 1966) and excess properties appropriate to calculate the phase diagram were estimated for the solid phase such that $\Omega = 3T - 11141 + 8076X_{Pd}$ (with units of cal/mol and T in kelvins). Although the Okamoto and Massalski (1985) model is temperature and composition dependent, very good agreement with our value of -0.4 kcal/mol is found when considering Ω 's

between 60 and 80 mol % Pd where our solubility for the solid phase applies. For the liquid phase the Okamoto and Massalski (1985) parameterization predicts slightly less non-ideality compared to the solid, whereas our measurements indicate, perhaps, slightly more ideal behavior. Nevertheless, the method illustrated seems to produce reasonable agreement considering the scarcity of data pertinent to these conditions.

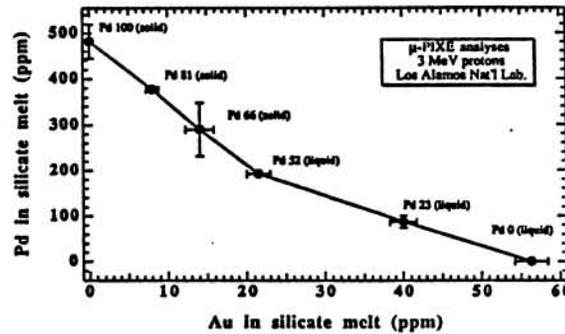


Figure 1. Solubilities in silicate melt (in ppm) of Pd versus Au at 1450°C determined by PIXE analysis. Equilibrated alloy molar concentrations noted on plot.

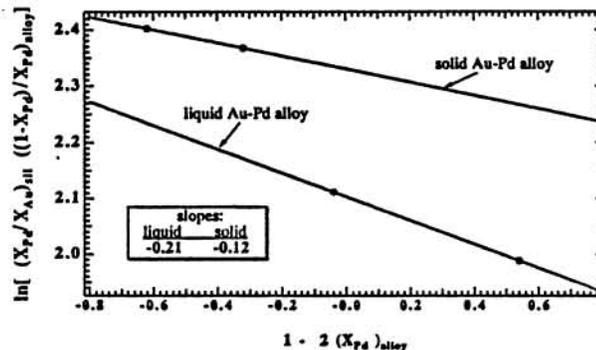


Figure 2. Data from Figure 1 replotted with equation (5). The slope of the solid and liquid lines are the reduced interaction parameter $\Omega' = \Omega/RT$.

References: Capobianco *et al.* (1990) *Solubility and partitioning of noble metals in molten silicate systems an experimental study.* (This volume). Darby, J. B. (1966) *The relative heats of formation of solid gold-palladium alloys.* Acta Metallurgica, 14, 265-270. Okamoto, H. and Massalski, T. B. (1985) *The Au-Pd (gold-palladium) system.* Bulletin of Alloy Phase Diagrams, 6, 229-235.

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