

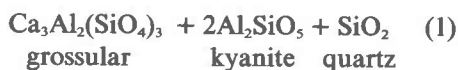
Experimental determination of univariant equilibria using divariant solid-solution assemblages: a discussion¹

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Schmid *et al.* (1978) recently published a method for experimentally determining the pressure-temperature coordinates of univariant reactions by adding an additional component that is soluble in *one* of the phases of the divariant assemblage and monitoring the composition of that phase with changing pressure (or temperature). They state that this procedure "has a number of advantages over that normally used for determining univariant equilibria." It is true that this method may be advantageous in some instances, but uncertainties can also arise, and it is the major purpose of this note to air these.

The reaction selected for illustration by Schmid *et al.* is as follows:



Standard experimental procedures involve running the reactants or a mixture of reactants and products and monitoring the appearance and disappearance of phases or changes in the relative proportions of phases. The configuration of the univariant reaction curve is established with experiments over a range of pressures and temperatures, as shown diagrammatically in Figure 1.

The method discussed by Schmid *et al.* is best explained using Figure 2, which illustrates an isothermal section. Schmid *et al.* added Fe to the univariant assemblage of reaction (1), converting grossular (Gr) to $\text{Gr}_{0.97}\text{Alm}_{0.03}$ crystalline solution. For runs at pressures below the heavy binary reaction curve, the equilibrium composition of the garnet for "0.97"

composition would be richer in Alm component than the starting material; the reverse would be true at pressures above the curve. Thus, monitoring the composition of the garnets establishes the heavy curve and the pressure P for the *divariant* assemblage. The position of the *univariant* reaction (1) (pressure P_0) at the temperature of Figure 2 was calculated using the well-known relationship,

$$P_0 - P = \Delta P = \frac{3RT}{\Delta V^0} \ln X_{\text{Gr}} \quad (2)$$

which assumes that Raoult's Law prevails for this composition, that there is mixing of Fe and Ca ions on three sites for each formula unit in the garnet structure, and that ΔV is constant between P and P_0 .

One point that must be amplified is that it is assumed that Fe is soluble only in one phase, namely, garnet in this instance. However, if some of the ferrous ion enters the anorthite, the anorthite solid solution (An_{ss}) in equilibrium at the binary reaction boundary would be dissimilar to that of pure An in reaction (1) at P_0 , and the procedure would not be rigorously valid. This is illustrated in Figure 3, where $P^1 \neq P$ in Figure 2. In fact, of course, it would be possible in some systems to have the situation in Figure 4, where $P > P_0$, although this configuration is dissonant with the experimental data of Schmid *et al.*

The values of ΔP determined for reaction (1) by Schmid *et al.* ranged from 0.07 to 0.21 kbar for five experiments. The uncertainty in these values, *coupled* with the uncertainty in the precision of the experimental determination of the pressure P at any temperature, could conceivably be larger than that obtainable with standard methods. For example Essene *et al.* (1972) were able to obtain brackets on the following two reactions that were precise to 0.25 to 0.50 kbar, using a 2.54-cm diameter piston in a piston-cylinder apparatus with a 12.7-cm diameter master ram:

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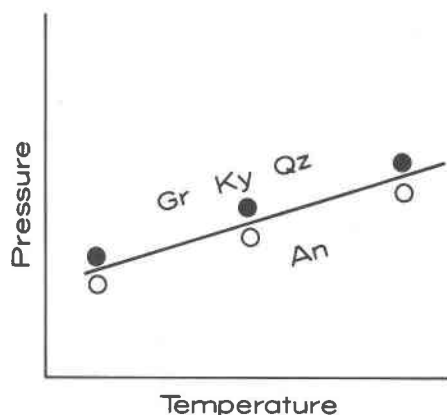
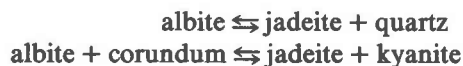


Fig. 1. Pressure-temperature projection of reaction (1). The results of hypothetical experiments are shown as circles.



More precise brackets were obtained on a determination of the high-pressure stability of ferrosilite and manganese ferrosilite relative to fayalite and quartz (Bohlen and Boettcher, 1978; Bohlen *et al.*, 1978). Here, using a 2.54-cm piston and a 8.9-cm master ram monitored with a 40-cm Heise gauge, a precision of about ± 50 bars was possible. I realize, however, that a comparison of these methods using different reactions is not entirely fair, particularly because reaction (1) is particularly sluggish.

In conclusion, my criticism of the Schmid *et al.* paper is based on the following points. They criticize

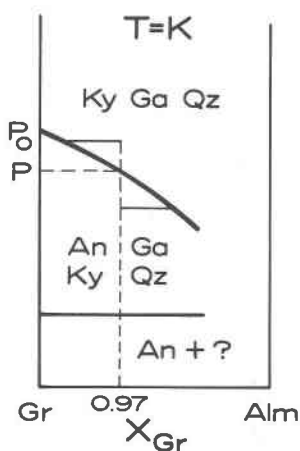


Fig. 2. Isothermal section of reaction (1) with 3 mole percent almandine (Alm) added to the grossular (Gr). The heavy curve gives the composition of garnet in equilibrium with anorthite, kyanite, and quartz. This assumes no solubility of Fe in anorthite.

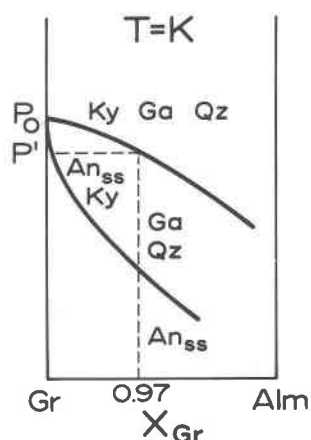


Fig. 3. Similar to Figure 2, assuming crystalline solution of Fe in An.

the standard methods that can be very precise, but they fail to bring to light the intrinsic weaknesses of their method, namely (1) uncertainties in the approach to ideal or Raoultian behavior; (2) uncertainties in the nature of which mixing model to select, *e.g.*, ionic or molecular; (3) uncertainties in the determination of the composition of the crystalline solution (garnet in this case), in part the result of zoning, which is commonly a problem in experiments with garnets; and (4) the assumption that crystalline solution occurs in only one phase. Schmid *et al.* did not address the possibility of solubility of Fe in the anorthite. It would have been interesting to search for an Fe-bearing phase coexisting with anorthite at pressures below the stability of grossular. Also, they

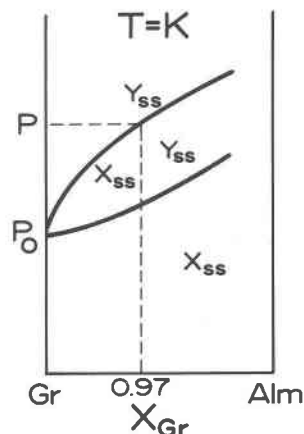


Fig. 4. Similar to Figure 3, assuming extensive crystalline solution in phase X, with lesser amounts in Y.

state that the addition of small proportions of another component [$\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$ in this instance] to change the reaction from univariant to divariant increases reaction rates. I know of no compelling thermodynamic argument to support this claim, and there are examples to the contrary. Their claim is difficult to evaluate because of a lack of data on homogeneity and grain size of their garnets.

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