Experimental determination of univariant equilibria using divariant solid-solution assemblages

Rolf Schmid
Institut für Kristallographie und Petrographie, ETH Zentrum
8092 Zürich, Switzerland

Gordon Cressey and Bernard J. Wood
Department of Geology, The University
Manchester M13 9PL, England

Abstract

A precise method for the determination of univariant equilibria is described. This makes use of the fact that small concentrations of a component in solid solution may shift a reaction curve by an appreciable amount, if the component in question enters only one of the solid phases. The direction of reaction can be determined by analysis of the solid-solution phase, and the position of the end-member curve calculated by assuming that this phase obeys Raoult’s Law.

The method has a number of advantages over that normally used for determining univariant equilibria: (a) the small amounts of additional components tend to increase reaction rates; (b) small degrees of reaction can be detected; (c) metastable univariant equilibria could be determined by studying stable divariant assemblages of the appropriate phases.

The method is illustrated by the reaction: anorthite \(\rightleftharpoons\) grossular + kyanite + quartz. The univariant boundary describes the following line in \(P-T\) space: \(P = 214 + 22.5T\) (°C) bars.

Introduction

The experimental methods most commonly used to determine univariant equilibria are as follows:

(a) Crystalline mixtures of the two-phase assemblages stable on each side of the reaction boundary are recrystallized under physical conditions near to the equilibrium values. Experiments are performed such that the observed changes in proportions of phases bracket the equilibrium boundary.

(b) The stable low-temperature assemblage is recrystallized at progressively higher temperatures until the high-temperature assemblage appears. The inverse procedure with the high-temperature assemblage brackets the equilibrium boundary.

(c) One of the phases involved in the reaction is added to the charge as a single crystal. The direction of reaction at any pressure and temperature is determined by the change in weight of this crystal.

The “modal” methods (a) and (b) often result in very large uncertainties, particularly at low temperatures in volatile-free systems where reaction rates are very low. In addition, the use of relatively inaccurate X-ray methods to determine proportions of phases necessitates, as the criteria of reaction, the observation of large changes in peak-height ratios. At low temperatures such large extents of reaction may only be observed under conditions far removed from the equilibrium phase boundary. The weight-change method (c) is precise, but not suitable under anhydrous conditions, because of the difficulty of separating the single crystal.

In cases where (c) is impracticable we believe that increased precision over (a) and (b) may be obtained by using starting materials in which one of the phases is a solid solution of two components. In such cases the criteria of reaction are small changes in the composition of the solid-solution phase. Since phase compositions can, in general, be determined far more accurately than the proportions of the phases present, this method is considerably more sensitive than the “modal” approaches.

The solid-solution method

For most univariant reactions at least one of the phases involved is an end-member of an extensive
solid-solution series. As an example consider the reaction:

\[ 3\text{CaAl}_2\text{Si}_2\text{O}_8 \rightleftharpoons \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 2\text{Al}_2\text{SiO}_5 + \text{SiO}_2 \]  

(1)

plagioclase garnet kyanite quartz

in which plagioclase and garnet may be readily turned into solid solutions by the addition of other components. We shall consider the divariant equilibrium in which only garnet is a solid solution. Taking standard states of all components to be the pure phase at the temperature and pressure of interest, the standard free energy change of reaction (1) is given by:

\[
(\Delta G^o)_{\text{p},T} = \Delta H^o_{\text{bar},T} - T\Delta S^o + \int_{\text{bar}}^{P} \Delta V^o \cdot dP
= -RT \ln \left( \frac{a_{\text{CaAl}_2\text{Si}_3\text{O}_{12}}^{x} \cdot a_{\text{SiO}_2}^{x}}{a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{x}} \right)
\]

(2)

where \( a_i \) is the activity of component \( i \) in phase \( j \). If all phases are pure then:

\[
\Delta H^o_{\text{bar},T} - T\Delta S^o + \int_{\text{bar}}^{P} \Delta V^o \cdot dP = -RT \ln 1 = 0
\]

(3)

where \( P_0 \) is the equilibrium pressure of the univariant reaction (1). If all phases are pure except the garnet \( (a_{\text{gro}} < 1) \) then we have:

\[
\Delta H^o_{\text{bar},T} - T\Delta S^o + \int_{\text{bar}}^{P} \Delta V^o \cdot dP = -RT \ln a_{\text{gro}}^{x}
\]

(4)

For mixing on three cation sites per formula unit, the activity–composition relationships for the \( \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} \) component of the garnet solid solution are given by:

\[
a_{\text{gro}}^{x} = (X_{\text{gro}} \cdot \gamma_{\text{gro}})^a
\]

(5)

where \( X_{\text{gro}} \) is the mole fraction of grossular component in the garnet solid solution and \( \gamma_{\text{gro}} \) is the activity coefficient. At constant temperature the change of \( X_{\text{gro}} = 1 \) to \( X_{\text{gro}} < 1 \) results in a pressure change which is negative. Then assuming \( \Delta V^o \) to be constant in the pressure range \( P_0 \) to \( P \), we obtain from (3) and (4):

\[
(P_0 - P) = \frac{RT}{\Delta V^o} \ln (X_{\text{gro}} \cdot \gamma_{\text{gro}})^a
\]

(6)

For concentrated solutions where \( X_{\text{gro}} \) approaches unity, Raoults’s Law can be assumed to hold. Applying this assumption to (6) yields:

\[
(P_0 - P) = \frac{3RT}{\Delta V^o} \ln X_{\text{gro}}
\]

(7)

For the investigation of reaction (1), we suggest that \( \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} - \text{Fe}_2\text{Al}_2\text{Si}_3\text{O}_{12} \) garnet solid solution crystals of composition \( X_{\text{gro}} \approx 0.97 \) are first synthesized and mechanically mixed with suitable amounts of pure anorthite, pure kyanite, and pure quartz. Crystalline reversal runs can then be carried out using this starting mix. The first experiment should be run at a pressure somewhat lower than the expected equilibrium pressure of the univariant end-member reaction. If the resulting garnet solid solution in this divariant assemblage has a lower \( X_{\text{gro}} \) than 0.97, the run pressure should be increased by a few tenths of a kilobar for the next experiment, and this procedure repeated until an increase in \( X_{\text{gro}} \) is observed. A slight decrease followed by a slight increase in \( X_{\text{gro}} \) relative to the starting composition, in response to only a few tenths of a kilobar pressure difference between consecutive runs, indicates close approach to the true univariant equilibrium pressure \( P_0 \), the latter can be calculated by adding \( (P_0 - P) \) obtained from (7) to the run pressure \( P \). The same procedure could also be followed with pure \( \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} \) garnet and anorthite-rich plagioclase solid solution. This would enable close bracketing of the univariant curve from both sides by the use of two different divariant assemblages.

**Experimental techniques**

All experiments were carried out in a conventional piston-cylinder apparatus (Boyd and England, 1960), using talc and pyrex glass as pressure media. Piston-out procedure was used throughout; the run was initially brought to the required temperature at a pressure 5 kbar above the nominal run pressure, before lowering and maintaining at the desired pressure with constant surveillance. The uncertainty in pressure gauge reading is ±0.05 kbar.

The apparatus has been calibrated with respect to other laboratories and good agreement with previously published data has been found (Hensen and Barton, 1975). Johannes et al. (1971), in their interlaboratory pressure calibration of piston-cylinder apparatus, report an average preferred value for the albite breakdown reaction of 16.3 kbar at 500°C. With the same jadeite starting material as Johannes et al., the albite breakdown reaction was reversed be-
between 16.5 and 16.7 kbar at 600°C on this apparatus using the "modal" method. This suggests that a pressure correction of -2 percent applied to our nominal piston-out values would be appropriate.

Although we have applied this correction to our nominal pressures (Table 1), it should be noted that its magnitude is within the generally accepted reproducibility of piston-cylinder pressures (±0.5 kbar approximately). Our results do not necessarily imply a precision in pressure measurement of better than ±0.5 kbar, although we consider that continual adjustment to the nominal pressure may improve reproducibility. As evidence of good precision we can cite runs at 16.5 and 16.7 kbar (at 600°C see above) and at 23.0 and 23.2 kbar (at 1000°C, Table 1), in which the nominal pressure differences of 0.2 kbar produced results in accord with pressure differences of the correct sign.

Temperatures were controlled using Pt100-PtRh13 thermocouples, and the effect of pressure on the emf has been neglected. The temperature on top of the capsule is controlled throughout the run to ±1°C. However, in view of longitudinal temperature gradients and assembly variations, temperature precision is probably not better than ±5×10⁻³°C.

Synthetic crystalline starting material was used in all experiments and consisted of 60 percent anorthite, 18 percent almandine-grossular solid solution (Xca = 0.978), 12 percent kyanite, and 10 percent quartz. The iron-bearing starting material was dried at 110°C and run in unsealed graphite capsules. Individual parts of the pressure cell were carefully dried in a bunsen flame before each run.

Run products were examined optically and by X-ray powder diffraction to ensure that the full mineral assemblage of interest was present. Garnet unit-cell parameters were determined from X-ray powder diffractometer tracings made at 4° 2θ per min, using NaCl as internal standard (checked against silicon).

The (420) garnet peak was measured against the (200) NaCl peak for 10 to 20 oscillations and the results averaged.

In order to obtain garnet compositions from cell-edge measurements, pure grossular and pure almandine were also synthesised and their cell edges determined. Pure synthetic grossular crystallized from a gel at 700°C and 1 kbar and recrystallized at 1000°C and 20 kbar had a cell-edge of 11.849A (±0.001). Almandine synthesised from a glass was found to have a cell edge of 11.526A (±0.001) in agreement with many previously-reported values. This suggests that the fO₂ is sufficiently low to ensure the absence of any Fe₂Fe₃Si₃O₁₂ component when using graphite capsules. For the small concentrations of almandine component of interest here, a linear relationship between cell edge and composition was assumed.

Experimental data

Reaction (1) has been determined experimentally by Hays (1966) and Hariya and Kennedy (1968) in the temperature range 950-1400°C. Their experimental data yield the following expression for the equilibrium pressure (Schmid and Wood, 1976)

\[ P = \frac{37.73T - 13740 \pm 1060}{1.582} \]  

where \( T \) is in °K and \( P \) is in bars. This corresponds to a slope of the reaction of 23.85 bars/°C and a pressure of 30.02 ±0.7 kbar at 1350°C. Our own piston-cylinder experiments carried out with pure phases at the same temperature using the "modal" method indicate an uncorrected piston-out pressure of 31.0 ±0.5 kbar. At temperatures slightly below 1300°C, reaction (1) becomes very sluggish and can only be bracketed to ±1.0 kbar using the "modal" method.

Experiments on divariant assemblages have been carried out at 900, 1000, and 1100°C and the equilibrium pressure for reaction (1) at these temperatures

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp °C</th>
<th>Pressure Kb</th>
<th>Time hr</th>
<th>starting garnet a₀ Xca</th>
<th>garnet after run a₀ Xca</th>
<th>ΔP = ( \frac{3RT}{\Delta V} ) ln Xca</th>
<th>P + ΔP = P₀</th>
<th>P₀ - 2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>900</td>
<td>20.77</td>
<td>12</td>
<td>11.849 0.978</td>
<td>11.837 0.963</td>
<td>0.17</td>
<td>20.94</td>
<td>20.52</td>
</tr>
<tr>
<td>138</td>
<td>900</td>
<td>20.90</td>
<td>12</td>
<td>&quot; &quot;</td>
<td>11.841 0.977</td>
<td>0.10</td>
<td>21.00</td>
<td>20.58</td>
</tr>
<tr>
<td>125</td>
<td>1000</td>
<td>23.00</td>
<td>14</td>
<td>&quot; &quot;</td>
<td>11.840 0.973</td>
<td>0.13</td>
<td>23.13</td>
<td>22.67</td>
</tr>
<tr>
<td>128</td>
<td>1000</td>
<td>23.16</td>
<td>12</td>
<td>&quot; &quot;</td>
<td>11.844 0.985</td>
<td>0.07</td>
<td>23.23</td>
<td>22.76</td>
</tr>
<tr>
<td>124</td>
<td>1000</td>
<td>23.90</td>
<td>12</td>
<td>&quot; &quot;</td>
<td>11.847 0.993</td>
<td>&quot;</td>
<td>25.51</td>
<td>25.00</td>
</tr>
<tr>
<td>130</td>
<td>1000</td>
<td>24.20</td>
<td>10</td>
<td>&quot; &quot;</td>
<td>11.847 0.993</td>
<td>&quot;</td>
<td>25.51</td>
<td>25.00</td>
</tr>
<tr>
<td>131</td>
<td>1100</td>
<td>25.30</td>
<td>12</td>
<td>&quot; &quot;</td>
<td>11.836 0.960</td>
<td>0.21</td>
<td>25.51</td>
<td>25.00</td>
</tr>
</tbody>
</table>

Table 1. Experimental data on the reaction An = gro + ky + qz
Table 2. A comparison of data on the anorthite breakdown reaction

<table>
<thead>
<tr>
<th>Present study</th>
<th>Heat of solution data (970K - Newton) combined with the present data</th>
<th>Entropy of grossular data Perkins &amp; Essene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °C</td>
<td>P o - 2%</td>
<td>dp/dT = 9400 (+ 570) + P$_{bars}$AVO</td>
</tr>
<tr>
<td>900</td>
<td>20.6</td>
<td>22.6 ($\pm$ 0.3)</td>
</tr>
<tr>
<td>1000</td>
<td>22.7</td>
<td>22.5 ($\pm$ 0.3)</td>
</tr>
<tr>
<td>1100</td>
<td>25.0</td>
<td>22.3 ($\pm$ 0.2)</td>
</tr>
<tr>
<td>1350</td>
<td>30.4 ($\pm$ 0.5)</td>
<td>22.4 ($\pm$ 0.5)</td>
</tr>
</tbody>
</table>

* Determined by the "modal" method using pure phases.

Recent calorimetric measurements of the entropy of grossular by Perkins and Essene (personal communication) together with data from Robie and Waldbaum (1968) also enable the slope of reaction (1) to be calculated. A comparison of data on the anorthite breakdown reaction is shown in Table 2, indicating good agreement between the present data and those of Newton and Perkins and Essene. As can be seen from Figure 1, the present study is consistent with the earlier experiments of Hays (1966), Hariya and Kennedy (1968), and Newton (1966). Our results at 1350°C also bracket the 30 kbar equilibrium point reported by Boyd (1964).

Conclusions

The solid-solution method for the determination of univariant equilibria seems to be more sensitive and less ambiguous than conventional "modal" methods, because it allows the direction of a reaction to be observed not only by changing amounts of phases but also by changing solid-solution composition. The small amounts of additional components in solid solution tend to increase reaction rates and enable small degrees of reaction to be detected, even at relatively low temperatures. It thus provides a reasonably precise method of determining univariant boundaries under P-T conditions for which reaction rates are very low.

Acknowledgments

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References


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