American Mineralogist, Volume 63, pages 511–515, 1978

Experimental determination of univariant equilibria using divariant solid-solution assemblages

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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 ⇆ 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

0003–004X/78/0506–0511$02.00

solid-solution series. As an example consider the reaction:

$$3\mathrm{CaAl_2Si_2O_8} \leftrightharpoons \mathrm{Ca_3Al_2Si_3O_{12}} + 2\mathrm{Al_2SiO_5} + \mathrm{SiO_2} \quad (1)$$
$$\text{plagioclase} \qquad \text{garnet} \qquad \text{kyanite} \quad \text{quartz}$$

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:

$$(\Delta G^0)_{P,T} = \Delta H^0_{1\mathrm{bar},T} - T\Delta S^0_T + \int_{1\mathrm{bar}}^{P} \Delta V^0 \cdot \mathrm{d}P$$
$$= -RT \ln \left(\frac{a^{\mathrm{gt}}_{\mathrm{gro}^1} \cdot a^{\mathrm{ky}^2}_{\mathrm{Al_2SiO_5}} \cdot a^{\mathrm{qz}}_{\mathrm{SiO_2}}}{a^{\mathrm{plag}^3}_{\mathrm{CaAl_2Si_2O_8}}} \right) \qquad (2)$$

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

$$\Delta H^0_{1\mathrm{bar},T} - T\Delta S^0 + \int_{1\mathrm{bar}}^{P_0} \Delta V^0 \cdot \mathrm{d}P = -RT \ln 1 = 0 \qquad (3)$$

where P_0 is the equilibrium pressure of the univariant reaction (1). If all phases are pure except the garnet ($a^{\mathrm{gt}}_{\mathrm{gro}} < 1$) then we have:

$$\Delta H^0_{1\mathrm{bar},T} - T\Delta S^0_T + \int_{1\mathrm{bar}}^{P} \Delta V^0 \cdot \mathrm{d}P = -RT \ln a^{\mathrm{gt}}_{\mathrm{gro}} \qquad (4)$$

For mixing on three cation sites per formula unit, the activity–composition relationships for the $\mathrm{Ca_3Al_2Si_3O_{12}}$ component of the garnet solid solution are given by:

$$a^{\mathrm{gt}}_{\mathrm{gro}} = (X_{\mathrm{gro}} \cdot \gamma_{\mathrm{gro}})^3 \qquad (5)$$

where X_{gro} is the mole fraction of grossular component in the garnet solid solution and γ_{gro} is the activity coefficient. At constant temperature the change of $X_{\mathrm{gro}} = 1$ to $X_{\mathrm{gro}} < 1$ results in a pressure change which is negative. Then assuming ΔV^0 to be constant in the pressure range P_0 to P, we obtain from (3) and (4):

$$(P_0 - P) = \frac{RT}{\Delta V^0} \ln (X_{\mathrm{gro}}\, \gamma_{\mathrm{gro}})^3 \qquad (6)$$

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

$$(P_0 - P) = \frac{3RT}{\Delta V^0} \ln X_{\mathrm{gro}} \qquad (7)$$

For the investigation of reaction (1), we suggest that $\mathrm{Ca_3Al_2Si_3O_{12}}$–$\mathrm{Fe_3Al_2Si_3O_{12}}$ garnet solid solution crystals of composition $X_{\mathrm{gro}} \simeq 0.97$ are first synthesised 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_{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_{gro} is observed. A slight decrease followed by a slight increase in X_{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 $\mathrm{Ca_3Al_2Si_3O_{12}}$ 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 inter-laboratory 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-

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[1] gro = $\mathrm{Ca_3Al_2Si_3O_{12}}$.

tween 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 Pt_{100}–$Pt_{87}Rh_{13}$ 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°C.

Synthetic crystalline starting material was used in all experiments and consisted of 60 percent anorthite, 18 percent almandine–grossular solid solution (X_{Ca} = 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 $\frac{1}{4}^{\circ}$ 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 fO_2 is sufficiently low to ensure the absence of any $Fe_3Fe_2Si_3O_{12}$ 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)

$$P = \frac{37.73T - 13740 \pm 1060}{1.582} \qquad (8)$$

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 1. Experimental data on the reaction An = gro + ky + qz

Run No.	Temp °C	Pressure Kb	Time hr	starting garnet		garnet after run		$\Delta P = \frac{3RT}{\Delta V^o} \ln X_{Ca}$	$P + \Delta P = P_o$	P_o - 2%
				a_o	X_{Ca}	a_o	X_{Ca}			
135	900	20.77	12	11.842	0.978	11.837	0.963	0.17	20.94	20.52
138	900	20.90	12	"	"	11.841	0.977	0.10	21.00	20.58
125	1000	23.00	14	"	"	11.840	0.973	0.13	23.13	22.67
128	1000	23.16	12	"	"	11.844	0.985	0.07	23.23	22.76
124	1000	23.90	12	"	"	11.847	0.993	bulk Ca/Ca+Fe = 0.993 above curve		
120	1000	24.20	10	"	"	11.847	0.993			
131	1100	25.30	12	"	"	11.836	0.960	0.21	25.51	25.00

Table 2. A comparison of data on the anorthite breakdown reaction

Present study		Heat of solution data (970K - Newton) combined with the present data	Entropy of grossular data Perkins & Essene
Temp ^{o}C	P_{o} - 2%	$\frac{dP}{dT} = \frac{9400\ (\pm 570) + P_{bars}\ \Delta V^{o}}{(\Delta V^{o})\ T^{o}K}$	$\frac{dP}{dT} = \frac{\Delta S^{o}_{600}{}^{*}}{\Delta V^{o}}$
900	20.6	22.6 (± 0.3)	
1000	22.7	22.5 (± 0.3)	
1100	25.0	22.5 (± 0.3)	22.0 (± 0.6)
1350†	30.4 ± 0.5	22.4 (± 0.5)	

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

* S^{o}_{600} values for anorthite, kyanite and quartz and V^{o}_{298} are taken from Robie & Waldbaum (1968).

has been calculated for this apparatus using the solid-solution approach. The results are shown in Table 1, for which the uncertainties of cell-edge measurements range between ±0.001 and ±0.0016, corresponding to an error in mole fraction of ±0.003 to ±0.005 respectively. It should be noted that the garnet composition has only been reversed at 1000°C thus far.

Heat of solution data of Newton (personal communication) for anorthite, grossular, kyanite, and quartz (at 1000°K) enable calculation of the slope of reaction (1) at each of our experimental data points. The corrected piston-out data yield the following expression for the anorthite breakdown reaction:

$$P\ (\text{bars}) = 214 + 22.5T(°\text{C})$$

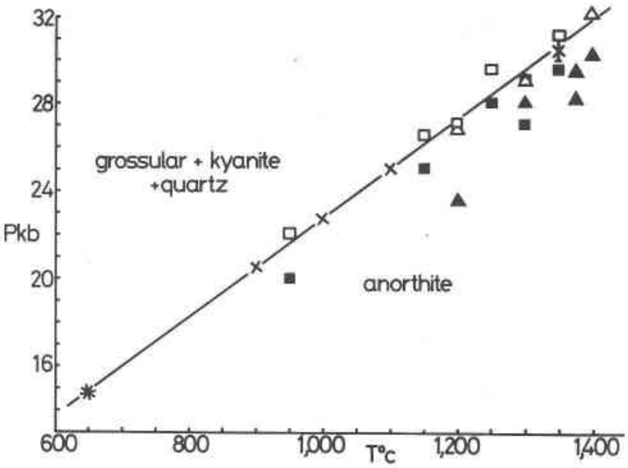

Fig. 1. A comparison of experimental data on the anorthite breakdown reaction. Open squares (Hariya & Kennedy, 1968) products grew, closed squares reactants grew. Open triangles (Hays, 1966) products grew, closed triangles reactants grew. Crosses (this study), equilibrium points determined by the solid-solution approach (by the "modal" method at 1350°C) from reaction in both directions at 1000°C and in one direction at 900 and 1000°C. Star, calculated equilibrium point of Newton (1966).

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

We are grateful to Dr. R. C. Newton for the personal communication of his heat of solution data, and also to Dr. D. Perkins and Dr. E. J. Essene for their personal communication. The work was supported by the Natural Environment Research Council, and by Schweizerischer Nationalfonds grant 2.373-0.75.

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Manuscript received, June 7, 1977; accepted for publication, December 20, 1977.