THE AMERICAN MINERALOGIST, VOL. 52, MAY-JUNE, 1967

DETERMINATION OF THERMODYNAMIC PROPERTIES OF SILICATES FROM LOCATIONS OF CONJUGATION LINES IN TERNARY SYSTEMS[1]

ARNULF MUAN, *The Pennsylvania State University, University Park, Pennsylvania.*

ABSTRACT

Directions of conjugation lines between coexisting solid-solution phases in ternary systems provide valuable information on activity-composition relations of the solid solutions and on stabilities of the end-member compounds of the solid solutions. Formulas are presented by which these relations can be derived quantitatively for important rock-forming minerals.

INTRODUCTION

Much of the information contained in phase diagrams for oxide and silicate systems is being used to good advantage by mineralogists, geologists and geochemists. However, there is at least one important aspect of such phase diagrams which is not being utilized to the fullest extent by workers in these fields. This is the direction of the conjugation lines between coexisting solid phases, from which important information may be derived regarding thermodynamic properties of mineralogically important solid solutions and stabilities of end-member compounds. The objective of the present paper is to focus attention on this use of phase-diagram information. The paper deals only with basic thermodynamic derivations relative to this problem. Experimental procedures for determining directions of conjugation lines, as well as data obtained for specific systems, are described elsewhere (Schwerdtfeger and Muan, 1966; Biggers and Muan, 1967; Nafziger and Muan, 1967).

THERMODYNAMIC RELATIONS

We will use as an example a hypothetical system AO-BO-SiO_2 in which AO and BO are oxides of the divalent cations A^{2+} and B^{2+}, respectively. We will asusme that both these two oxides react with SiO_2 to form orthosilicates (A_2SiO_4 and B_2SiO_4, respectively), whereas only AO reacts with SiO_2 to form metasilicate ($ASiO_3$). Furthermore, we will assume that A^{2+} and B^{2+} can substitute for each other in all proportions in the solid phases present in the system. Hence, there appear in the system the two complete solid-solution series (A,B)O and $(A,B)_2SiO_4$, and the incomplete

---

[1] Contribution No. 66-1 from College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania. Presented (by title) at the 45th Annual Meeting of The Mineralogical Society of America, Miami Beach, Florida, November 19-21, 1964.

solid-solution series $(A,B)SiO_3$. We will designate these series "oxide solid solution" (=Ox), "olivine" (=Ol) and "pyroxene" (=Pyr), respectively. The relations are shown graphically in the sketch of Figure 1.

In the following, we will be concerned primarily with the composition areas in which oxide solid solution+olivine, or olivine+pyroxene, respectively, are the stable phase assemblages at subsolidus temperatures.

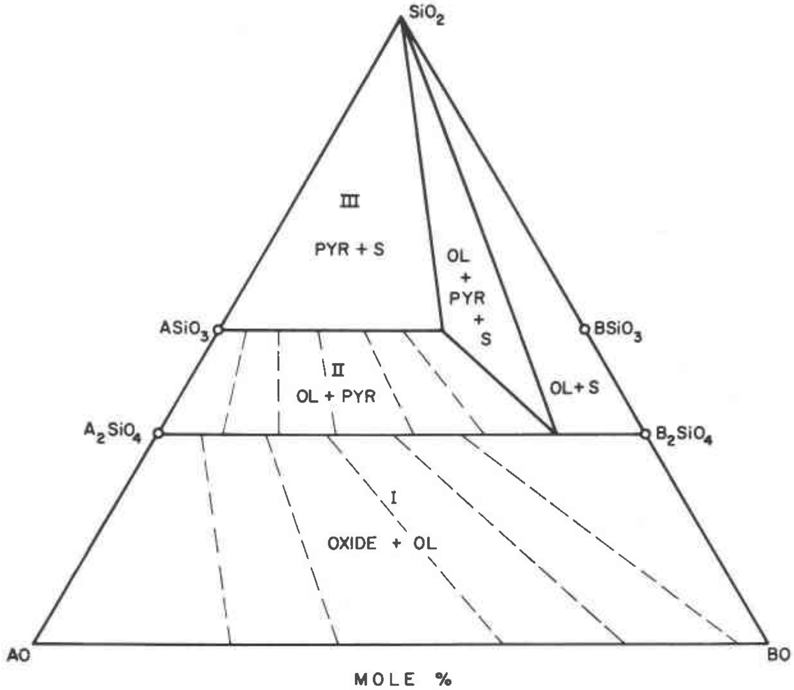

FIG. 1. Sketch showing solid solution series and equilibrium phase assemblages at subsolidus temperatures in the hypothetical ternary system AO-BO-SiO_2. Solid lines outline composition areas for the various phase assemblages, as labelled on the diagram, and light, dash lines are hypothetical conjugation lines for coexisting solid-solution phases. Abbreviations have the following meanings: S=silica, Ol=olivine, Pyr=pyroxene.

The oxide+olivine equilibrium. The composition of olivine coexisting in equilibrium with the oxide phase (area I of Fig. 1) depends on the activity-composition relations in the two solid solutions, and on the standard free energies of formation of A_2SiO_4 and B_2SiO_4 from the oxide components ($2AO+SiO_2$ and $2BO+SiO_2$, respectively). Qualitatively, it is easily recognized that for given activity-composition relations in the two solid solution series, the olivine phase will have a higher B/A ratio the more stable the B_2SiO_4 end members is relative to A_2SiO_4, and vice versa.

Quantitatively, the relations may be derived by procedures similar to those described by Wagner (1952) for alloy phases. In the present case, caution must be exercised in choosing appropriate activity expressions for the olivine solid solution. Darken and Schwerdtfeger, in an appendix to a paper by Schwerdtfeger and Muan (1966), have shown that for a solution $(A,B)_2SiO_4$ activities defined by the equations

$$a_{\mathrm{ASi_{0.5}O_2}} = \text{const.}\ (a_{\mathrm{AO}} \cdot a_{\mathrm{SiO_2}}{}^{1/2}) \tag{1}$$

and

$$a_{\mathrm{BSi_{0.5}O_2}} = \text{const.}\ (a_{\mathrm{BO}} \cdot a_{\mathrm{SiO_2}}{}^{1/2}) \tag{2}$$

vary linearly with mole fraction if the solution is ideal. Choosing the constants such as to make the activity equal to unity for the olivine end members, we obtain for an ideal solution

$$a_{\mathrm{ASi_{0.5}O_2}} = N_{\mathrm{ASi_{0.5}O_2}} \tag{3}$$

and

$$a_{\mathrm{BSi_{0.5}O_2}} = N_{\mathrm{BSi_{0.5}O_2}} \tag{4}$$

where the N's with appropriate subscripts are mole fractions. For non-ideal solid solutions, similarly, we may then write

$$a_{\mathrm{ASi_{0.5}O_2}} = \gamma_{\mathrm{ASi_{0.5}O_2}} \cdot N_{\mathrm{ASi_{0.5}O_2}} \tag{5}$$

and

$$a_{\mathrm{BSi_{0.5}O_2}} = \gamma_{\mathrm{BSi_{0.5}O_2}} \cdot N_{\mathrm{BSi_{0.5}O_2}} \tag{6}$$

where $\gamma_{\mathrm{ASi_{0.5}O_2}}$ and $\gamma_{\mathrm{BSi_{0.5}O_2}}$ are activity coefficients.

For the equilibrium between oxide and olivine solid solutions within area I of Figure 1 we may write

$$(\mathrm{AO})_{\mathrm{Ox}} + (\mathrm{BSi_{0.5}O_2})_{\mathrm{Ol}} = (\mathrm{BO})_{\mathrm{Ox}} + (\mathrm{ASi_{0.5}O_2})_{\mathrm{Ol}} \tag{7}$$

and

$$\Delta G^\circ = \tfrac{1}{2}G^\circ_{\mathrm{A_2SiO_4}} - \tfrac{1}{2}G^\circ_{\mathrm{B_2SiO_4}} = -\,2.303\ RT \log \frac{a_{\mathrm{BO}} \cdot N_{\mathrm{ASi_{0.5}O_2}}}{a_{\mathrm{AO}} \cdot N_{\mathrm{BSi_{0.5}O_2}}} \cdot \frac{\gamma_{\mathrm{ASi_{0.5}O_2}}}{\gamma_{\mathrm{BSi_{0.5}O_2}}} \tag{8}$$

where ΔG° is the change in standard free energy for the reaction, $G^\circ_{\mathrm{A_2SiO_4}}$ and $G^\circ_{\mathrm{B_2SiO_4}}$ are the standard free energies of formation per mole of each of the olivine end members from their oxide components, and a_{AO} and a_{BO} are activities of the components in the oxide solid solution.

Activity-composition data are available for a number of (A,B)O oxide solid solutions (see for instance papers by Hahn and Muan, 1961, 1962; by Aukrust and Muan, 1963; and by Schwerdtfeger and Muan, in press). Hence the quotient

$$\frac{a_{BO}\cdot N_{ASi_{0.5}O_2}}{a_{AO}\cdot N_{BSi_{0.5}O_2}} \tag{9}$$

of equation (8) can usually be determined experimentally. For the sake of simplicity this quotient will be called C, and equation (8) may then be rewritten in the form

$$\log \gamma_{BSi_{0.5}O_2} - \log \gamma_{ASi_{0.5}O_2} = \frac{\Delta G^\circ}{2.303\ RT} + \log C \tag{10}$$

where C in the general case of non-ideal solid solutions is a function of composition. Using the method developed by Wagner (1952), and as applied to oxide phases by Muan (1965), the differentiated form of equation (10) is combined with the Gibbs-Duhem equation for the olivine solid solution, and the equations

$$\log \gamma_{ASi_{0.5}O_2} = N_{BSi_{0.5}O_2} \log C - \int_0^{N_{BSi_{0.5}O_2}} \log C dN_{BSi_{0.5}O_2} \tag{11}$$

and

$$\log \gamma_{BSi0.5O_2}$$

$$= -(1 - N_{BSi_{0.5}O_2}) \log C - \int_{N_{BSi_{0.5}O_2}}^{1} \log C dN_{BSi_{0.5}O_2} \tag{12}$$

are obtained. Graphical integration of these equations yields the γ-values, and by substituting these into equztion (10), a value of ΔG° is obtained. If the free energy of one of the end members ($G^\circ_{A_2SiO_4}$ or $G^\circ_{B_2SiO_4}$) is known, the free energy of the other may be calculated from the relation $\Delta G^\circ = \frac{1}{2}\ G^\circ_{B_2SiO_4} - \frac{1}{2}\ G^\circ_{A_2SiO_4}$ (see equation (8)).

The olivine+pyroxene equilibrium. For the equilibrium coexistence of olivine and pryoxene in area II of Fig. 1 we may proceed in a manner analogous to that shown above. For the reaction

$$(ASiO_3)_{Pyr} + (BSi_{0.5}O_2)_{Ol} = (BSiO_3)_{Pyr} + (ASi_{0.5}O_2)_{Ol} \tag{13}$$

we may write

$$\Delta G^\circ = \tfrac{1}{2}G^\circ_{A_2SiO_4} - \tfrac{1}{2}G^\circ_{B_2SiO_4} + G^\circ_{BSiO_3} - G^\circ_{ASiO_3}$$

$$= -\ 2.303\ RT \log \frac{a_{ASi_{0.5}O_2} \cdot N_{BSiO_3}}{a_{BSi_{0.5}O_2} \cdot N_{ASiO_3}} \cdot \frac{\gamma_{BSiO_3}}{\gamma_{ASiO_3}} \qquad (14)$$

where $G^\circ_{BSiO_3}$ and $G^\circ_{ASiO_3}$ are the standard free energies of formation of the two pyroxene end members from their oxide components, and the other symbols with appropriate subscripts have the same meanings as explained previously. Assuming that the activity-composition relations in the olivine solid solutions are known from the preceding treatment of the oxide-olivine equilibrium, and using the same mathematical treatment as that described for the olivines, we derive for the activity coefficients of the pryoxene solid solutions the following expressions:

$$\log \gamma_{ASiO_3} = N_{BSiO_3} \log C' - \int_0^{N_{BSiO_3}} \log C' dN_{BSiO_3} \qquad (15)$$

and

$$\log \gamma_{BSiO_3} = -\ (1 - N_{BSiO_3}) \log C' - \int_{N_{BSiO_3}}^{1} \log C' dN_{BSiO_3} \qquad (16)$$

where C' is the experimentally determined quotient

$$\frac{a_{ASi_{0.5}O_2} \cdot N_{BSiO_3}}{a_{BSi_{0.5}O_2} \cdot N_{ASiO_3}} \qquad (17)$$

By graphical integration of equations (15) and (16) we obtain the values of the activity coefficients, and ΔG° is then obtained by substitution of the γ-values into equation (14). If the G°-values for the olivine end members and one of the pyroxene end members are known, the stability of the other pyroxene end member may be calculated from the relation

$$\Delta G^\circ = \tfrac{1}{2}G^\circ_{A_2SiO_4} - \tfrac{1}{2}G^\circ_{B_2SiO_4} + G^\circ_{BSiO_3} - G^\circ_{ASiO_3} \qquad (18)$$

(compare equation (14)).

Simplified equations. The equations derived above for olivine and pyroxene solid solutions may be greatly simplified if the solutions are ideal or regular in their activity-composition behavior. For ideal solutions, the log γ-terms are zero, and hence C and C' are constants. Equations (8) and (14) then reduce to the following simple forms

$$\Delta G^\circ = \tfrac{1}{2}G^\circ{}_{\mathrm{A_2SiO_4}} - \tfrac{1}{2}G^\circ{}_{\mathrm{B_2SiO_4}} = -\,2.303\;RT\log C \qquad (19)$$

and

$$\begin{aligned}\Delta G^\circ = \tfrac{1}{2}G^\circ{}_{\mathrm{A_2SiO_4}} - \tfrac{1}{2}G^\circ{}_{\mathrm{B_2SiO_4}} + G^\circ{}_{\mathrm{BSiO_3}}& \\ - G^\circ{}_{\mathrm{ASiO_3}} = -\,2.303\;RT\log C'& \qquad (20)\end{aligned}$$

respectively.

If the solutions are regular, the activity coefficients may be expressed as

$$\log \gamma_{\mathrm{ASi_{0.5}O_2}} = b\cdot N_{\mathrm{BSi_{0.5}O_2}}{}^2 \qquad (21)$$

$$\log \gamma_{\mathrm{BSi_{0.5}O_2}} = b\cdot N_{\mathrm{ASi_{0.5}O_2}}{}^2 \qquad (22)$$

$$\log \gamma_{\mathrm{ASiO_3}} = b'\cdot N_{\mathrm{BSiO_3}}{}^2 \qquad (23)$$

and

$$\log \gamma_{\mathrm{BSiO_3}} = b'\cdot N_{\mathrm{ASiO_3}}{}^2 \qquad (24)$$

where b and b' are constants at constant temperature. Equations (8) and (14) then reduce to

$$\begin{aligned}-\frac{\Delta G^\circ}{2.303\;RT} &= \frac{G^\circ{}_{\mathrm{A_2SiO_4}} - G^\circ{}_{\mathrm{B_2SiO_4}}}{2\times 2.303\;RT} \\ &= \log C + b(N_{\mathrm{ASi_{0.5}O_2}} - N_{\mathrm{BSi_{0.5}O_2}}) \qquad (25)\end{aligned}$$

and

$$\begin{aligned}-\frac{\Delta G^\circ}{2.303\;RT} &= \frac{\tfrac{1}{2}G^\circ{}_{\mathrm{A_2SiO_4}} - \tfrac{1}{2}G^\circ{}_{\mathrm{B_2SiO_4}} + G^\circ{}_{\mathrm{BSiO_3}} - G^\circ{}_{\mathrm{ASiO_3}}}{2.303\;RT} \\ &= \log C' + b'(N_{\mathrm{BSiO_3}} - N_{\mathrm{ASiO_3}}) \qquad (26)\end{aligned}$$

respectively. For regular solutions, therefore, a plot of experimentally determined values of log C versus $(N_{\mathrm{ASi_{0.5}O_2}} - \mathrm{N}_{\mathrm{BSi_{0.5}O_2}})$, or of log C' versus $(N_{\mathrm{BSiO_3}} - N_{\mathrm{ASiO_3}})$, will give straight lines from which b and b', respectively, are determined from the slopes of the curves, and $-(\Delta G^\circ/2.303\;RT)$ is the value of log C at $N_{\mathrm{ASi_{0.5}O_2}} = N_{\mathrm{BSi_{0.5}O_2}} = 0.5$, or $N_{\mathrm{BSiO_3}} = N_{\mathrm{BSiO_3}} = 0.5$, respectively.

General considerations. In the present derivations it was assumed that activity-composition relations were known for the oxide solid solution

((A,B)O). The activity-composition relations in the olivine solid solution were then derived from the olivine-oxide equilibrium (composition area I in Fig. 1), and subsequently the activity-composition relations in the pyroxene solid solution were derived from the olivine-pyroxene equilibrium (composition area II in Fig. 1). The derivations would be similar, however, if one starts instead with the assumption that activity-composition relations for the pyroxene solid solution are known (for instance from equilibrations involving pyroxene solid solutions and silica in composition area III of Fig. 1). The available data for the pyroxenes are then used to derive activity-composition relations for the olivines from the pyroxene-olivine equilibrium in composition area II, and the data thus calculated for the olivines are in turn used to calculate activity-composition relations for the oxide solid solution from the olivine-oxide equilibrium in composition area I of Fig. 1. In practice, it is highly desirable to have available activity-composition data determined independently for the oxide solid solution and for the pyroxene solid solution, and then carry out the above calculations in both directions to provide a check on the accuracy and the internal consistency of the data.

It is often more difficult to obtain as a starting point activity-composition data for the pyroxene solid solution than for the oxide solid solution. This is because in many mineralogically important systems the pyroxene solid solution is not complete between the two end members. A case in point are iron oxide-containing systems (for instance MgO-"FeO"-SiO_2), where the $FeSiO_3$ end member is unstable relative to the phase assemblage Fe_2SiO_4 (fayalite) plus silica. However, even in such a case it is possible to derive activity-composition relations for the pyroxene phase, provided the solid solution behaves simply enough to permit extrapolation of the data to the unstable end member. An example of this approach to $(Mg,Fe)SiO_3$ solid solutions has been published elsewhere (Muan, Nafziger and Roeder, 1964).

ACKNOWLEDGEMENTS

The ideas and derivations presented in this paper originated from experimental studies of thermodynamic properties of solid solutions at high temperatures sponsored by the United States Atomic Energy Commission under Contract No. AT(30-1)-2781. The author is indebted to Carl Wagner for valuable suggestions.

REFERENCES

AUKRUST, E. AND A. MUAN (1963) Activities of components in oxide solid solutions: the systems CoO-MgO, CoO-MnO, and CoO-"FeO" at 1200°C *Trans. AIME* **227**, 1378–1380.

BIGGERS, J. V. AND A. MUAN (1967) Activity-composition relations in orthosilicate and metasilicate solid solutions in the system MnO-CoO-SiO_2 *J. Amer. Ceram. Soc.* **50** (in press).

HAHN, W. C., JR. AND A. MUAN (1961) Activity measurements in oxide solid solutions: the systems NiO-MgO and NiO-MnO in the temperature interval 1100–1300°C *Phys. Chem. Solids* **19,** 338–48.

MUAN, A., R. H. NAFZIGER AND P. L. ROEDER (1964) A method for determining the instability of ferrosilite: *Nature* **202,** 688–689.

MUAN, A. (1965) Equilibria among cobalt oxide-containing phases with NaCl-type, spinel-type and olivine-type structures, *In* G.-M. Schwab, ed. *Reactivity of Solids*, Elsevier Publ. Co., p. 596–605.

NAFZIGER, R. H. AND A. MUAN (1967) Equilibrium phase compositions and thermodynamic properties of solid solutions in the system MgO-"FeO"-SiO_2, *Amer. Mineral.* **52** (in press).

SCHWERDTFEGER, K. AND A. MUAN (1966) Activities in olivine and pyroxenoid solid solutions of the system Fe-Mn-Si-O at 1150°C, with Appendices by L. S. Darken and K. Schwerdtfeger. *Trans. AIME* **236,** 201–211.

SCHWERDTFEGER, K. AND A. MUAN (in press) Equilibria in the system Fe-Mn-O involving "(Fe,Mn)O" and $(Fe,Mn)_3O_4$ solid solutions, *Trans. AIME.*

WAGNER, C. (1952) *Thermodynamics of Alloys.* Addison-Wesley Press, Reading, Mass.

Manuscript received July 21, 1966; accepted for publication September 27, 1966.