Thermodynamics of melting of anorthite deduced from phase equilibrium studies

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Abstract

Application of freezing-point depression theory to experimentally-determined melting relations of anorthite in binary systems with silica, orthoclase, leucite, albite, wollastonite, and diopside yields results which are consistent with an enthalpy of fusion for anorthite of 81000 J/mol, the best estimate of Robie *et al.* (1978). The calculations are made using the 8-oxygen model of silicate melts suggested by Burnham (1975). They also incorporate solid-solution data among anorthite, quartz, and orthoclase. All temperatures are converted to the International Practical Temperature Scale of 1968.

The binary silicate systems studied do not appear to mix ideally, but they may be described by regular solution theory. The deviations from ideal behavior are related to the ionic potential of the cations.

Introduction

This study originated in an attempt to define the enthalpy of fusion of anorthite by application of freezing-point depression theory to experimental phase-equilibrium studies. These data might then be applied to problems involving the estimation of heat contents of crystal-melt mixtures for use in the delineation of geothermal energy reserves. Hopes for success were based in part on the suggestion by Burnham (1975) that many silicate melts might, by judicious choice of components and standard states, be viewed as ideal mixtures. Subsequent to initiation of the project, calorimetric studies on anorthite have more closely delineated the bounds on the possible range of values for its enthalpy of fusion. This communication seeks to answer some questions about the nature of silicate melts, given some known thermodynamic quantities as boundary conditions, and to show that the melting behavior of a phase does not closely constrain its enthalpy of fusion.

Thermodynamic framework

The state of a pure solid phase, A, in equilibrium with a liquid of its own composition at its melting temperature, T_m, may be described as follows. For the reaction, A(s) = A(l), $\Delta G_m = G_{A(l)} - G_{A(s)} = 0$. ΔG_m, the free energy of fusion, may also be written as:

$$\Delta G_m = H_{A(l)} - H_{A(s)} - T_m(S_{A(l)} - S_{A(s)}) \quad (1)$$

Thus,

$$H_{A(l)} - H_{A(s)} = \Delta H_m^A = T\Delta S_m^A \quad (2)$$

If a component of composition A is present in a solution, and a solid and liquid coexist at equilibrium at any temperature T, the chemical potential of A in both phases is equal, and we may write $\mu_{A(s)} = \mu_{A(l)}$. But $\mu_{A(s)} = \bar{G}_{A(s)} + RT \ln a_{A(s)}$, and $\mu_{A(l)} = \bar{G}_{A(l)} + RT \ln a_{A(l)}$. Equating the last two expressions, we have:

$$\Delta G_m = RT \ln (a_{A(s)}/a_{A(l)}) \quad (3)$$

A first approximation to the temperature and compositional dependence of the enthalpy of fusion is to assume that the heat capacity difference, ΔC_p, between the liquid and solid is constant. Thus equation (1) holds at any temperature and, combining (1) and (3), we have:

$$\Delta H_m - T(\Delta H_m/T_m) = RT \ln (a_{A(s)}/a_{A(l)}) \quad (4)$$

Rearranging, we get:

$$\Delta H_m = R[\ln (a_{A(s)}/a_{A(l)})]/[(1/T) - (1/T_m)] \quad (5)$$

More complex equations which incorporate fewer simplifying assumptions about heat capacities may be made, but they can be shown to have a much smaller effect on calculated enthalpies or entropies than do the uncertainties of the data used in this study.

Precision and accuracy of calculations

Adoption of the new temperature scale, IPTS-68, requires that accurate thermochemical data be refer-

Table 1. Some primary calibration points on the IPTS-68 and GL-12 temperature scales

No.	Element	IPTS-68	GL-12	Difference
1	Zn	419.58	419.4	0.18
2	S	444.674	444.55	0.124
3	Sb	630.74	630.0	0.74
4	Ag	961.93	960.2	1.73
5	Au	1064.43	1062.6	1.83
6	Cu	1084.5	1082.8	1.7
7	Pd	1554	1549.5	4.5
8	Pt	1772	1755	17

The calibration points in the table correspond to the numbered symbols in Figure 1. All temperatures are melting points, expressed in degrees Celsius, except sulfur, which is the boiling point at one atmosphere. IPTS-68 temperatures are from Powell et al. (1974). GL-12 temperatures are from (1952).

enced to the new temperatures. Temperatures reported in phase equilibrium studies are generally referenced in three ways: (1) IPTS-48 international temperature scale, (2) 1912 Carnegie Institution of Washington, Geophysical Laboratory (hereafter GL-12) temperature scale, and (3) unspecified. The preponderance of the data are GL-12 temperatures, chiefly because of the wide acceptance of the melting point of diopside (1391.5°C, GL-12) as a calibration
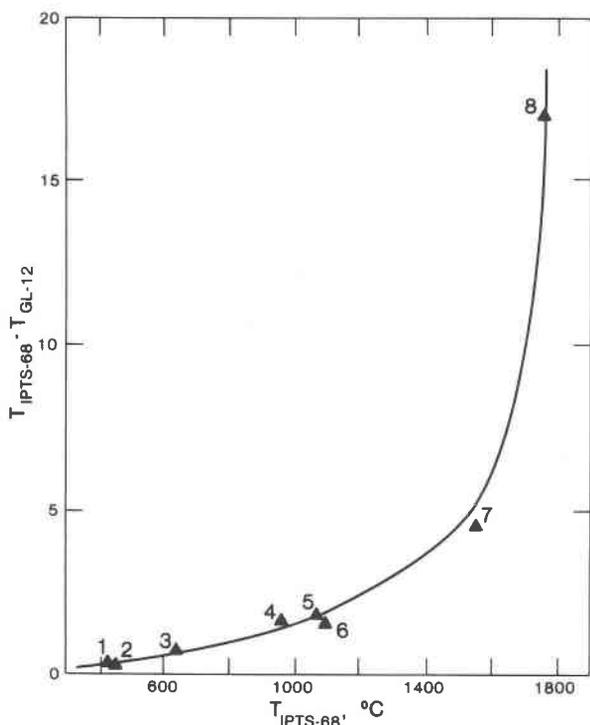

Fig. 1. The discrepancy between IPTS-68 and GL-12 temperature scales. Numbered symbols correspond to the calibration points listed in Table 1.

point. Differences between GL-12 and IPTS-68 are strongly temperature-dependent, and while for hydrothermal experiments below 1200 K the differences may perhaps be ignored, at the high liquidus temperatures of the studied systems the differences are significant. Table 1 and Figure 1 show the difference between the two scales as a function of temperature; Figure 1 was used to convert the temperatures used in this study.

Liquidus temperatures reported in melting experiments are commonly bracketed by two runs anywhere from 4 to 30 degrees apart, one in which all glass is obtained, and one in which some crystals are present. Such experiments are seldom reversed. Starting materials are generally crystalline, occasionally glass. In very few cases is a temperature well defined above which crystals melt completely, and below which glass starting materials yield some crystals. In this study I assumed that reported liquidus temperatures were more likely to be too high, because of lack of reversal, than too low, because of lack of equilibrium. Accordingly, the general procedure was to choose an upper bracket 2° higher than the lowest temperature at which all glass was obtained, and a lower bracket 7° below the upper bracket. Table 2 and Figure 2 show the results of calculations used to test the resultant uncertainties in enthalpies of fusion, given commonly encountered temperature and compositional uncertainties in the input data.

Equation (5) is very sensitive to activities of the solids. However, few quantitative compositional data are known about solid solutions in silicate systems at near-liquidus temperatures. Since most of the studies considered here were made without the benefit of the electron microprobe, anorthite has been commonly assumed to have end-member composition.

Figure 3 illustrates the effects of solid solution in phase A (Table 2, Fig. 2) on calculated enthalpies of fusion at 1750 K. The compositional effects can be relatively large, and may easily overshadow temperature uncertainties. In calculating enthalpies of fusion, all melt and crystal components were assumed to mix ideally, and activities were set equal to mole fractions. Departures from ideal mixing are thus reflected in the extracted data.

The ability to calculate mole fractions correctly depends critically on understanding the structure of silicate melts. Such a melt consists of an array of cations, free oxygen ions, and silicate ions displaying various degrees of polymerization. Polymer theory has been applied to silicate melts by Masson (1972), but the theory has not been extended to ternary and

Table 2. Sample calculation to show constraints on precision of calculated enthalpies of melting

T(K)	X(an) liquid	ΔH_m	$\Delta H1$	$\Delta H2$	$\Delta H3$	$\Delta H4$	$\Delta H5$
1750	0.852	83.89	87.49	97.95	90.08	93.93	107.65
			80.50	73.30	77.78	74.73	67.95
–	–	–	–	–	–	–	–
1700	0.720	83.60	85.85	90.25	87.15	89.04	93.89
			81.84	77.78	80.08	78.41	74.52
–	–	–	–	–	–	–	–
1650	0.602	83.55	84.77	87.99	86.32	87.57	90.02
			82.34	79.50	80.83	79.66	76.90

Numbers in the table were obtained as follows: phase A was assumed to have a melting temperature of 1800 K, and a true enthalpy of melting of 83.68 KJ/mol. Mole fractions of A in the melt were calculated from equation (5), then the enthalpy was recalculated from those mole fractions, which are accurate to the nearest .001. $\Delta H1$ represents ±2 deg uncertainty in temperature, $\Delta H2$ represents ±7 deg. $\Delta H3$ represents ±1 mol % uncertainty in composition. $\Delta H4$ and $\Delta H5$ represent combined maximum uncertainties of methods 1 and 3, and 2 and 3, respectively.

higher-order systems with any great success, so I did not attempt to apply it in the present study, which deals with ternary and higher-order oxide systems of appreciable alumina content. Though various models were explored, the procedure adopted was to consider the unit of silicate melt to be 8 oxygen atoms and the cations associated with them (Burnham, 1975).

Results

Previous work

Bowen (1913) demonstrated that freezing-point depression theory applied to the plagioclase phase diagram yields a value for the enthalpy of fusion of anorthite of approximately 121000 J/mol. The results of Peck *et al.* (1977), based on thermal modeling of the Alae Lava Lake, Hawaii, are consistent with Bowen's estimate. Ferrier (1969) made a calorimetric determination of 167000 J/mol for the enthalpy of fusion of anorthite. Klein and Uhlmann (1974), using a kinetic study of anorthite crystallization, estimated an enthalpy of fusion of between 117000 and 188000 J/mol. Yoder (1975) reported unpublished data of O. J. Kleppa and T. V. Charlu, who determined enthalpies of solution of anorthite and anorthite glass in molten lead borate, which yield an enthalpy difference at 973 K of 78200 J/mol. Robie *et al.* (1978), using the heat capacities of Krupka, Robie, and Hemingway (in preparation) and the standard enthalpies of anorthite and anorthite glass measured at 298 K (Kracek and Neuvonen, 1952), report a value of 81000 J/mol. The apparent lack of agreement in the calorimetric studies suggests the utility of an examination of the phase equilibria studies.
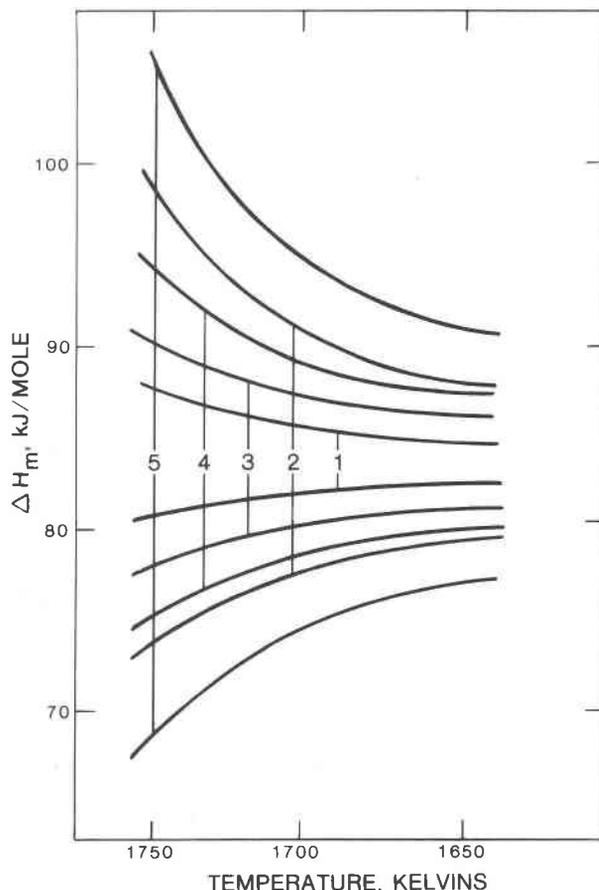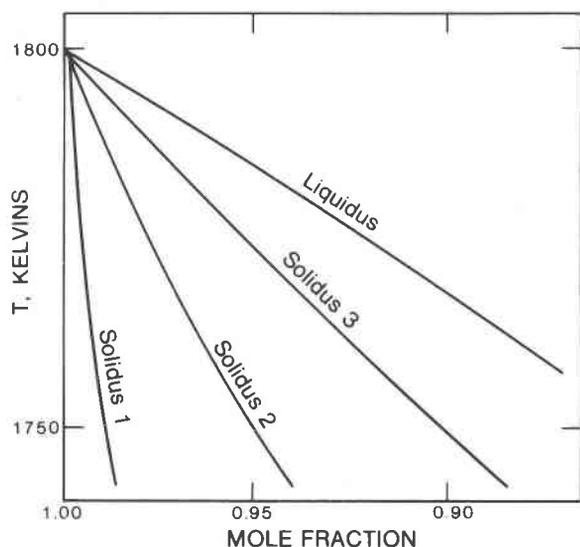

Fig. 2. Uncertainties in ΔH_m resulting from (1) ±2° temperature uncertainty, (2) ±7° temperature uncertainty, (3) ±1 mole percent compositional uncertainty, (4) a combination of 1 and 3, and (5) a combination of 2 and 3.

Anorthite–albite

Data were extracted from Bowen's (1913) study in the following manner. Bowen was so thorough as to publish his galvanometer readings, and it was possible to convert his temperature to IPTS-68 in a very rigorous manner. A graph of EMF vs. temperature was constructed, based on a straight line between his low and high calibration points of lithium metasilicate (m. p. 1208°C, IPTS-68), and anorthite (m. p. 1558.5°C, IPTS-68). Reversal brackets for the liquidus were constructed by noting the lowest temperature at which all glass was obtained from crystalline starting materials (upper bracket), and the highest temperature at which crystals were observed starting with glass (lower bracket). Maximum and minimum permissible liquidi were then drawn through the resulting brackets. Data for discrete temperature inter-

ΔH_m (1750K)	SOLIDUS
83.7 kJ	No ss
78.7 kJ	1
56.9 kJ	2
28.9 kJ	3

Fig. 3. Calculated enthalpies of fusion for the hypothetical phase considered in Table 2, showing the effect of different amounts of solid solution.

vals were then read from the resulting phase diagram. The solidus was assumed to be accurate.

Other systems

Data for anorthite–leucite, anorthite–orthoclase, and anorthite–silica were taken from Schairer and Bowen (1947), except for solidus data on anorthite-silica from Longhi and Hays (1976). Schairer and Bowen used thermocouple calibration points of palladium (m. p. 1554°C, IPTS-68) and gold (m. p. 1064.43°C, IPTS-68) to correct the temperatures. For solidus data in the system anorthite–silica, a solid composition was estimated by interpolation from the data of Longhi and Hays for each liquidus point reported by Schairer and Bowen. Leucite was assumed to exhibit no solid solution with anorthite. Orthoclase, however, dissolves in anorthite to some extent. Some lunar feldspars (Ryder *et al.*, 1975) are reported to exhibit extensive ternary solid solution. To test this hypothesis, two experiments were performed with the help of B. R. Lipin. Mixtures of 60 mole percent anorthite and 40 mole percent orthoclase (both crystalline) were equilibrated for 5 hours, one sample at 1673 K and one at 1698 K. Electron

microprobe and X-ray diffraction analysis of the resulting feldspars show no more than 2 mole percent solid solution at those temperatures. Probe analyses of the glass agree, within analytical uncertainty, with Schairer and Bowen's liquidus curve. Accordingly, the solid phase in equilibrium with liquids in the anorthite field was assigned a composition of $An_{97}Or_3$ at the eutectic (1641 K) and assumed to vary linearly with temperature to An_{100} at pure anorthite. Interpolated values were then assigned to each of Schairer and Bowen's liquidus points.

Data for anorthite–diopside and anorthite–wollastonite were taken from Osborn (1942). In the absence of any quantitative data on solid solution among these phases, mole fractions of crystalline anorthite were taken to be unity.

Discussion of results

Calculated enthalpies are presented in Table 3 and plotted as a function of anorthite content of the melt in Figures 4 through 6. The enthalpies do not present a coherent pattern nor easily lend themselves to a comprehensive model. Particularly disturbing is the fact that some of the enthalpy data tend to approach pure anorthite in an asymptotic manner instead of extrapolating to a common value for the enthalpy of fusion. High-temperature data might be less reliable for the following reasons:

(1) Temperature measurement above 1700 K is less precise than at lower temperatures; thermal gradients may be larger because of greater thermal conductivities at high temperatures.

(2) Small temperature errors near T_m have a large effect on calculated enthalpies because the absolute temperature variation is a much larger percentage of $T_m - T$.

(3) Experiments at high temperatures tend to be very short and may not always reach equilibrium.

Extrapolation of these data to pure anorthite composition fall into two groups. Binary systems with albite, leucite, and diopside indicate a heat of fusion near 109000 J/mol, while the orthoclase, silica, and wollastonite data point to a figure near 146000 J/mol. The large uncertainty may be a result of poor data or poor modeling. Probably the uncertainty is as large as the uncertainties of the highest temperature points (±25000 J/mol). If such an uncertainty is assigned, all the values overlap and the "determined" enthalpy of fusion of anorthite is approximately 126000±54000 J/mol, which includes all the disparate calorimetric data reported. The conclusion is that this method does not closely delineate enthalpies of fusion.

Table 3. Calculated enthalpy of fusion of anorthite

TEMP(K)	SOLID	LIQUID	ΔH_m (J/MOL)	TEMP(K)	SOLID	LIQUID	ΔH_m (J/MOL)
Anorthite-albite				1752	0.980	0.600	157674
1823	0.983	0.950	135307	1745	0.980	0.600	153251
1823	0.983	0.961	89689	1730	0.980	0.500	177134
1813	0.960	0.887	128333	1723	0.980	0.500	164876
1813	0.960	0.906	93942	1694	0.980	0.400	159326
1793	0.915	0.772	125300	1687	0.980	0.400	150845
1793	0.915	0.800	99031	1679	0.980	0.350	174192
1773	0.874	0.689	112563	1672	0.980	0.350	155781
1773	0.874	0.701	104391	1657	0.970	0.300	171018
1753	0.836	0.581	126045	1650	0.970	0.300	153673
1753	0.836	0.609	109741	1641	0.970	0.250	179115
1733	0.799	0.508	123108	1634	0.970	0.250	171981
1733	0.799	0.529	112097	Anorthite-silica			
1713	0.763	0.442	121619	1814	0.995	0.886	200147
1713	0.763	0.461	112243	1807	0.995	0.886	138696
1693	0.728	0.383	120762	1784	0.980	0.776	137726
1693	0.728	0.402	111658	1777	0.980	0.776	119067
1673	0.692	0.329	120551	1735	0.965	0.668	102215
1673	0 692	0.348	111448	1728	0.965	0.668	94816
1653	0.656	0.279	121484	1715	0.955	0.616	99490
1653	0.656	0.298	112122	1708	0.955	0.616	93399
1633	0.619	0.234	122691	1694	0.940	0.564	96811
1633	0.619	0.254	112348	1687	0.940	0.564	91592
1613	0.581	0.191	125818	1673	0.935	0.514	97009
1613	0.581	0.212	114021	1666	0.935	0.514	92479
Anorthite-leucite				1654	0.915	0.473	94348
1809	1.000	0.904	132282	1647	0.915	0.473	90355
1802	1.000	0.904	98827	Anorthite-diopside			
1784	1.000	0.807	126533	1814	1.000	0.903	176009
1777	1.000	0.807	109390	1807	1.000	0.903	121968
1765	1.000	0.709	142083	1769	1.000	0.806	95163
1758	1.000	0.709	127760	1762	1.000	0.806	85029
1740	1.000	0.610	145403	1720	1.000	0.708	82153
1733	1.000	0.610	134367	1713	1.000	0.708	76924
1712	1.000	0.510	148640	1669	1.000	0.609	78223
1705	1.000	0.510	139743	1662	1.000	0.609	74549
1706	1.000	0.485	151474	1604	1.000	0.509	72925
1699	1.000	0.485	142791	1597	1.000	0.509	70425
Anorthite-orthoclase				Anorthite-wollastonite			
1814	0.990	0.900	164412	1790	1.000	0.817	137517
1807	0.990	0.900	113932	1783	1.000	0.817	116663
1800	0.990	0.800	194535	1745	1.000	0.722	101745
1793	0.990	0.800	157118	1738	1.000	0.722	93626
1776	0.980	0.700	168374	1605	1.000	0.527	69523
1769	0.980	0.700	148465	1598	1.000	0.527	67131

Data for anorthite-albite are from Bowen (1913); for anorthite-leucite, anorthite-orthoclase, and anorthite-silica from Schairer and Bowen (1947); for anorthite-diopside and anorthite-wollastonite from Osborn (1942). Columns entitled 'solid' and 'liquid' refer to mole fractions of anorthite.

Our imperfect knowledge of the structure of calcium-rich plagioclase at high temperature complicates the picture (see Smith, 1975). For pure anorthite, a completely disordered crystal has 23.05 J/mol·K of configurational entropy (Ulbrich and Waldbaum, 1976). A 42000 J/mol difference thus exists between the enthalpy of fusion of completely ordered and completely disordered anorthite, with the ordered phase exhibiting a higher value. On the basis of TEM (transmission electron microscopy) observations, G. L. Nord suggests (1977, oral communications) that pure anorthite formed at temperatures higher than 1700 K probably crystallizes in the disordered $C\bar{1}$ structure. However, it is the high-temperature data in Figures 4 through 6 which suggest anomalously high enthalpies of fusion, and hence

crystallization as the ordered phase. This contradiction remains unresolved.

Granted that Kracek and Neuvonen's (1952) determination of the heat of solution of anorthite crystals and glass is approximately correct, one is led to agree with Robie et al. (1978) and to conclude that the difference in enthalpy between anorthite glass and crystals at the melting point is very near 81000 J/mol. Data of Krupka and others (in preparation) do require a long extrapolation, but the heat content difference, $\Delta(H_{1830} - H_{298})$, between glass and crystals must lie between about 6000 and 15000 J/mol. An enthalpy of fusion in the neighborhood of 150000 J/mol is untenable in the light of the best available calorimetric data.
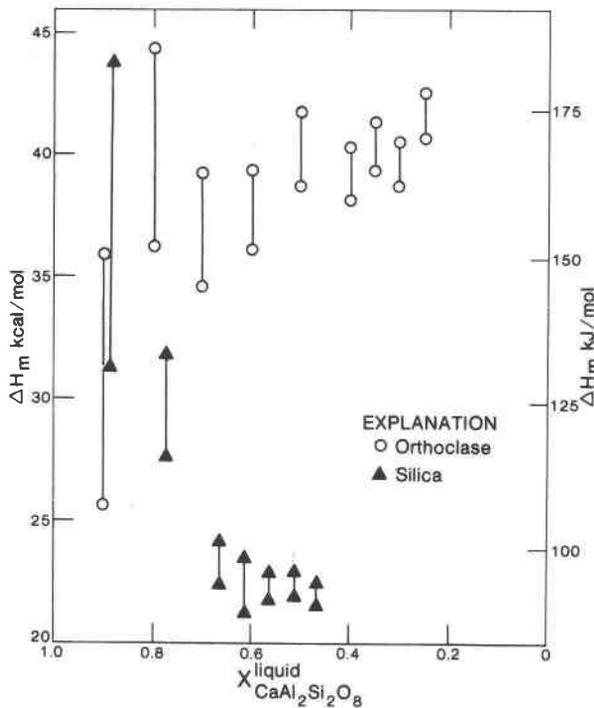
If the enthalpy of fusion of anorthite is near 81000

Fig. 4. Calculated enthalpies of fusion for the systems anorthite-orthoclase and anorthite–silica.
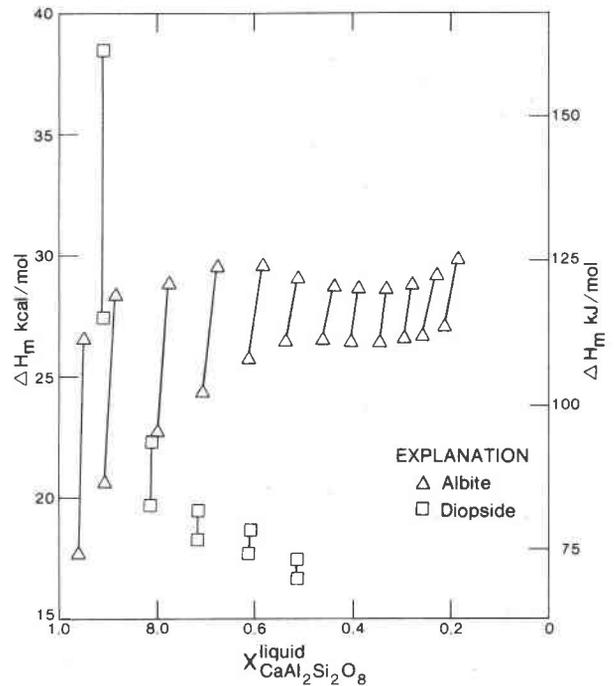

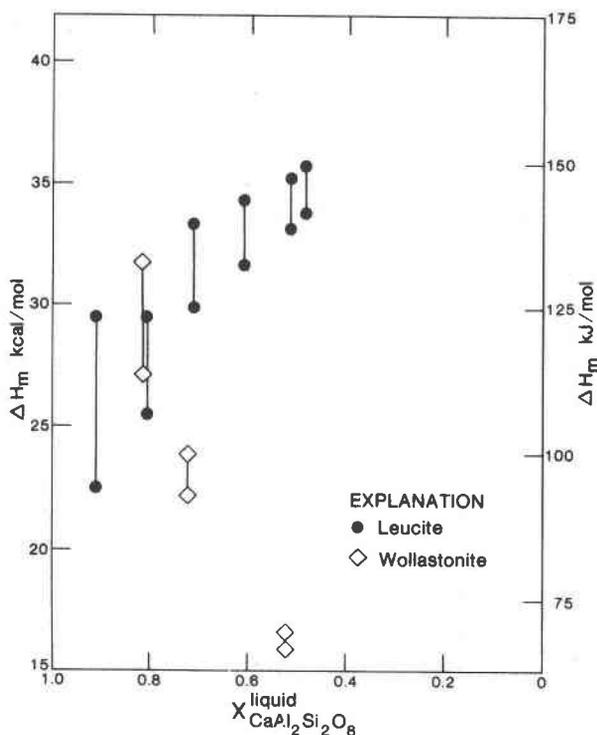Fig. 6. Calculated enthalpies of fusion for the systems anorthite-albite and anorthite–diopside.

Fig. 5. Calculated enthalpies of fusion for the systems anorthite-leucite and anorthite–wollastonite.

J/mol, the discrepancies in the enthalpies calculated in this paper might be ascribed to non-ideal mixing in the silicate liquids. To assess the nature and degree of this possible non-ideality, activities of anorthite in liquid were calculated for the various binary systems, assuming the enthalpy of fusion of anorthite to be 81000 J/mol. Solid activities were assumed to be equal to mole fractions, and the temperature used was the midpoint of the temperature range of the original data. The resulting activities and activity co-efficients are shown in Figures 7 and 8, respectively. The activity coefficient is simply the quotient of the calculated activity and the liquid composition.

Figure 8 looks remarkably like similar plots for metal alloys (Richardson, 1974, chapter 4), implying that the data are compatible with a regular solution model. The model seems to hold for mole fractions of <0.75, but the behavior of the activity coefficients at mole fractions of anorthite >0.75 is very uncertain and subject to large perturbations as the result of small changes in the assumed enthalpies of fusion and melting point of anorthite.

The slope of the lines in Figure 8 can be roughly correlated with the ionic potential of the cations in the solutions, with the largest positive deviations from ideality shown by systems containing potassium, the ion with the lowest potential.
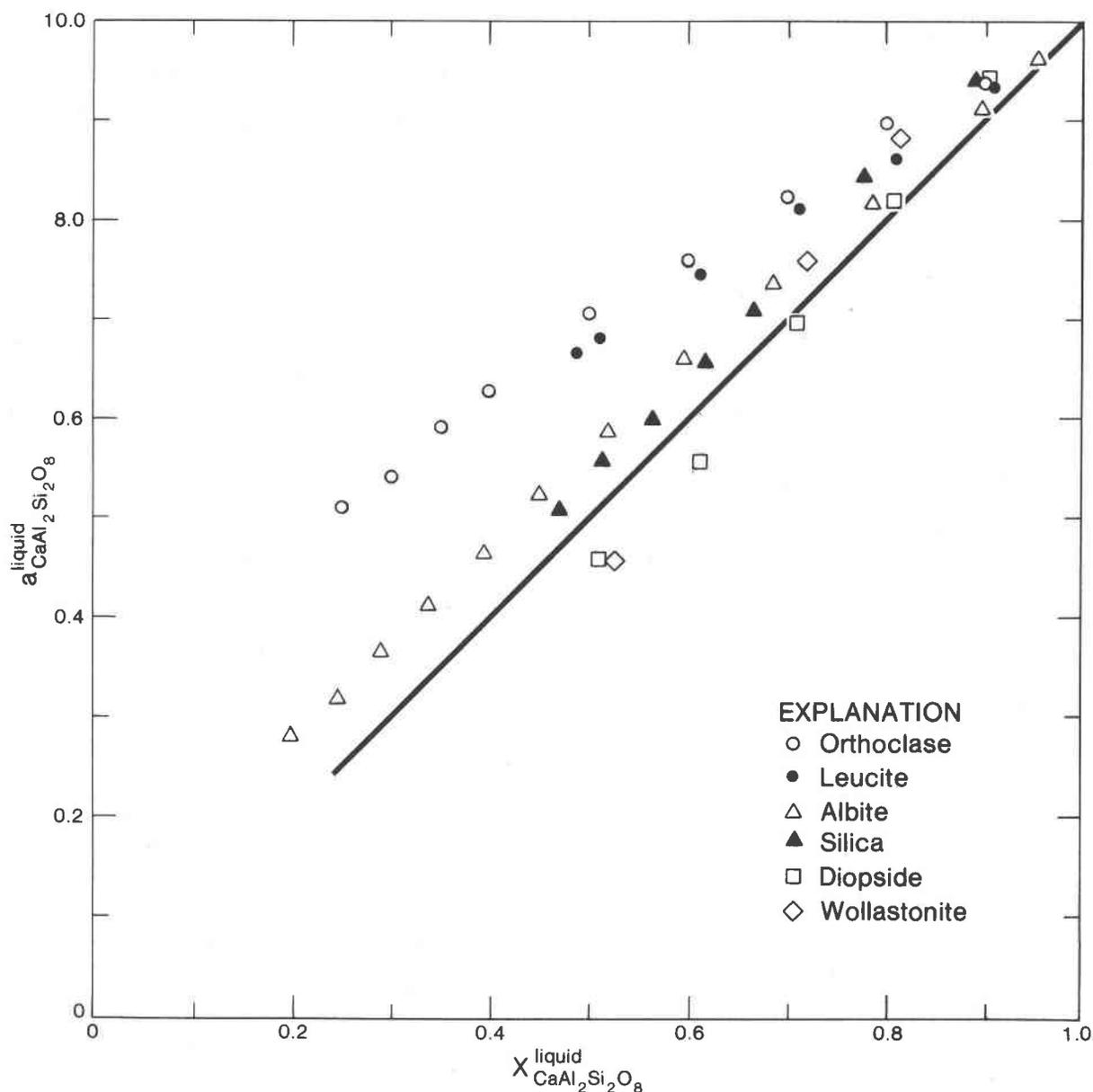
Fig. 7. Calculated activity–composition relations using the assumptions that the enthalpy of fusion of anorthite is 81000 J/mol and that its melting point is 1830 K. Size of the symbols for anorthite–albite reflects the uncertainty. The other symbols are about one half the size of their uncertainties for clarity. The straight line represents ideal mixing behavior.

The intent of this communication is to suggest that a regular solution model may be applicable to silicate melts; analysis of the model will require more extensive testing with more data and perhaps more sophisticated thermodynamic models. The great variation in the slopes of the lines in Figures 8 and 9, however, strongly suggests that a simple abandonment of the assumption of constant ΔC_p will not greatly simplify the situation.

An interesting implication of this data for experimental petrology is that valuable thermodynamic data may be gathered from close-spaced and precise data on liquidus surfaces. It could be very illuminating to study one of the systems considered in this study at 2 to 5 mole percent intervals, along with a careful determination of the melting point of anorthite. A necessity in such a study would be careful determination of the structural state of the calcic
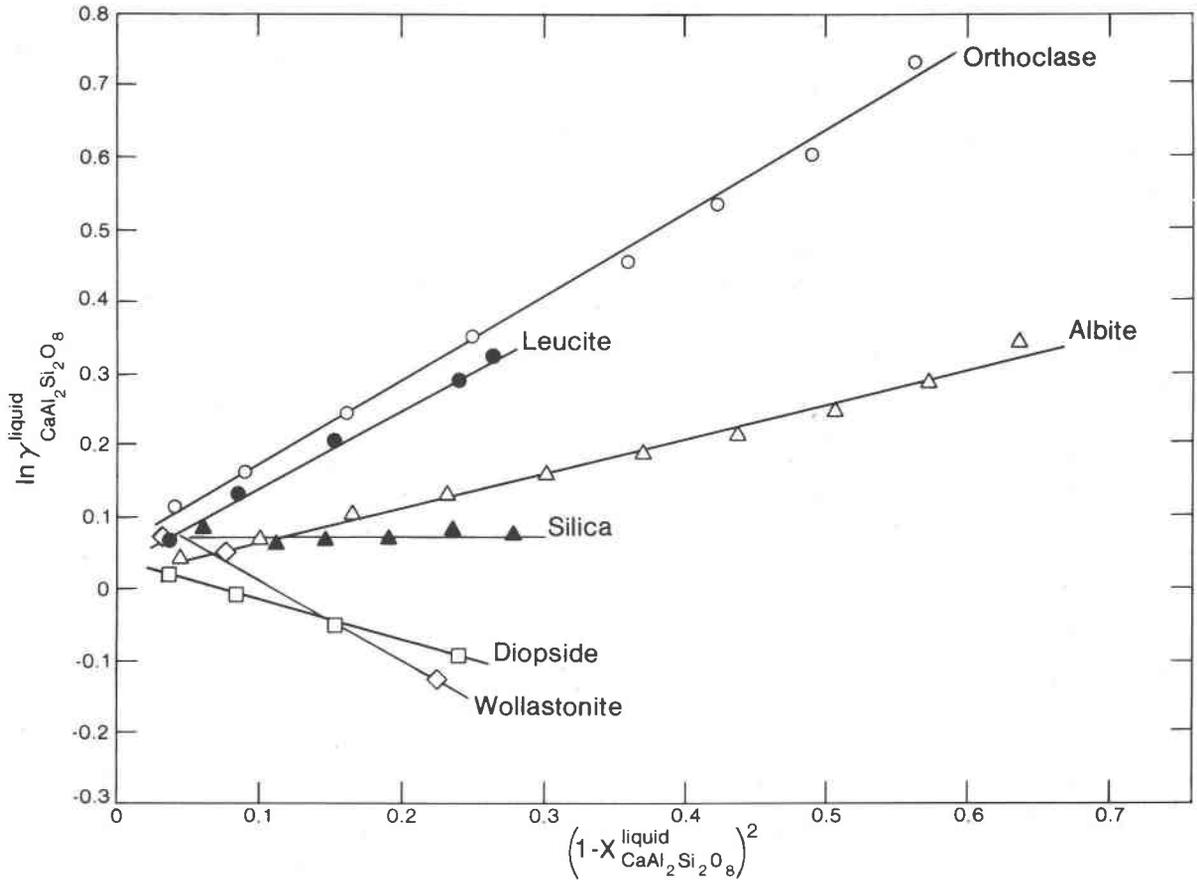
Fig. 8. Natural logarithm of calculated activity coefficients plotted *vs.* the square of the mole fraction of the solute. Straight lines are eyeball best fits to the data over the range in which they appear to exhibit regular solution behavior. Points at $(1 - X_{CaAl_2Si_2O_8}^{liquid}) < 0.2$ are omitted for clarity.

plagioclase. It might also be particularly revealing to study the molar volume of a series of glasses in some of these binary systems to see if such data could be correlated with the mixing behavior deduced from phase diagrams.

Summary and conclusions

An examination of the thermodynamics of melting of anorthite in binary systems suggests some basic conclusions about silicate melts containing anorthite as a component.

(1) Calculated enthalpies of fusion based on an ideal solution model are not compatible in detail with each other or with the calorimetrically-constrained figure of 81000 J/mol suggested by Robie *et al.* (1978).

(2) Calculated activity–composition relations for anorthite-bearing melts suggest that the binary systems under study may be described by regular solu-

tion theory, with mixing parameters controlled by the ionic potentials of the ions in the melt.

References

Bowen, N. L. (1913) The crystallization of the plagioclase feldspars. *Am. J. Sci., 35,* 577–599.

Burnham, C. W. (1975) Water and magmas; a mixing model. *Geochim. Cosmochim. Acta, 39,* 1077–1084.

Ferrier, A. (1969) Etude experimentale de l'enthalpie de l'anorthite synthetique entre 298 et 1950 K. *C. R. Acad. Sci. (Paris), Ser. C, 269,* 951–954.

Klein, L. and D. R. Uhlmann (1974) Crystallization behavior of anorthite. *J. Geophys. Res., 79,* 4869–4874.

Kracek, F. C. and K. J. Neuvonen (1952) Thermochemistry of

plagioclase and alkali feldspars. *Am. J. Sci., Bowen Volume,* 293–318.

Longhi, J. and J. F. Hays (1976) Solid solution and phase equilibria on the join anorthite–silica (abstr.). *Am. Geophys. Union Trans., 57,* 340.

Masson, C. R. (1972) Thermodynamics and constitution of silicate slags. *J. Iron Steel Inst., 210,* 89–96.

Osborn, E. F. (1942) The system $CaSiO_3$–diopside–anorthite. *Am. J. Sci., 240,* 751–788.

Peck, D. L., M. S. Hamilton and H. R. Shaw (1977) Numerical analysis of lava lake cooling models. Part II, application to Alae lava lake, Hawaii. *Am. J. Sci., 277,* 415–437.

Powell, R. L., W. J. Hall, C. H. Hyink, Jr., L. L. Sparks, G. W. Burns, G. Scroger and H. H. Plum (1974) Thermocouple reference tables based on the IPTS-68. *National Bureau of Standards Monograph 125.*

Richardson, F. D. (1974) *Physical Chemistry of Melts in Metallurgy, v. 1.* Academic Press, London and New York.

Robie, R. A., B. S. Hemingway and W. H. Wilson (1978) Low-temperature heat capacities of $KAlSi_3O_8$, Na $AlSi_3O_8$, and $CaAl_2Si_2O_8$ glasses and of anorthite. *Am. Mineral., 63,* 109–123.

Ryder, G., D. B. Stoeser, U. B. Marvin and J. F. Bower (1975) Lunar granites with unique ternary feldspars. *Proc. 6th Lunar Sci. Conf., Geochim. Cosmochim. Acta Supp. 6,* 435–449.

Schairer, J. F. and N. L. Bowen (1947) The system anorthite–leucite–silica. *Bull. Comm. Geol. Finlande, 140,* 67–87.

Smith, J. V. (1975) Phase equilibria of plagioclase. In P. H. Ribbe, Ed., *Feldspar Mineralogy,* Chapter 7. Mineral. Soc. Am. Short Course Notes 2.

Sosman, R. B. (1952) Temperature scales and silicate research. *Am. J. Sci., 250A,* pt. 2, 517–532.

Ulbrich, H. H. and D. R. Waldbaum (1976) Structural and other contributions to the third-law entropies of silicates. *Geochim. Cosmochim. Acta, 40,* 1–24.

Yoder, H. S., Jr. (1975) Heat of melting of some simple systems related to basalts and eclogites. *Carnegie Inst. Wash. Year Book, 74,* 515–519.