Heats of mixing of silicate liquid in the systems diopside-anorthite-akermanite, diopside-anorthite-forsterite, and diopside-silica

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ABSTRACT

Fusion enthalpies were measured by differential scanning calorimetry (DSC) for mineral mixtures of eutectic composition in the systems anorthite-diopside ($An_{42}Di_{58}$, wt%), anorthite-akermanite ($An_{46}Ak_{54}$), akermanite-diopside ($Ak_{42}Di_{58}$), diopside-silica ($Di_{84}Qt_{16}$), and anorthite-diopside-forsterite ($Di_{49}Fo_{7.5}An_{43.5}$), along with akermanite. Heats of mixing of silicate liquid in those systems were calculated based on the DSC data. The liquids of $Di_{49}Fo_{7.5}An_{43.5}$, $An_{42}Di_{58}$, $An_{46}Ak_{54}$, and $Ak_{42}Di_{58}$ have negative excess enthalpies of –4 to –10 ($\pm$5) kJ/mol, whereas the $Di_{84}Qt_{16}$ liquid has positive excess enthalpy of 5.0($\pm$1.7) kJ/mol. Those values are consistent with the heats of mixing estimated by thermodynamic analyses of phase equilibria of the above systems. The results suggest that the differential scanning calorimetry is useful and sufficiently accurate for direct calorimetric measurement of small endothermic or exothermic heat of mixing in silicate liquid.

INTRODUCTION

Knowledge of energetics of silicate liquid is necessary for thermodynamic analyses of mineral-melt equilibria and calculation of heat balance in magmatic processes. Comparison of thermodynamic parameters (fusion enthalpy, entropy, and heats of mixing, etc.) of silicate liquids with different compositions also gives insight into structure and speciation of silicate liquids on the microscopic scale (Stebbins et al. 1984; Navrotsky 1995). Although heats of mixing for silicate liquids have been derived as functions of composition based on thermodynamic analyses of multicomponent phase equilibria (e.g., Berman and Brown 1984; Ghiorso and Sack 1995; Andersson et al. 2002), those values depend on the method chosen for calculation of configurational entropy of the liquid and on the selection of phase-equilibrium experiments used in these analyses. Calorimetric measurements of silicate liquids are essential to test the assumptions in models and to validate (or disprove) mixing properties obtained from thermodynamic analyses of phase equilibria.

In early calorimetric studies, heats of mixing of silicate liquids were estimated by indirect methods based on a combination of solution calorimetry and traditional drop calorimetry (Stebbins et al. 1982; Richet and Bottinga 1984; Kosa et al. 1992). Furthermore, heats of mixing of silicate glasses instead of liquids had been investigated in detail by oxide melt solution calorimetry (e.g., Navrotsky et al. 1980, 1983; Hervig and Navrotsky 1984; Hervig et al. 1985). The thermodynamics of phase equilibria in the system anorthite-albite-diopside had been examined based on the calorimetric data of the glasses in those systems (Weill et al. 1980; Henry et al. 1982). However, subsequent studies by direct calorimetric measurements at high temperature (~1773K) have revealed that the heats of mixing of silicate liquids are significantly different from those of glasses

(Navrotsky et al. 1989; Navrotsky 1997). Direct measurements by transposed-temperature drop calorimetry have suggested that mixing in the liquid in the system Di-An-Ab is less exothermic than in the glass (Navrotsky et al. 1989). Heats of mixing of liquids in the system An-Fo (Navrotsky et al. 1989), Di-An-Wo (Tarina et al. 1994), and An-Di-Fo-En (Kojitani and Akaogi 1995, 1997) are very small or zero. Other methods of direct calorimetric measurement for silicate liquid are scanning calorimetry by step-scan and differential scanning calorimetry (DSC). Scanning calorimetry conveniently provides more accurate data of heats of fusion of silicate samples compared with the drop method. Richet et al. (1993) measured heats of fusion of forsterite and spinel by DSC method. Scanning calorimetry by step-scan method was performed to measure heats of fusion for diopside (Lange et al. 1991), olivine basalt and ugandite (Lange et al. 1994), and An-Di mixtures (DeYoreo et al. 1995). DeYoreo et al. (1995) reported that the heat of fusion of liquid of 10 mol% An + 90 mol% Di ($An_{12.5}Di_{87.5}$ wt%) is 114 $\pm$ 6 kJ/mol, 6% less than values calculated assuming athermal mixing. This result suggests that heat of mixing of the $An_{12.5}Di_{87.5}$ liquid is exothermic.

We have performed direct measurements of heats of fusion by differential scanning calorimetry for silicate liquids of eutectic composition in the systems anorthite-diopside-forsterite, anorthite-diopside-akermanite, and diopside-silica and of akermanite. This paper reports heats of mixing (excess enthalpy) of silicate liquids in those systems and discusses the consistency between heats of mixing measured by calorimetry and those predicted from thermodynamic analyses of the phase equilibria.

EXPERIMENTAL METHOD

Synthetic crystalline anorthite ($CaAl_2Si_2O_8$, An), diopside ($CaMgSi_2O_6$, Di), akermanite ($Ca_2MgSi_2O_7$, Ak), and forsterite (Mg_2SiO_4, Fo), and reagent-grade quartz (SiO_2, Qt) were used for the DSC measurements. The Di and An are from the same batches used by Sugawara and Akaogi (2003). The Ak was prepared

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from a stoichiometric mixture of reagents of $CaCO_3$, Al_2O_3, and SiO_2, and 5g of the pelletized mixture was heated on Pt foil at 1623 K for 72 hours. The Fo was made similarly from a mixture of MgO and SiO_2. The synthesized An, Di, and Fo were confirmed to be single-phase crystalline materials by powder X-ray diffraction (XRD) and electron microprobe analysis (EPMA). In the analysis of Ak, phases other than Ak were not detected by XRD, whereas a small quantity of wollastonite (Wo) was observed in the EPMA analysis. Mechanical mixtures of weighed An, Di, Ak, Qt, and Fo [with the compositions of $An_{42}Di_{58}$, $An_{46}Ak_{54}$, $Ak_{42}Di_{58}$, $Di_{84}Qt_{16}$, and $Di_{49}Fo_{7.5}An_{43.5}$ (wt%)] were made by grinding in an agate mortar with alcohol for one hour and were dried at about 450 K for a few hours. Powdered samples (~30 mg) of the mineral mixtures of the above proportions were encapsulated in 0.03 mm thick Pt foil, and used for calorimetry.

Differential scanning calorimetry was made with a Setaram MHTC high-temperature calorimeter at Gakushuin University. The DSC detector has two chambers for a sample and a reference. Both of the chambers are made of alumina and are of the same size, and they are placed side by side in symmetrical positions in the central part of a vertical graphite furnace. To measure fusion enthalpies of silicates, a pure Pt crucible was inserted into each alumina chamber to avoid reaction between silicate melt and alumina. The DSC detector can be used for calorimetric measurements up to 1873 K. The sample and reference chambers are each surrounded by twenty thermocouples. When an endothermic or exothermic reaction occurs in the sample cell, heat flow between the two chambers is detected as the change of e.m.f. of the thermocouples. Enthalpy of the reaction is measured by integrating the change of e.m.f. with time. All the enthalpy measurements were made during heating at a rate of 2 K/min. Figure 1 shows a typical endothermic peak ($An_{42}Di_{58}$ sample) during melting.

The heat of fusion (ΔH_{sample}) is obtained using the following relationship:

$$\Delta H_{sample} = A_{sample} \times (\Delta H_{STD}/A_{STD}) \qquad (1)$$

where the A_{sample} and A_{STD} represent integrated areas of endothermic peaks for the sample and the standard material, respectively, and the ΔH_{STD} is the published fusion enthalpy of the standard material. Calibration of enthalpy for the DSC detector was made using fusion enthalpies of Zn, Al, Ag, Au (JANAF 1998), and diopside (see below). In the melting of diopside, the abnormal increase in enthalpy (premelting) has been observed from around 1635K (Ziegler and Navrotsky 1986), 1605K (Lange et al. 1991), and 1580K (Richet and Fiquet 1991), which is 30–85 K below the melting point ($T_m = 1665$ K). Starting temperature T_p of endothermic reaction peak observed in our experiments was 1640 ± 5 K in average of seven measurements. Differences of premelting temperature in the previous experiments and the present study are probably caused by differing sensitivities of the calorimetric techniques. As shown in Figure 2, fusion enthalpy observed in DSC measurement, ΔH_{sample}, is related to fusion en-

thalpy at melting point, ΔH_{Tm}, as follows:

$$\Delta H_{Tm} = \Delta H_{measured} + \left(H_{Tp}^{Real\ Sol} - H_{Tp}^{Calc\ Sol}\right) - \int_{Tp}^{Tm} C_p^{Sol} \qquad (2)$$

where C_p^{Sol} is isobaric heat capacity, $H_{Tp}^{Real\ Sol}$ and $H_{Tp}^{Calc\ Sol}$ are real enthalpy during premelting (and/or incongruent melting) and enthalpy calculated from C_p^{Sol} at T_p, respectively. To obtain ΔH_{Tm} of diopside for calibration of the DSC detector, values of $H_{Tp}^{Real\ Sol}$-$H_{Tp}^{Calc\ Sol}$ and the ΔH_{Tm}(137.7 kJ/mol) by Lange et al. (1991) were used. The magnitude of the $H_{Tp}^{Real\ Sol}$-$H_{Tp}^{Calc\ Sol}$ in our experiments for Di calculated from the data in Table 2 of Lange et al. (1991) was about +6.3 kJ/mol (5% of ΔH_{Tm}) . As shown in Figure 3, the measured data of Zn, Al, Ag, Au, and diopside indicate that the calibration factor, $\Delta H_{STD}/A_{STD}$, of Equation 1 increases with increasing temperature, that is, the detector becomes less sensitive with increasing temperature. In this study, the following relationship obtained by linear regression of the data for the standard materials was used to calculate fusion enthalpies of samples:

$$\Delta H_{STD}/A_{STD} = 0.974 + 3.899 \times 10^{-4} \times T \text{ (K)} \qquad (3)$$

The combination of Equations 1 and 3 provides fusion enthalpy of sample material with accuracy of approximately ±2–3% between 700 and 1700 K.

RESULTS

The results are shown in Table 1. Four individual measurements were performed for each sample. One standard deviation of the data was 1–4 kJ/mol. It is observed that the melting reaction appears to 15–25 K below the eutectic temperatures of the reported phase diagrams for all the samples. The solidus (partial melting) and liquidus (eutectic) temperatures for $An_{42}Di_{58}$ and $Di_{49}Fo_{7.5}An_{43.5}$ are consistent with those reported in previous studies (see Table 1). Although solidus temperatures for $An_{46}Ak_{54}$, $Ak_{42}Di_{58}$, and $Di_{84}Qt_{16}$ still remain unknown, presumably those are not invariant points, but piercing points similar to the $An_{42}Di_{58}$ and $Di_{49}Fo_{7.5}An_{43.5}$. Another possibility is that partial melting could occur due to a small amount of impurity (Wo) in the Ak sample. To confirm incongruent melting reaction, melting experiments were performed for the sample of $An_{42}Di_{58}$, $Ak_{42}Di_{58}$, and $Di_{84}Qt_{16}$ using vertical quenching furnace under Ar gas with a heating rate of 2 K/min. Run
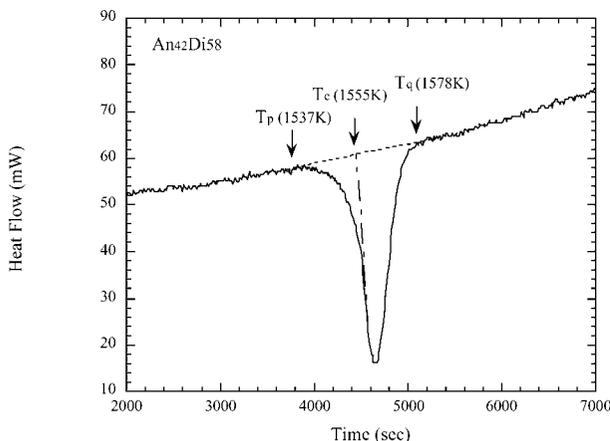

FIGURE 1. Typical endothermic peak (example of $An_{42}Di_{58}$ sample) during melting reaction observed in differential scanning calorimetry. Solidus and liquidus temperatures are defined by temperature T_p at which the heat flow falls from baseline (dotted line) and by onset temperature T_e, respectively. Endothermic heat content due to melting reaction is calculated based on integration of the peak area between T_p and T_q.
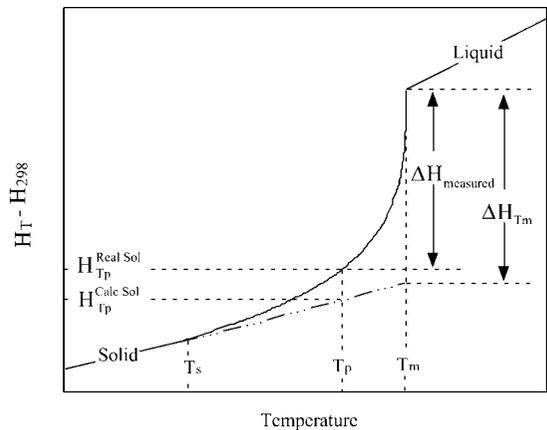

FIGURE 2. Schematic relationship between measured enthalpy by differential scanning calorimetry, ΔH_{sample}, and fusion enthalpy, ΔH_{TM}, for a material showing premelting. Temperature T_s, T_p, and T_m represent starting temperature of premelting, temperature at which the heat flow falls from baseline (see T_p in Fig. 1), and melting temperature, respectively.
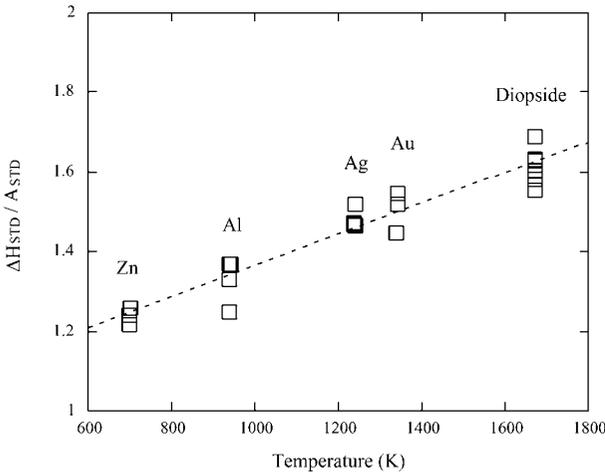
FIGURE 3. Relationship between calibration factors ($\Delta H_{STD}/A_{STD}$) and melting temperatures of standard materials in the DSC measurements.

products quenched at temperatures 5–13 K below the liquidus temperatures observed by DSC were glass plus a small amount of An for the $An_{42}Di_{58}$ at 1543 K, only glass for the $Ak_{42}Di_{58}$ at 1634 K, and glass plus a small amount of Qt for the $Di_{84}Qt_{16}$ at 1634 K. All glasses analyzed by EPMA were compositionally homogeneous, and the standard deviations based on the six measurements for different points in the same glass were less than 0.3 wt% in all oxides. This result suggests that endothermic reaction during DSC measurements had also occurred homogeneously throughout samples.

Fusion enthalpies for $Di_{49}Fo_{7.5}An_{43.5}$ and akermanite were calculated from Equation 2 using the $\Delta H_{measured}$ of this study and C_P^{Sol} from Berman (1988), assuming $H_{Tp}^{Real\ Sol}-H_{Tp}^{Calc\ Sol} = 0$, and are 113.5 ± 3.9 and 133.1 ± 2.4 kJ/mol, respectively. The former value agrees with that determined by transposed-temperature drop calorimetry for $Di_{49}Fo_{7.5}An_{43.}$ (116.8 ± 8.9 kJ/mol, Kojitani and Akaogi 1995). The latter datum is slightly larger than the fusion enthalpy of akermanite obtained by a combination of drop calorimetry and HF solution calorimetry for Ak (123.9 ± 3.2 kJ/mol, Proks et al. 1976). If small amount

of Wo in the Ak sample affected the endothermic heat content and/or premelting occurred during the DSC measurements, the real ΔH_{Tm} would probably be larger than 133.1 kJ/mol, as the ΔH_{Tm} of Wo is smaller than that for the Ak and $H_{Tp}^{Real\ Sol}-H_{Tp}^{Calc\ Sol}$ in Equation 1 is positive. Therefore, our reported ΔH_{Tm} for the Ak sample (133.1 kJ/mol) is regarded as a minimum estimate.

Excess enthalpy of liquid at composition X_1 and temperature T_1, H_{ex}^{Liq}, is defined as the difference between enthalpy of the liquid ($H_{T_1}^{Liq}$) and sum of enthalpies of end-members:

$$H_{ex}^{Liq} = H_{T_1}^{Liq} - \sum_i X_i H_{T_1}^{i,Liq}. \tag{4}$$

For a solid phase at T_2 ($T_2 < T_1$), $0 = H_{T_2}^{Sol} - \sum_i X_i H_{T_2}^{i,Sol}$, therefore,

$$H_{ex}^{Liq} = \left(H_{T_1}^{Liq} - H_{T_2}^{Sol}\right) - \sum_i X_i \left(H_{T_1}^{i,Liq} - H_{T_2}^{i,Sol}\right). \tag{5}$$

When T_1 is liquidus (eutectic) temperature (T_e), and T_2 is the solidus temperature (T_p), the $H_{Te}^{i,Liq}$ is expressed by

$$H_{Te}^{i,Liq} = H_{Tp}^{i,Sol} + \int_{Tp}^{Tm_i} C_{Pi}^{Sol} dT + \Delta H_{Tm}^i - \int_{Te}^{Tm_i} C_{Pi}^{Liq} dT. \tag{6}$$

Substitution of the Equation 6 and $\Delta H_{measured} = H_{Te}^{Liq} - H_{Tp}^{Sol}$ into Equation 5 yields

$$H_{ex}^{Liq} = \Delta H_{measured} - \sum_i X_i \left[\int_{Tp}^{Tm_i} C_{Pi}^{Sol} dT - \int_{Te}^{Tm_i} C_{Pi}^{Liq} dT + \Delta H_{Tm}^i\right]. \tag{7}$$

The excess enthalpies of the liquids were calculated from Equation 7 using thermodynamic data of end-member components (Table 2) and the ΔH_{sample} (Table 1). Two different values for ΔH_{Tm}^{Ak}, 133.1 kJ/mol (ΔH_{Tm}^{Ak} assuming no premelting) and 139.8 kJ/mol (a value 5% higher than 133.1 kJ/mol considering possible effect of premelting), were tested in calculation of the H_{ex}^{Liq} in order to examine the effect of the ΔH_{Tm}^{Ak} on the H_{ex}^{Liq}. Accuracy for the H_{ex}^{Liq} was calculated based on error propagation using errors of respective thermodynamic data. The calculated H_{ex}^{Liq} values are shown in Table 1.

All the excess enthalpies of silicate liquids investigated here are small values within from +5 to –10 kJ/mol. The liquids of $Di_{49}Fo_{7.5}An_{43.5}$, $An_{42}Di_{58}$, $An_{46}Ak_{54}$, and $Ak_{42}Di_{58}$ have negative H_{ex}^{Liq} of –4 to –10 (±5) kJ/mol. The H_{ex}^{Liq} for the $An_{46}Ak_{54}$ and

TABLE 1. Solidus (T_p) and liquidus (T_e) temperatures, measured endothermic heat content ($\Delta H_{measured}$) between T_p and T_e, and calculated excess enthalpy (H_{excess}^{Liq})

Composition	Reported T_p and T_e		Measured T_p and T_e		$\Delta H_{measure}$		H_{excess}^{Liq}
	T_p (K)	T_e (K)	T_p (K)	T_e (K)	(kJ/mol)	averages	(kJ/mol)
$An_{43.5}Di_{49}Fo_{7.5}$	1533*	1543†	1534 ± 3	1547 ± 2	120.0, 112.8, 114.2, 121.7	117.2 ± 4.3	–3.8 ± 5.0
$An_{42}Di_{58}$	1538‡	1547‡	1532 ± 3	1550 ± 2	122.9, 124.3, 123.6, 120.6	122.8 ± 1.6	–4.3 ± 2.6
$Di_{58}Ak_{42}$		1638§	1618 ± 1	1638 ± 2	139.6, 136.3, 136.7, 136.4	137.2 ± 1.6	–1.1±2.3††, –3.6±2.3‡‡
$An_{46}Ak_{54}$		1507ll	1499 ± 4	1518 ± 2	111.7, 115.4, 108.3, 116.7	113.0 ± 3.8	–6.2±5.7††, –9.8±5.7‡‡
Ak_{100}		1727#	1711 ± 2	1731 ± 2	139.5, 141.4, 136.0, 140.8	139.4 ± 2.4	
$Di_{84}Qt_{16}$		1635**	1622 ± 2	1647 ± 2	93.4, 90.4, 91.8, 93.5	92.3 ± 1.4	5.0 ± 1.7

Notes: Four measurements were made for each sample.
* T_p calculated from T_e by Osborn and Tait (1952) and temperature range of partial melting (10 K, Kojitani and Akaogi 1995).
† Osborn and Tait (1952).
‡ Osborn (1942).
§ Ferguso and Merwin (1919).
ll De Wys and Foster (1956).
Proks et al. (1977).
** Schairer and Bowen (1938).
†† H_{excess}^{Liq} calculated assuming $\Delta H_{Tm}^{Ak} = 133.1$ kJ/mol.
‡‡ H_{excess}^{Liq} calculated assuming $\Delta H_{Tm}^{Ak} = 139.8$ kJ/mol.

TABLE 2. Thermodynamic data of pure end-members used in the calculation of excess enthalpy of liquid

	$CaMgSi_2O_6$	$Ca_2MgSi_2O_7$	Mg_2SiO_4	SiO_2	$CaAl_2Si_2O_8$
C_P-liquid [J/(K·mol)]	334±7*	382±27†	271±6.2 ‡	85.772±1§	400.772+0.020243 × T(K) ±10‖
ΔH_{Tm} (kJ/mol)	137.7±1*	133.1±2.4#	142±14**	8.92±1††	133±4‖
T_m (K)	1665*	1731#	2174**	1999††	1830‖

The C_P for solid phase is calculated from Berman (1988) assuming error of ±1% [~±3J/(K·mol)].
* Lange et al. (1991).   ‖ Richet and Bottinga (1984).
† Proks et al. (1977).   # This study.
‡ Lange and Navrotsky (1992).   ** Richet et al. (1993).
§ JANAF (1984).   †† Cristobalite, Richet et al. (1992).

$Ak_{42}Di_{58}$ liquids become more exothermic when the larger ΔH_{Tm}^{Ak} is adopted. In contrast, the liquid of $Di_{84}Qt_{16}$ has a positive H_{ex}^{Liq} of 5.0±1.7 kJ/mol.

DISCUSSION

The H_{ex}^{Liq} also can be estimated by thermodynamic analysis of phase equilibria using thermodynamic data of end-members and activity-composition relationships of solid phases. The H_{ex}^{Liq} values of multicomponent silicate liquids have been derived as functions of composition based on the analysis of phase equilibria of simple two- and three-component systems (e.g., Andersson et al. 2002) and of natural magmatic systems (Ghiorso and Sack 1995). However, they are to be considered model parameters simply to reproduce phase equilibria rather than thermodynamic properties with energetic meaning, because the H_{ex}^{Liq} derived by thermodynamic analyses depend on the method chosen for calculation of configurational entropy of the liquid and on the selection of phase-equilibrium experiments used in these analyses. For silicate liquids corresponding to $An_{42}Di_{58}$, $An_{46}Ak_{54}$, $Ak_{42}Di_{58}$, and $Di_{84}Qt_{16}$, we calculated the effect of assuming zero heats of mixing ($H_{ex}^{Liq} = 0$) on phase equilibria and compared the H_{ex}^{Liq} estimated by the thermodynamic analysis with those obtained from calorimetric measurements.

The difference between the partial molar Gibbs free energies of component i in a solid and a liquid in a binary system, ΔG_i, is expressed by

$$\Delta G_i = G_i^{Liq} - G_i^{Sol} + RT \ln X_i^{Liq} - RT \ln a_i^{Sol}$$
$$+\left(1 - X_i^L\right)^2 \left[\left(1 - 2X_i^L\right)W_{ij}^{Liq} + 2X_i^L W_{ji}^{Liq}\right] \quad (8)$$

where ΔG_i^{Liq} and ΔG_i^{Sol} are molar Gibbs free energies of the liquid and solid of pure component i, respectively, and a_i^{Sol} is the activity of the solid. The W_{ij}^{Liq} and W_{ji}^{Liq} are asymmetric solution parameters of the liquid. The ΔG_i must be zero under equilibrium condition. Assuming that the liquid is an ideal solution ($W_{ij}^{Liq} = W_{ji}^{Liq} = 0$) and the solid is a pure phase ($a_i^{Sol} = 1$), the eutectic temperature at a given eutectic composition can be calculated using data of Table 2. The results are shown in Table 3. Two different values of a_{Di}^{Sol}, 1 and 0.8, were tested for the composition $An_{42}Di_{58}$, because the Di in the An-Di system includes a small amount of the $CaAl_2SiO_6$ component (Osborn 1942), and thereby the activity of diopside is likely less than unity. Also, the two ΔH_{Tm}^{Ak} values, 133.1 and 139.8 kJ/mol, were tested in the calculation. The calculated eutectic temperatures differ from the actual temperatures by about 50–150 K irrespective of the adopted a_{Di}^{Sol} and ΔH_{Tm}^{Ak}. It is clear that those discrepancies are caused by the existence of excess enthalpies of mixing of the silicate liquids.

In a binary system, substituting a known eutectic composition and temperature for Equation 5 provides both the W_{ij}^{Liq} and W_{ji}^{Liq}. Then the H_{ex}^{Liq} is calculated using the following relationship:

$$H_{ex}^{Liq} = X_i\left(1 - X_j\right)\left[\left(1 - X_i^L\right)W_{ij}^L + X_i^L W_{ji}^L\right] . \quad (9)$$

The calculated results are also given in Table 3. Two different models, a two-lattice model (e.g., Weill et al. 1980) and a simple oxide model, were tested in calculating the partial molar configurational entropy ($RT \ln X_i^{Liq}$) in Equation 5. The configurational entropy of mixing Si and Al in tetrahedral sites and of mixing divalent cations in non-framework sublattice are calculated using the two-lattice model. Navrotsky (1995) concluded that a combination of athermal mixing and the two-lattice model reproduces the diopside saturation surface well when the liquid composition has Al/(Al + Si) < 0.25 and Ca/(Mg + Ca) < 0.5. In the simple oxide model, the configurational entropy is calculated assuming random mixing of end-member components such as Di, An, and Ak etc.

The calculated H_{ex}^{Liq} is listed in Table 3. Regardless of the simple oxide or two-lattice model, the calculated H_{ex}^{Liq} for the $An_{42}Di_{58}$ and $An_{46}Ak_{54}$ compositions are negative values of –3 to –10 kJ/mol. The H_{ex}^{Liq} of the $Ak_{42}Di_{58}$, is positive or negative, when the simple oxide or two-lattice model is adopted, respectively. Because of errors in calorimetric measurements and uncertainty in the ΔH_{Tm}^{Ak} and activity of diopside, although it is impossible to discuss the configurational entropy of the liquid quantitatively based on the comparisons of the measured and calculated H_{ex}^{Liq}, it appears that the values of the H_{ex}^{Liq} calculated assuming the two-lattice model are generally consistent with those obtained from calorimetry (Table 1). Our result that the

TABLE 3. Saturation temperatures at eutectic compositions calculated assuming $H_{excess}^{Liq}=0$, and the H_{excess}^{Liq} calculated by thermodynamic analyses of phase equilibria assuming simple oxide model or two lattice model

Eutectic comp. (wt%)	Saturation temperature (K) calculated assuming $H_{excess}^{Liq}=0$	Calculated H_{excess}^{Liq} (kJ/mol) Simple oxide model	Two lattice model
$An_{42}Di_{58}$*	(An)1626; (Di)1592†, 1628‡	–4.4†, –6.2‡	–2.7†, –4.6‡
$An_{46}Ak_{54}$§	(An)1671; (Ak)1637‖, 1641#	–10.3‖, –10.8#	–10.1‖, –10.6#
$Di_{58}Ak_{42}$**	(Di)1591; (Ak)1568‖, 1576#	4.5‖, 4.4#	–3.9‖, –4.1#
$Di_{84}Qt_{16}$ ††	(Di)1580	7.2	

* Osborn (1942).
† $a_{Di}^{Sol}=1$.
‡ $a_{Di}^{Sol}=0.8$.
§ De Wys and Foster (1956).
‖ H_{excess}^{Liq} calculated assuming $\Delta H_{Tm}^{AK}=133.1$ kJ/mol.
H_{excess}^{Liq} calculated assuming $\Delta H_{Tm}^{AK}=139.8$ kJ/mol.
** Ferguso and Merwin (1919).
†† Schairer and Bowen (1938).

$An_{42}Di_{58}$ liquid has negative H_{ex}^{Liq} is consistent with that obtained by scanning calorimetry for $An_{12.5}Di_{87.5}$ liquid reported by DeYoreo et al. (1995). Calculated H_{ex}^{Liq} for the $Di_{84}Qt_{16}$ is a positive value (7.2 kJ/mol), which almost agrees with that obtained by DSC measurements (5.0 ± 1.7 kJ/mol). The positive H_{ex}^{Liq} in the system diopside-silica is also supported by existence of liquid immiscibility in this system.

SUMMARY REMARKS

The liquids in the systems Di-Fo-An and Di-An-Ak have negative excess enthalpies (minimum about –10 kJ/mol) and the liquid in the system Di-Qt has a positive excess enthalpy (maximum about 7 kJ/mol). Those values are smaller than the error in typical transposed-temperature drop calorimetry (±10–15 kJ/mol, Navrotsky et al. 1989; Tarina et al. 1994). As shown in Table 3, however, such small differences of enthalpy (+10 to –10 kJ/mol) affect phase equilibria considerably, resulting in differences of 50–150 K for saturation temperatures of minerals. Therefore, the small H_{ex}^{Liq} of multicomponent silicate liquid cannot be ignored in petrological applications based on thermodynamic calculation.

We have shown that differential scanning calorimetry can provide precise data of small heats of mixing of silicate liquids within ±10 kJ/mol, and those data are consistent with values obtained from thermodynamic analyses of phase equilibria. It is concluded that the DSC measurement, as well as transposed-temperature drop calorimetry, is useful for direct calorimetric measurement of the heats of mixing of silicate liquids.

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