

## The high temperature liquid and glass heat contents and the heats of fusion of diopside, albite, sanidine and nepheline

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### Abstract

We have measured the relative enthalpy,  $H_T - H_{300K}^{\text{glass}}$ , and the heat capacities of  $\text{CaMgSi}_2\text{O}_6$  (Di) stable liquid and glass; of  $\text{KAlSi}_3\text{O}_8$  (Sa) stable and supercooled liquid and glass; of  $\text{NaAlSi}_3\text{O}_8$  (Ab) liquid derived directly by melting solid albite; of crystalline, disordered albite itself; and of  $\text{NaAlSiO}_4$  (Ne) liquid and glass. We have also determined the effect of annealing at 981 K on the enthalpy of the glasses quenched from liquids at high temperature. This effect is relatively small, ranging from 0 to 1100 cal/mol. These data can be combined with published results on heats of vitrification and the heat capacities of solids to yield heats of fusion, in kcal/mol: Di  $33.0 \pm 0.5$  (1665 K); Ab:  $15.0 \pm 0.5$  (1373 K); Sa:  $13.8 \pm 1.0$  (metastable, 1473 K); and Ne:  $11.7 \pm 0.5$  (metastable, 1750 K).

Albite liquid prepared by melting of the crystalline phase has a heat capacity and relative enthalpy indistinguishable from those of a liquid produced by heating the glass. The enthalpy of crystalline, disordered albite (probably monoclinic) is equal to that predicted by heat capacity data collected below 1000 K for the triclinic phase by Hemingway *et al.* (1981). The liquid heat capacities of Ab and Sa (88.2 and 89.5 cal/mol · K) are nearly equal and are much lower than that for An liquid (113 cal/mol · K), suggesting that the latter undergoes greater structural changes, possibly depolymerization, with increasing  $T$ . The entropies of fusion of Ab and Sa (10.9 and 9.4 cal/mol · K) are similar, and much of the difference between these values and that for An (17.7 cal/mol · K) could be due to Al/Si order in crystalline An.

### Introduction

Accurate values of the heats of fusion of minerals are required in a variety of problems in igneous petrology, including the modeling of energy budgets of cooling magmas and the definition of standard states for the components of more complex silicate liquid and solid solutions.

We have recently reported on the heat of fusion ( $\Delta H_f$ ) of anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) (Weill *et al.*, 1980b) and have presented data on liquids and glasses of plagioclase composition (Stebbins *et al.*, 1982). Here we introduce new data to define better the heats of fusion of disordered albite ( $\text{NaAlSi}_3\text{O}_8$ ), diopside ( $\text{CaMgSi}_2\text{O}_6$ ), sanidine ( $\text{KAlSi}_3\text{O}_8$ ), and nepheline ( $\text{NaAlSiO}_4$ ). The calculations presented here, which use enthalpy and heat capacity results for the stable liquids, should produce much more reliable estimates than those based on data for glasses alone (*e.g.*, Robie *et al.*, 1979; Yoder 1976).

It has been suggested (Boettcher *et al.*, 1980) that albite liquid which is produced by reheating of the glass above its liquidus temperature may not come to equilibrium during high temperature calorimetric experiments. We present here direct evidence that places strong limits on the magnitude of such an effect on the measured thermal properties.

Finally, we have measured the heat content of disordered crystalline albite near its melting point.

### Experimental methods

Preparation of starting materials, and the techniques and instruments used in drop and differential scanning calorimetry (DSC), have been described in detail earlier (Stebbins *et al.*, 1982; Weill *et al.*, 1980b). A Perkin-Elmer DSC-2 was used for direct heat capacity measurements. A diphenyl ether drop calorimeter with a 300 K reference temperature, coupled to a platinum–40% rhodi-

um wire-wound furnace, provided high temperature data. Air was removed from the diphenyl ether by repeated freezing under vacuum. Sample size for the DSC was about 30 mg, and about 1.6 g for the drop calorimeter. NBS 720 sapphire standard reference material was used to calibrate both calorimeters, with one standard run for every one or two sample runs. Samples were examined after measurement by petrographic microscope and by X-ray diffraction to check for crystallization. Glasses were analyzed after runs by electron microprobe to insure that compositional changes were insignificant. The frequent calibration, and the good agreement of our drop and DSC data on albite glasses and liquid with results from other laboratories (Stebbins *et al.*, 1982) suggest that systematic errors are not significant in the results presented here.

Inverse drop and drop-solution calorimetric measurements were made with a twin, Calvet-type microcalorimeter operating at 981 K (described by Navrotsky and Coons, 1976, Navrotsky and Kleppa, 1968, *etc.*). Glasses were prepared by quenching liquids in the drop calorimeter, using the same capsules and sample sizes as in the high temperature enthalpy runs. Samples were generally removed from capsules by diamond core drill, producing cylinders about 3 mm in diameter and between 60 and 190 mg in weight. In most experiments, unencapsulated glass pieces were dropped from room temperature into an empty silica crucible in the calorimeter. Heat effects were observable for about 50 minutes. Calibration by dropping pieces of platinum wire allowed accurate absolute measurements. Samples were weighed before and after inverse drop experiments. Weight changes were less than 0.1%, indicating that vaporization of absorbed water did not make an important contribution to the measured enthalpy changes.

Several experiments were also made in which glasses were dropped into and dissolved in  $\text{Pb}_2\text{B}_2\text{O}_5$  flux at 981 K from 298 K in order to bring samples to a well defined, equilibrium final state.

### The determination of heats of fusion

Most determinations of the heats of fusion ( $\Delta H_f$ ) of high melting point materials have been made by drop calorimetry on materials (such as metals and salts) that rapidly and reproducibly crystallize upon quench. The interpretation of measurements in such cases is straightforward, because the liquid returns to the same final crystalline state as the solid after cooling in the calorimeter to the reference temperature  $T_r$  (generally near 298 K). Equations are fitted to heat content measurements on the liquid (l) above the melting point  $T_f$  and on the solid (s) below  $T_f$ , and the results at some temperature  $T$  are simply subtracted:

$$\Delta H_{f,T} = H_T^l - H_T^s = (H_T^l - H_{T_r}^l) - (H_T^s - H_{T_r}^s) \quad (1)$$

Many silicate liquids, however, form glasses on quenching. Several techniques have been used to calcu-

late  $\Delta H_f$  for such glass formers; and all depend on solution calorimetric measurements in addition to heat content data. First, the heat of vitrification,  $\Delta H_v$ , is simply computed as the difference between the heats of solution of the glass (g) and the solid at the temperature of solution,  $T_{sc}$ :

$$\begin{aligned} \Delta H_{v,T_{sc}} &= H_{T_{sc}}^g - H_{T_{sc}}^s \\ &= (H_{T_{sc}}^g - H_{in\ solution}) - (H_{T_{sc}}^s - H_{in\ solution}) \quad (2) \end{aligned}$$

In order to calculate  $\Delta H_f$  accurately at and above the liquidus temperature,  $\Delta H_v$  must then be combined with high temperature data for the solid and for the stable liquid. If the temperature of transition ( $T_g$ ) between glass and supercooled liquid, and the heat capacity of the supercooled liquid, can be estimated, then the heat of fusion can be calculated from the relationship:

$$\begin{aligned} \Delta H_{f,T} &= \Delta H_{v,T_{sc}} + \int_{T_{sc}}^{T_g} (C_P^g - C_P^s) dT \\ &\quad + \int_{T_g}^T (C_P^l - C_P^g) dT \quad (3) \end{aligned}$$

This method was used by Weill *et al.* (1980a) to determine  $\Delta H_f$  for albite, anorthite, and diopside, and provided better estimates than those based on glass data alone. The calculation was somewhat limited, however, because it was necessary to assume (1) that the heat capacity of the liquid was constant at some average value over a large temperature range below the melting point, and (2) that the glass transition temperatures determined by dilatometry are identical to the transition temperatures in heat capacity. The accuracy of the first assumption is difficult to assess for those liquids which crystallize instead of supercooling (such as anorthite and diopside liquids), thus making calorimetric measurements on the liquid below  $T_f$  impossible. Since the transition behavior of glasses can be significantly affected by their thermal histories (Moynihan *et al.*, 1974), the latter assumption may not always be adequate.

Calorimetric measurements on the stable liquid (above  $T_f$ ) can improve the estimate of the heat of fusion in the stable liquid region. However,  $\Delta H_v$  is often best known at a temperature  $T_{sc}$  much higher than the drop calorimetry quench temperature  $T_r$ . The enthalpy change in the glass and solid from  $T_r$  to  $T_{sc}$  must then also be measured and combined with the other data:

$$\begin{aligned} \Delta H_{f,T} &= \Delta H_{v,T_{sc}} + (H_T^l - H_{T_r}^l) - (H_T^s - H_{T_r}^s) \\ &\quad - (H_{T_{sc}}^g - H_{T_r}^g) + (H_{T_{sc}}^s - H_{T_r}^s) \quad (4) \end{aligned}$$

$(H_{T_{sc}} - H_{T_r})$  can be measured by standard drop calorimetry from high to low  $T$ , by inverse drop calorimetry from low to high  $T$ , or by integration of direct heat capacity data from differential scanning calorimetry. Barring phase transitions, all such techniques should give the same

results for crystalline materials, since equilibrium is maintained. Measurements of enthalpy changes in the glass region by different techniques may not, however, be identical. The selection of data on  $H_{T_{sc}} - H_{T_r}$  for glasses of appropriate thermal histories is essential for accuracy in the heat of fusion calculation.

Published  $C_p$  equations for the crystalline phases often contain more terms than are needed to accurately reproduce the data at high temperatures, where  $C_p$  changes slowly with  $T$ . Derived heat of fusion equations can thus be overly cumbersome. We therefore have refitted the enthalpies of the crystalline phases above 900 K with simple equations of the form  $H_T = aT + b/2 T^2 + c$ , with  $C_p = a + bT$ . The simplified expressions given below predict enthalpies that are the same within 0.1% of those calculated from the more complex expressions at temperatures between 900 and 2000 K. Heat of fusion expressions based on both types of equation are given in Table 7 for completeness.

### Glasses in calorimetry

Most previous studies by drop calorimetry on glass-forming liquids (Richet and Bottinga, 1980; Ferrier, 1968a,b; White 1919) have not considered the potential effects of variations in thermal history of the glasses on their calorimetric properties.

During the preparation of a glass, and during drop calorimetry on glass-forming liquids, a liquid is cooled rapidly from temperature  $T$ , through the stable and supercooled liquid regions, down through the glass transition range, to a final temperature of about 300 K. At some point during cooling, the response of the structural configuration of the sample to temperature begins to lag behind adjustment to equilibrium. The temperature at which this lag begins depends on the cooling rate. The enthalpy vs. temperature curve followed therefore begins to depart from that which it would follow if it were cooled very slowly (Fig. 1, curve 1–2–3 as opposed to curve 1–4–5–6).

Navrotsky *et al.*, (1982) discovered a thermal history effect of this type with inverse drop calorimetry from 298 to 985 K on albite glass. Unannealed samples were dropped into the calorimeter, then retrieved after 3–8 hours at 985 K. Second drops on the same samples gave values of  $H_{985}^g - H_{300}^g$  that were 500–800 cal/mol greater than the values from the first runs, with no additional increases on subsequent drops. The interpretation of the experiments is illustrated by Figure 1. The glass initially produced by rapid quenching of the liquid has a heat content corresponding to point 3 at the beginning of an inverse drop sequence. Fifty minutes at 985 K anneals the glass so that  $H_{985}^g$  corresponds to 5 rather than 2. Cooling back to room temperature results in state 6 at the beginning of the second drop, but the final state at the end of the second drop is again 5. The difference  $(H_5 - H_6) - (H_5 - H_3)$ , which is the difference between the results of the

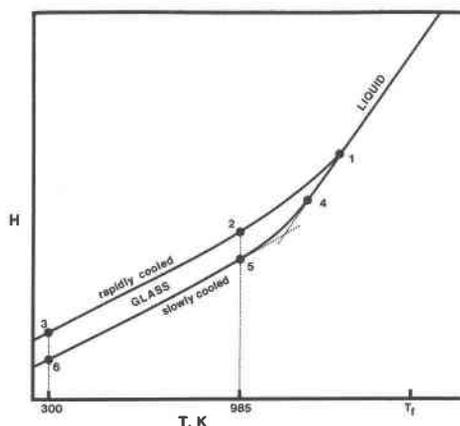


Fig. 1. Schematic diagram of the effect of cooling rate on the enthalpy of a glass (relative to some arbitrary, thermodynamically well-defined point).  $\Delta C_p$  between glass and liquid is greatly exaggerated, as is the magnitude of the cooling rate effect relative to the change in  $H$  with  $T$ . See text for explanation.

first and second inverse drops, can be considered the "enthalpy of annealing" at this temperature. Other possible changes in the samples cannot explain this effect. Weill *et al.* (1980a) showed that devitrification does not occur under these run conditions used. Absorbed water was shown by weighing to be negligible (see "experimental methods"), and in any case would produce a value for  $H_{T_{sc}} - H_{300}$  greater for first drop than for the second. The opposite change was observed.

To calculate accurately heats of fusion using Equation 4, values of the quantity  $(H_{T_{sc}}^g - H_{300}^g)$  that are appropriate to the glasses formed during drop calorimetry are needed. We have therefore carried out inverse drop calorimetric experiments on unannealed glass samples actually produced in the drop calorimeter, and on annealed samples corresponding to those for which the heat of vitrification was measured. Results are given for albite, anorthite, and diopside glasses in Table 1. The calorimeter temperature for these experiments was 981 K, not 985 K, but this difference is not important. Our data for albite glass agree well with those of Navrotsky *et al.* (1982) and the inverse drop measurements of  $H_{981}^g - H_{300}^g$  on annealed samples are very close to those derived by integrating DSC heat capacity data. Referring again to Figure 1, it is obvious that the annealing effect, if large, should be included in the heat of fusion equation: the actual calorimetric cycle represented by Equation 2 proceeds from liquid at  $T$  to unannealed glass 3 at 298 K to annealed glass 5 at the temperature of solution calorimetry, to crystals at  $T_{sc}$ , to crystals at  $T$ .

It is important to note that thermal history effects in glasses may be undetectable by several common calorimetric techniques. The quantity  $H_T^g - H_{300}^g$  measured by standard drop calorimetry (from *high* to *low* temperature)

may be unaffected by the previous history of the glass if the  $H$  vs.  $T$  curves followed by the glass samples during the rapid cooling imposed by the drop are always parallel to curves such as 1–2–3 and 4–5–6 in Figure 1. Similarly, if in some cases the rapid heating rates of typical differential scanning calorimeter runs do not allow significant annealing to take place while data are being recorded, differences in the state of annealing due to the previous thermal history may not be seen. It is possible that annealing of a glass could be observed with a DSC in the form of a baseline drift during long heating at a constant, high temperature, if instrumental stability was unusually good.

Finally, derivation of the heat capacity of a glass-forming liquid from a series of drop calorimetric data requires that minor differences in the cooling rate, due to different initial liquid temperatures  $T$ , result in only negligible differences in the reference state reached in the calorimeter after each drop of the liquid. To determine if this is a good approximation, we prepared glass samples by quenching liquids from different temperatures in the high temperature drop calorimeter. We then measured, by inverse drop calorimetry, the enthalpy differences between an initial state of unannealed glass at room temperature and a final state of glass heated at 981 K for 50 minutes. Results for unannealed albite, anorthite, and diopside glasses are given in Table 1. Differences in the relative enthalpies for glasses made from high and low temperature liquids are within experimental error, and therefore, no corrections of the derived heat capacities are necessary. Several additional experiments by the

drop solution technique on Ab, Di, and  $Ab_{50}Di_{50}$  glasses (with somewhat lower precision), give enthalpies of annealing that are  $500 \pm 1000$  cal/mol less than those derived from the inverse drops without solution. Within error, then, no additional enthalpy changes occur on further heating of the glasses for times greater than 50 minutes and less than 8 hours at 981 K. The 300 K glass reference states produced on quenching liquids of these compositions (in this sample size and at this quench rate) are therefore not significantly dependent on the initial temperature of the liquid. This conclusion is supported by HF solution calorimetry on  $CaSiO_3$  and  $Ca_2MgSi_2O_7$  glasses produced by quenching liquids from a range of initial temperatures (Adamkovičová *et al.*, 1980; Proks *et al.*, 1977). In these studies, no systematic dependence of the heat of solution on quench temperature was observed.

## Results and heat of fusion calculations

### Diopside

Our DSC data on diopside glass are summarized in Tables 2 and 4. Each point is the average of two to four measurements at the temperature given. Previous heat content measurements on this material were made by drop calorimetry below 973 K by White (1919). Although his results were labeled as "preliminary," they agree within 200 cal/mol with the integration of the equation derived from our DSC data alone. Our drop data at 985 K are about 500 cal/mol higher for unknown reasons (possibly related to the onset of glass transition behavior). All three sets of data were combined as described by Stebbins *et al.*, (1982) to yield the regression equation. In general, addition of a fourth term in  $T^{-1/2}$  to the standard Meier-Kelley  $C_p$  equation for the glasses produces the best fit without producing inflections on extrapolation. A fifth,  $T^2$  term may be warranted when more constraints are added.

Drop calorimetric data for stable diopside liquid are given in Table 3 (these data are actual measurements, not averages as for DSC results), and the resulting linear equation in temperature is given in Table 4. A very few crystals (less than 0.1%) were detected optically in the glass after the drop runs, but their number was too small to affect the accuracy of the measurements. The data can be compared with two other published studies. The results of Ferrier (1968a) are presented in a form which suggests that a large capsule allowed slow cooling and near-complete crystallization of the sample in the calorimeter. Because our samples quenched to form a glass, a direct comparison of  $H_T - H_{300}$  is impossible. However, our derived equation:

$$H_T^l - H_{300}^l = 84.41 T - 50345 \text{ cal/mol} \quad (5)$$

results in a heat capacity very close to that reported by Ferrier, (85.0 cal/mol · K). Stout and Piwinski (1980b) report drop calorimetric data for  $CaMgSi_2O_6$  liquid from

Table 1. Inverse drop calorimetric measurements of heats of annealing. Ab:  $NaAlSi_3O_8$  glass. An:  $CaAl_2Si_2O_8$  glass. Di:  $CaMgSi_2O_6$  glass.  $T$  in K. enthalpies in cal/mol. All data corrected to initial temperature of 300 K.

sample	initial quench T	$H_{981} - H_{300}$ unannealed (first run)	$H_{981} - H_{300}$ annealed (subsequent runs)	$H_{981} - H_{300}$ predicted from DSC and standard drop results
Ab-1	1816	45293	46009 46296	46145
Ab-2	1815	45558	46126 46018	
Ab-3	1540	45796	45732	
Ab-4	1536	45171	45880	
	means	45455	46010	
	annealed - unannealed ; unannealed, high T - low T: -58 annealed - predicted :		555 -135	
Di-1	1840	35385	37011	36430
Di-2	1845	35304	36578	
Di-3	1724	35624	36316	
Di-4	1725	35850	36776	
	means	35541	36670	
	annealed - unannealed ; unannealed, high T - low T: -392 annealed - predicted :		1129 240	
An-1	1861	46249	46381	46357
An-2	1862	46270	46270	
	means	46260	46416	
	annealed - unannealed ; annealed - predicted :		156 59	

Table 2. DSC results on the  $C_P$  of  $\text{CaMgSi}_2\text{O}_6$  glass, in cal/mol/K. Each point is the average of 2–4 measurements.

CaMgSi <sub>2</sub> O <sub>6</sub>									
T(K)	C <sub>P</sub>	T(K)	C <sub>P</sub>	T(K)	C <sub>P</sub>	T(K)	C <sub>P</sub>	T(K)	C <sub>P</sub>
405.0	46.81	544.4	52.29	683.9	55.59	794.2	57.29	914.0	60.10
409.9	47.07	549.4	52.39	688.8	55.72	799.1	57.43	915.4	60.13
414.9	47.29	554.4	52.54	693.8	55.86	804.1	57.58	918.9	60.20
419.9	47.53	559.4	52.66	694.9	55.71	809.1	57.81	920.3	60.16
424.9	47.78	564.3	52.77	698.8	55.92	814.0	57.72	924.0	60.38
429.9	48.01	569.3	52.88	699.9	55.80	814.7	57.66	925.3	60.26
434.8	48.23	574.3	53.04	703.7	56.02	819.0	57.83	928.9	60.42
439.8	48.45	579.3	53.13	704.8	55.92	819.6	57.74	930.2	60.32
444.8	48.68	584.3	53.27	708.7	56.11	824.7	57.81	933.9	60.60
449.8	48.86	589.2	53.41	709.8	55.90	829.6	57.94	935.2	60.35
454.8	49.03	594.3	53.53	713.6	56.24	834.6	58.04	938.8	60.69
459.7	49.28	599.3	53.68	714.7	55.83	839.5	58.11	940.2	60.31
464.7	49.45	604.3	53.74	718.6	56.32	844.5	58.22	943.8	60.78
469.7	49.69	609.3	53.83	719.7	55.94	849.5	58.37	945.1	60.40
474.7	49.85	614.2	54.00	724.7	56.01	854.4	58.48	948.7	60.85
479.7	50.03	619.2	54.14	729.6	56.14	859.4	58.58	950.1	60.43
484.6	50.21	624.2	54.26	734.6	56.26	864.3	58.68	953.7	60.93
489.6	50.42	629.2	54.37	739.6	56.27	868.3	58.80	955.0	60.38
494.6	50.60	634.1	54.48	744.5	56.23	874.2	58.92	958.6	61.02
499.6	50.82	639.1	54.61	749.5	56.41	879.2	59.05	960.0	60.49
504.6	51.00	644.1	54.70	754.5	56.63	884.2	59.15	963.6	61.19
509.6	51.16	649.1	54.78	759.4	56.71	889.1	59.29	965.0	60.45
514.5	51.29	654.1	54.87	764.4	56.75	894.1	59.47	968.5	61.20
519.5	51.49	659.0	55.07	769.4	56.74	899.0	59.60	969.9	60.57
524.5	51.65	664.0	55.19	774.3	57.03	904.0	59.77	973.5	61.35
529.5	51.77	669.0	55.38	779.3	57.06	905.5	59.96	974.9	60.66
534.5	51.92	673.9	55.41	784.3	57.04	909.0	59.96		
539.4	52.11	678.9	55.56	789.2	57.20	910.4	60.02		

1700 to 2500 K. Their results predict heat contents at 1680 and 1840 K that are lower than our values by 2.4 and 3.5 kcal/mol, respectively. The reason for such large discrepancies is not known. Neither the sample size nor the sample condition after their runs were reported, but in earlier work on elemental boron with the same instrument (Stout *et al.*, 1973), large capsules containing tens of grams were used. Their quenched samples may have been partly crystalline.

Three series of drop calorimetric measurements on crystalline diopside have been published. The compilations of Robie *et al.* (1979) and of Kelley (1960) combined the data of White (1919) and of Wagner (1932). Ferrier (1968a) made additional measurements, but reported only an equation fitted to 38 points with a standard error of 780 cal/mol. We have generated points at 100 K intervals from his equation, and combined these points with the earlier studies. Our fit equation, not very different from that of Kelley (1960), is:

$$C_P = 63.29 + 2.26 \times 10^{-4} T - 3.097 \times 10^6 T^{-2} \text{ cal/mol} \cdot \text{K} \quad (6)$$

The standard deviation in the enthalpy data used in the regression is 540 cal/mol. A simplified equation predicts essentially the same enthalpies between 900 and 2000 K:

$$H_T - H_{300} = 58.296 T + 1.2775 \times 10^{-3} T^2 - 22392.3 \text{ cal/mol} \quad (7)$$

The results of four measurements of the heat of vitrification of diopside are given in Table 6. When the data are adjusted to 985 K, and the measured enthalpy of annealing is considered when appropriate, the agreement is improved. Results from HF calorimetry could be complicated by the precipitation of fluorite. For this reason and for consistency, we have chosen the value for  $\Delta H_v$  reported by Weill *et al.* (1980a) for our heat of fusion calculation.

The estimate of  $H_{885}^{\text{liq}} - H_{300}^{\text{liq}}$  is derived from the combined  $C_P$  equation in Table 4. 1100 cal/mol was subtracted to include the enthalpy of annealing. With Equation 7 for

 Table 3. Drop calorimetric measurements of  $\Delta H = H_T - H_{300}^{\text{liq}}$  for liquids and glasses, in cal/mol.  $T$  in K

CaMgSi <sub>2</sub> O <sub>6</sub>				KAlSi <sub>3</sub> O <sub>8</sub>			
glass		liquid		glass		liquid	
T	ΔH	T	ΔH	T	ΔH	T	ΔH
848.5	28680	1680.6	91540	983.5	46210	1342.7	73670
849.1	28810	1681.0	91310	983.7	46420	1343.1	73520
984.1	37360	1760.4	98450	1094.2	54650	1519.6	89600
984.4	37110	1760.9	98570	1095.1	55000	1520.4	89700
984.6	36880	1833.0	104200	1223.5	64660	1702.4	105400
985.3	37300	1839.8	105610	1224.1	64730	1702.4	105520
985.6	37000	1840.5	104880			1862.7	120780
		1850.4	105880			1863.4	119880

NaAlSi <sub>3</sub> O <sub>8</sub>			
glass		liquid	
T	ΔH	T	ΔH
984.6	25967	1815.5	68104
984.6	25913	1815.5	68052
984.6	25810	1901.9	72492
		1901.6	72791

Table 4. Constants in the general equation,  $H_T - H_{300} = AT + BT^2 + CT^{-1} + DT^{1/2} + ET^3 + F$  (cal/mol) of  $\text{CaMgSi}_2\text{O}_6$ ,  $\text{KAlSi}_3\text{O}_8$ , and  $\text{NaAlSi}_3\text{O}_8$  glasses and liquids

Substance	$A \times 10^{-1}$	$B \times 10^3$	$C \times 10^{-5}$	$D \times 10^{-2}$	$E \times 10^6$	$F \times 10^{-3}$	T range and no. of $C_p$ pts. in fit	rmsd of $C_p$ data, cal/mol/K	T range and no. of $\Delta H$ pts. in fit	rmsd of $\Delta H$ data, cal/mol
<b><math>\text{CaMgSi}_3\text{O}_8</math></b>										
glass	6.1656	5.2012	3.5233	-6.5476	0	-8.7986	405-975 K 138	0.28	373-986 K 11	279
liquid <sup>1</sup>	8.4413	0	0	0	0	-50.345			1681-1850 K 8	169
<b><math>\text{KAlSi}_3\text{O}_8</math></b>										
glass	12.491	-4.6099	-1.2255	-25.388	0	7.3225	303-968 K 78	0.42	984-1224 K 6	368
liquid <sup>1</sup>	8.950	0	0	0	0	-46.568			1343-1863 K 8	332
<b><math>\text{NaAlSi}_3\text{O}_8</math></b>										
glass	10.822	3.2327	-0.1317	-20.61	-1.701	3.0297	307-968 K	0.42	373-1205 K 30	131
liquid <sup>1</sup>	8.820	0	0	0	0	-43.070			1249-1810 K 22	370
<b><math>\text{NaAlSiO}_4</math></b>										
glass	4.26	0	0	0	0	-16.064			985 K <sup>2</sup> 3	78 <sup>3</sup>
liquid <sup>1</sup>	5.290	0	0	0	0	-27.969			1816-1902 K 4	226

1. For the liquids,  $\Delta H = H_T^1 - H_{300}^g$ , referred to a glass that has been rapidly quenched relative to the more annealed glass which is the reference state for the  $\Delta H$  equation of the glass itself. The effect of adding the enthalpy of annealing to  $\Delta H$  for the liquids is discussed in the text.

2. The heat capacity of nepheline glass near to 985 K is taken as equal to that of the solid at 985 K (see text).

3. Standard deviation from the mean of the data at 985 K.

Table 5. Drop calorimetric results for crystalline analbite and for liquid derived by melting albite.  $T$  in K, enthalpies in kcal/mol. Values below underscores are means

crystalline analbite <sup>1</sup>			low albite, melted at T			
T	$H_T - H_{300}$ measured	$H_T - H_{300}$ predicted <sup>2</sup>	run#	T	$H_T - H_{300}$ measured	$H_T - H_{300}$ predicted <sup>3</sup>
1360.2	73.69		1	1413.8	81.20 <sup>4</sup>	
1360.5	73.76		2	<u>1412.5</u>	<u>80.75</u> <sup>5</sup>	
1360.5	74.73			1413.2	80.96	81.57
1361.5	73.78					
1360.5	<u>73.50</u>					
1360.5	73.89	73.93	3	1702.5	107.28 <sup>6</sup>	107.09
985.0	45.22					
985.0	<u>45.44</u>					
985.0	45.33	45.25				

<sup>1</sup>Hovis (1977); heated 1 hr. at T before drop

<sup>2</sup>equation of Hemingway, et al (1981)

<sup>3</sup>equation of Stebbins, et al (1982), based on drop data on homogeneous liquid produced by heating glass

<sup>4</sup>heated 120 hrs. at T before drop (presumably contained 10-15% crystals in glass)

<sup>5</sup>second drop of above sample after 24 hrs. more at T; contained 10-15% crystals in glass

<sup>6</sup>heated 12 hrs. at T prior to drop; no crystals observed

the solid, the heat of fusion calculated with Equation 4 (900-200 K), is given by:

$$\Delta H_{f,T} = 26.12T - 1.278 \times 10^{-3}T^2 - 6935.3 \text{ cal/mol} \quad (8)$$

The value at the melting point is  $33.0 \pm 0.5$  kcal/mol.

Ferrier (1968a) reported a direct attempt to measure  $\Delta H_f$  for diopside. Since his liquid apparently crystallized on quench, he could calculate the heat of fusion at  $T$  simply by subtracting the enthalpy equation for the solid from that of the liquid (Equation 1 above). His reported value for  $\Delta H_f$  at 1665 K is 30.7 kcal/mol. An underestimate of this quantity could result from about 7% residual glass in runs quenched from the liquid—a result which could easily have occurred in the experiment, and which would explain the discrepancy between Ferrier's and our value. Apparently, each of Ferrier's drops of the stable liquid returned to more-or-less the same phase or mixture of phases, because his derived  $C_p$  agrees well with ours.

Weill *et al.* (1980a) calculated  $\Delta H_f$  from  $\Delta H_v$ , heat capacity estimates for the supercooled liquid and data for the glass and solid, and the assumption of a sharp transition from glass to liquid heat capacity at the dilatometric glass transition temperature of 1026 K. As shown

Table 6. Heat of vitrification ( $\Delta H_v$ ) data, kcal/mol

	original T, K	$\Delta H_v$	corrected to 985 K	corrected to 985 K, with heat of annealing if applicable
<u>Diopside</u>				
Weill, et al (1980a)	985	20.46	20.46	20.46
Navrotsky and Coons (1976)	986	21.00	21.00	21.00
Ferrier (1968a)	353	22.22	22.28	21.18
Tamman (1903)	293	20.15	20.61	19.51
<u>Analbite</u>				
Weill, et al (1980a)	985	12.40	12.40	12.40
Waldbaum and Robie (1971)	323	11.66	12.82	12.27
Hlabee and Kleppa (1968), Holm and Kleppa (1968)	972	11.67	11.67	11.67
Kracek and Neuvonen (1952)	348	9.45	10.58	10.03
<u>Nepheline</u>				
Navrotsky, et al (1980)	985	6.13	6.13	6.13
			corrected to 300 K	corrected to 300 K, with heat of annealing estimate
<u>Sanidine</u>				
Waldbaum and Robie (1971)	323	10.70	10.67	10.12
Tamman (1903)	293	23±5	23±5	23±5

in Table 7, this technique produces a slight overestimate. As illustrated by Figure 2,  $T_g$  can also be estimated by extrapolating the stable liquid enthalpy down from  $T_f$  until  $H_T - H_{300}$  for liquid and the annealed glass are equal, giving  $T_g = 1115$  K. The difference between this and the dilatometric value is probably less than the errors inherent in the calculation of  $C_p$  in this manner.

Our heat of fusion equations, as given in Table 7, are based on stable liquid data and are therefore good estimates of the heat of fusion at temperatures above the melting point. It remains to be shown, however, that they are also good estimates below the melting point.  $\Delta H_f$  above  $T_f$  can be estimated in a different manner, using the value  $T_f$  and a value for the mean  $C_p$  of the supercooled liquid calculated from the enthalpy of the stable liquid at  $T_f$  and that of the annealed glass at the dilatometric  $T_g$  (assuming that the dilatometric samples were annealed):

$$C_p^l(T_g \text{ to } T_f) = [(H_{Tf}^l - H_{300}^g) - (H_g^g - H_{300}^g)] / (T_f - T_g) \quad (9)$$

Here, g refers to the annealed glass.  $C_p$  calculated in this way is 83.5 (cal/mol · K), not significantly different from the measured stable liquid value of 84.4. Differences between the heats of fusion estimated with the two choices of supercooled liquid  $C_p$  are less than 500 cal/mol, even 300 K below  $T_f$ . The comparison suggests that

Table 7. Recent estimates of heats of fusion at  $P = 1$  bar, in kcal/mol

	Diopside 1665 K	Albite 1373 K	Sanidine 1473 K (metastable)	Nepheline 1750 K (metastable)	Anorthite 1830 K
preferred estimate, based on $\Delta H$ and $C_p$ data for liquid and glass	33.0	15.0	13.8	11.7	32.4 <sup>4</sup>
estimate based on $C_p$ data for liquid and glass, and dilatometric $T_g$	34.1 <sup>1</sup>	15.4 <sup>1</sup>			
estimate based on $C_p$ for glass alone	18.5 <sup>2</sup>	14.0 <sup>3</sup>	11.9 <sup>3</sup>		19.4 <sup>3</sup>
"direct" measurement ( $\Delta H_T^l - \Delta H_T^g$ )	30.7 <sup>5</sup>				
Heats of fusion as functions of temperature, in cal/mol: <sup>6</sup>					
Diopside: $\Delta H_{f,T} =$	$21.122 T - 1.1320 \times 10^{-4} T^2 - 3.0968 \times 10^6 T^{-1} + 17$ $= 26.117 T - 1.2775 \times 10^{-3} T^2 - 6935$				
Albite: $\Delta H_{f,T} =$	$-72.27 T + 1.7531 \times 10^{-2} T^2 + 7.586 \times 10^5 T^{-1} + 3.8116 \times 10^3 T^{0.5} - 2.9151 \times 10^{-6} T^3 - 53110$ $= 21.195 T - 3.912 \times 10^{-3} T^2 - 6760$				
Sanidine: $\Delta H_{f,T} =$	$-76.23 T + 2.0519 \times 10^{-2} T^2 + 8.2749 \times 10^5 T^{-1} + 3.9701 \times 10^3 T^{0.5} - 3.9187 \times 10^{-6} T^3 - 58883$ $= 25.429 T - 5.2361 \times 10^{-3} T^2 - 12338$				
$\gamma$ Nepheline: $\Delta H_{f,T} =$	$11.795 T - 6.5966 \times 10^{-4} T^2 - 6948$				

1. Weill et al (1980a), adjusted to 1373 K for albite
2. Robie et al (1979)
3. Robie et al (1978), adjusted to 1373 K for albite
4. Weill et al (1980b)
5. Ferrier (1968a)

6. The first equation for each mineral is based directly on  $C_p$  equations for the crystalline phase as reported in the literature. The second equation uses  $P$  simplified fits of the enthalpy of the crystalline phase at high temperature. The simplified equations are recommended for use from 900 to 2000 K only. Over this interval, the two equations generally differ by less than 100 cal/mol.

the calorimetric and dilatometric data for diopside liquid and glass are at least consistent with each other, and that the  $C_P$  of the supercooled liquid can be accurately approximated by that of the stable liquid.

Other estimates of  $\Delta H_f$  for diopside have been derived from the initial slope of the high pressure fusion curve. Our calorimetric value of 33.0 kcal/mol lies well within the range of those calculated using various estimates of the volume of fusion (31.0 to 34.4) (Carmichael *et al.*, 1977; Ghiorso and Carmichael, 1980).

Finally, Figure 2 also illustrates the large underestimates of the heat of fusion that can result when the difference in  $C_P$  between liquid and glass is not known.

### Albite

The equations generated from DSC and drop calorimetric data for albite glass, and from drop data on the liquid, (Stebbins *et al.*, 1982) are given in Table 4. We have also measured the heat content of liquids resulting from the melting of natural, crystalline, low albite from a Franciscan formation vein deposit in Cazadero, California (composition about Ab<sub>99</sub>, Apps and Neil, 1978). The results are given in Table 5. Runs #1 and #3 were made on liquids that had never been in glass form prior to quenching in the calorimeter. At 1702.5 K, the sample melted completely, and its heat content was not significantly different from that predicted by the results of our data from runs with glassy starting material. At 1413 K (only 40 K above the melting point of albite given by Boettcher *et al.*, 1982), the mean of two runs was 0.6 kcal/mol less than that predicted. The sample was found to contain 10

to 20% residual, unmelted crystal fragments after the runs, despite continuous heating for five days, followed by quenching and heating for 24 hours. Since the heat capacity of the solid is considerably less than that of the liquid, a two phase mixture will indeed have a lower heat content than the liquid: 16% residual crystals would explain the observed discrepancy exactly, while 10–20% crystals would produce variations less than the experimental error of the calorimetry. No crystals or overgrowths were seen that had morphologies of rapid growth, indicating that crystallization did not take place during quench. The good agreement of these results with those from glassy starting materials indicates that any disequilibrium in the liquid at temperatures above the melting point (as suggested by Boettcher *et al.*, 1980, 1982) produces insignificant errors in the calorimetric data.

There is some disagreement about the energetics of the transition from disordered, triclinic albite (analbite) to the monoclinic phase (monalbite) which is stable near the melting point. Different interpretations of the available data could result in variations in the calculated heat of fusion. We have therefore measured the heat content of disordered albite at temperatures near its melting point and near to the temperature of earlier experiments reported in the literature. Our sample was heat-treated Amelia albite, described by Hovis (1977, heated 712 hours at 1325 K), and was heated for one hour prior to drop during calorimetric measurements. The results at both 1360 and 985 K (Table 5) are within 100 cal/mol of the values predicted by the equation given for analbite by Hemingway *et al.* (1981), which was based on DSC data below 1000 K, and was constrained at 300 K by the results of low temperature adiabatic calorimetry.

Our runs at 1360 K were made only 13 K below the melting point of albite (1373 K) as reported by Boettcher *et al.* (1982). If the disordered, triclinic feldspar transformed to a monoclinic phase at this temperature as would be expected from the results of Winters *et al.* (1979), then the agreement of our data with the extrapolation of the results of Hemingway *et al.* (1981) indicates that the change from monoclinic to triclinic symmetry has little or no effect on heat capacity. The near equality of the heat capacities of triclinic, disordered albite, and of ordered albite (Hemingway *et al.*, 1981), is similar to the corresponding relationship in the potassium feldspars (Robie *et al.*, 1978; Helgeson *et al.*, 1978).

Holm and Kleppa (1968), determined the heats of solution of Amelia albite that had been heat treated at 1320 K for varying periods of time. They concluded that *substitutional* disordering takes place in two steps on two different tetrahedral sites, as an abrupt jump in the heat of solution of about 900 cal/mol occurred after about 20 days of heating. The authors also measured  $H_{970} - H_{298}$  for low albite (ordered) and analbite (disordered triclinic) by the inverse drop technique, and found that the enthalpy change was about 790 cal/mol lower for the ordered

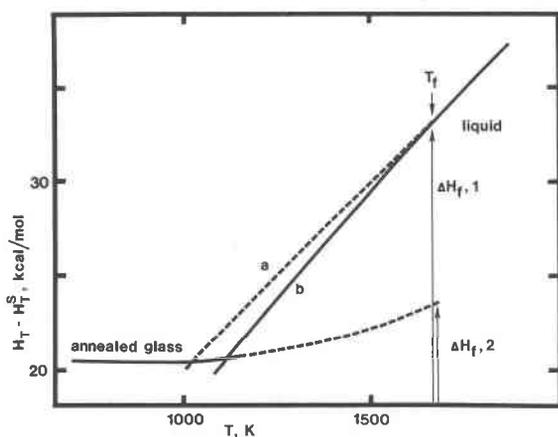


Fig. 2. The heats of vitrification and fusion of diopside. Solid curves portray the enthalpy differences between annealed glass and solid at the same  $T$ , and between liquid and solid. Curve a is based on a constant supercooled liquid  $C_P$  derived from the enthalpy of the liquid at  $T_f$  and that of the glass at the dilatometric  $T_g$  (Equation 9 in the text). Curve b is based on the stable liquid  $C_P$ .  $\Delta H_f, 1$  is the true heat of fusion,  $\Delta H_f, 2$  is that derived by extrapolation of the glass  $C_P$ .

phase. The equations of Hemingway *et al.* (1981), confirmed for the disordered phase by our drop calorimetry, predict a difference of only 95 cal/mol (less than experimental error of any of the techniques used). The latter authors suggest that the precision of the data of Holm and Kleppa (1968) is not high enough to substantiate either of the two transition effects, basing this conclusion on the improvements in the experimental techniques of solution chemistry described by Anderson and Kleppa (1969).

Helgeson *et al.* (1978), described a somewhat different two-step transition in albite, based on the results of Holm and Kleppa (1968). In this model, a rapid, unquenchable, displacive transition towards monoclinic symmetry begins after substitutional disordering is nearly complete. The displacive change would begin at roughly 600 K and continue until the albite was topologically as well as topochemically monoclinic at about 1238 K. Helgeson *et al.* (1978) suggested that the DSC data disagree with the inverse drop experiments because the rapid heating during the DSC runs did not allow the displacive change to take place. During our drop calorimetry, samples were maintained at 985 K long enough to reach the same state as the final state reached during the inverse drop study of Holm and Kleppa (1968), and therefore do not support their results or the interpretation of Helgeson *et al.* (1978). Because of the agreement of our results with the DSC data, we have chosen the equation of Hemingway *et al.* (1981) for our heat of fusion calculation. The predicted enthalpies between 900 and 1800 K are reproduced within 0.1% by the simplified expression:

$$H_T - H_{300} = 67.005 T + 3.911 \times 10^{-3} T^2 - 24442 \text{ cal/mol} \quad (10)$$

The hypothesis of Helgeson *et al.* (1978) would lead to a value for the enthalpy of disordered albite at the melting point that is about 1 kcal/mol higher than that predicted by us, and would result in a calculated heat of fusion which is less than our result by the same amount. Final resolution of the thermodynamics of the triclinic-monoclinic transition in albite probably awaits a study combining calorimetry, long-term annealing, and high temperature X-ray diffraction.

Measurements of the heat of vitrification of an albite glass by several research groups are compared in Table 6. The data have been corrected to 985 K with our equation for the glass and that of Hemingway *et al.* (1981) for the solid. (985 K was chosen because it was the temperature at which many of the heat of vitrification measurements were made.) If the heat of annealing (Table 1) is subtracted from the measurement of Waldbaum and Robie (1971), it agrees almost exactly with that reported by Weill *et al.* (1980a) and Navrotsky *et al.* (1980). As mentioned earlier, the experimental method of Holm and Kleppa (1968) was questioned by Anderson and Kleppa (1969). We have therefore chosen the value of  $\Delta H_f$  of Weill *et al.* (1980a). As with diopside, we have calculated  $H_{985}^E - H_{300}^E$  from the

equation in Table 4, subtracting the heat of annealing at 981 K. (This is equivalent to using a heat of vitrification measured near to 300 K on rapidly quenched, unannealed glass.) The heat of fusion equation, with Equation 10 for the solid, (900–2000 K) is:

$$\Delta H_{f,T} = 21.195 T - 3.912 \times 10^{-3} T^2 - 6760.1 \text{ cal/mol} \quad (11)$$

with  $\Delta H_f$  at 1373 K equal to  $15.0 \pm 0.5$  kcal/mol.

Again, the estimate of Weill *et al.* (1980a), adjusted to  $T_f = 1373$  K is slightly higher. Calculations using  $C_P$  data for the glass alone produce the underestimates of Waldbaum (1968) and of Robie *et al.* (1978). The range in the values is relatively small because of the small difference in  $C_P$  between glass and liquid, and the short temperature interval between  $T_g$  and  $T_f$ .

The heat of fusion of albite is well defined even below  $T_f$ , as drop calorimetry can be done on the supercooled liquid all the way down to the glass transition. The point of transition from glass to liquid heat capacity is poorly constrained by calorimetry, however, again because of the small change in  $C_P$  from glass to liquid. Dilatometric values of  $T_g$  range from 1018 K (Arndt and Haberle, 1973) to 1088 K (Vergano *et al.*, 1968). The intersection of the linear fit to the enthalpy data for the liquid (with the annealing enthalpy added) and our equation for the enthalpy of the glass lies at 1190 K (Fig. 2). (If the annealing effect is not considered, the intersection shifts to 1248 K, as reported by Stebbins *et al.*, 1982). Richet *et al.* (1980), using slightly different data sets for liquid and glass and not considering annealing, derived a value of  $T_g$  of 1166 K. This range of values simply indicates that it remains uncertain whether there is an abrupt increase in heat capacity from albite glass to liquid at the same temperature where an abrupt increase in thermal expansivity is detected by dilatometry, or whether the  $C_P$  change occurs at a higher temperature or over a range in temperature.

### Sanidine

We have combined our drop data on  $\text{KAlSi}_3\text{O}_8$  glass with the DSC data of Krupka *et al.* (1979, 350 to 1000 K) to yield the equation given in Table 4. Krupka *et al.* combined their data with the drop data of White (1919), whose data should not be used here, as they were collected for a glass derived by melting a natural microcline whose  $\text{KAlSi}_3\text{O}_8$  content was only 75% (Day and Allen, 1905).

Sanidine melts incongruently at about  $1423 \pm 20$  K to leucite and liquid (Schaerer and Bowen, 1955), and the metastable, congruent, one bar melting point can therefore not be directly determined. As with albite liquid, though, the high viscosity of the liquid allows calorimetry to be done over the entire temperature range from glass to stable liquid above 1800 K, without crystallization. Our drop data show a definite increase in heat capacity between 1225 and 1340 K, with a constant  $C_P$  above 1340

K. We have therefore made the operational distinction between glass at temperatures of 1225 K and below, and liquid at 1340 K and above.

For crystalline sanidine, we have chosen the heat capacity equation of Hemingway *et al.* (1981), based on DSC data to 1000 K. We assume that as for albite, extrapolation to higher temperatures does not lead to large errors. Again, for convenience, we have refit enthalpies predicted by this equation above 900 K to a simplified expression to give:

$$H_T - H_{300} = 64.072 T + 5.236 \times 10^{-3} T^2 - 23001 \text{ cal/mol} \quad (12)$$

Relatively few measurements of the heat of vitrification of sanidine have been made. HF calorimetry on this calcium-free phase should be reliable, and we therefore use the results of Waldbaum and Robie (1971). The very large value of  $\Delta H_f$ , reported by Tamman (1903) seems to be in error for unknown reasons. The glass sample used by Waldbaum and Robie (1971) was, unfortunately for our purposes, thoroughly annealed, as it was synthesized by cation exchange from albite glass in KCl at 1173 K. The glass should therefore be somewhat lower in enthalpy than the glass produced during the rapid quench of sanidine liquid in our drop calorimeter. No data on the annealing enthalpy are available, so there is some added uncertainty in the heat of fusion calculation. Analogy to albite glass suggests a correction of about 555 cal/mol, which we have added to the heat of  $\Delta H_{v,300}$  derived from the data of Waldbaum and Robie (1971). Our equation (900–2000 K) becomes:

$$\Delta H_{f,T} = 25.429 T - 5.236 \times 10^{-3} T^2 - 12338 \text{ cal/mol} \quad (13)$$

The metastable, one bar, congruent melting point of sanidine cannot be measured directly. Waldbaum (1968) estimated a value of  $1473 \pm 40$  K by extrapolation from anhydrous and hydrous high pressure experiments where congruent melting is observed. This temperature serves as a convenient point of comparison for values of  $H_f$ . Waldbaum (1968) derived a value of 14.70 kcal/mol (tabulated in Robie *et al.*, 1979), while Robie *et al.* (1978) derived a value of 1.9 kcal/mol. Our estimate for the heat of fusion at 1473 K is  $13.8 \pm 1.0$  kcal/mol. Arndt and Haberle (1973) measured a glass transition temperature for sanidine glass of 1178 K by dilatometry, while the intersection of our equations for liquid and glass is at about 1300 K (Fig. 3). As for albite, however, the difference in  $C_p$  between glass and liquid is small and  $T_g$  is poorly defined by calorimetry.

### Nepheline

Synthetic sodium nepheline ( $\text{NaAlSi}_3\text{O}_8$ ) transforms from  $\alpha$  to  $\beta$  phase at 467 K, from  $\beta$  to  $\gamma$  at 1180 K, and to carnegieite at 1525 K, which finally melts at 1799 K

(Kelley *et al.*, 1953; Schairer and Bowen, 1956). Solution calorimetric data are not available on carnegieite, but the heat of vitrification of the  $\beta$  nepheline phase was measured at 985 K by Navrotsky *et al.* (1980). The heat capacities of all four polymorphs were determined by Kelley *et al.* (1953), who concluded that the enthalpy change from  $\beta$  to  $\gamma$  nepheline was zero.

In order to estimate the metastable heat of fusion of nepheline (as opposed to the stable liquidus phase carnegieite), we have measured  $H_T^l - H_{300}^l$  above the liquidus, and  $H_{85}^g - H_{300}^g$ . Results are given in Table 3. Despite the small temperature range of measurements on the liquid,  $C_p^l$  is fairly well constrained at  $52.9 \pm 1.9$  cal/mol · K. The glass transition temperature was defined at 1003 K by a viscosity of  $10^{13}$  poise by Taylor and Rindone (1970). The heat capacity of the supercooled liquid can be calculated from the glass enthalpy at  $T_g$  and the liquid enthalpy at 1799 K by using Equation 9, with the assumption that the glass  $C_p$  at about 1000 K is equal to that of the solid (a good approximation for many materials at high  $T$ ). The result of 50.9 cal/mol · K is slightly less than the directly measured value, the difference being just greater than one standard deviation.

No annealing enthalpy data are available for Ne glass, but analogy with An glass suggests that this correction could be negligible. Data on the solid, liquid, and glass can be combined to calculate the heat of fusion ( $\gamma$  nepheline, 1180–1800 K):

$$\Delta H_{f,T} = 11.80 T - 6.597 \times 10^{-4} T^2 - 6948 \text{ cal/mol} \quad (14)$$

The metastable melting point of  $\gamma$  nepheline can be roughly estimated as  $1750 \pm 50$  K from the phase diagrams

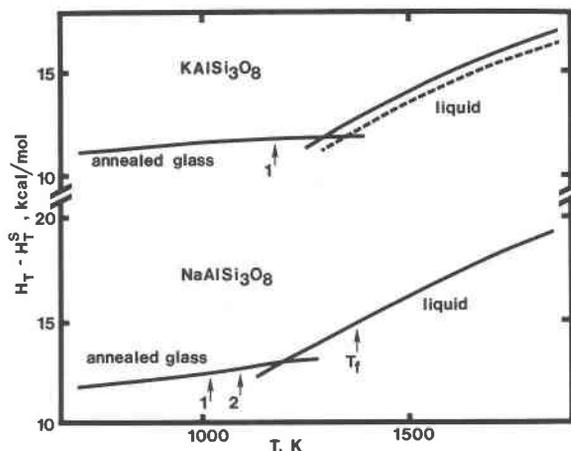


Fig. 3. The heats of vitrification and fusion of disordered albite and of sanidine. Points 1 are dilatometric  $T_g$  values from Arndt and Haberle (1973), point 2 is that from Vergano (1968). Solid curves for liquids include an annealing enthalpy of 55 cal/mol; dashed curve includes no enthalpy of annealing.

presented by Schairer and Bowen (1956). At this temperature,  $\Delta H_f$  is  $11.7 \pm 0.5$  kcal/mol.

The heat of fusion of  $\beta$  nepheline, stable below 1180 K, can also be calculated:

$$\Delta H_{f,T} = 26.11 T - 8.020 \times 10^{-3} T^2 - 13596 \text{ cal/mol} \quad (15)$$

Recent measurements of the heat capacity of Ne liquid by Richet (Thesis, University of Paris, 1982) confirm the data given here.

### Discussion

For liquids which cannot be supercooled easily over a large temperature range, the most important remaining uncertainties are in the extrapolations of the heats of fusion below the melting point. Such data are of obvious importance in the calculation of phase equilibria in systems where an added component lowers the liquidus temperature. As discussed above, an additional constraint (of somewhat uncertain merit) can be placed upon the heat capacity of the supercooled liquid by taking the dilatometric  $T_g$  as the point of transition from glass to liquid  $C_p$ . For diopside (Fig. 2), albite, and sanidine (Fig. 3), such a choice makes little difference in the derived heat of fusion below  $T_f$ . The situation is different for anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) (Fig. 4). The heat of fusion at  $T_f$  was relatively well constrained by drop calorimetry on the stable liquid reported by Weill *et al.* (1980b), but the temperature range of measurements was insufficient to define the heat capacity of the liquid directly. The supercooled liquid  $C_p$  was therefore determined from  $H_{T_g}^L$  and  $H_{T_f}^L$  (Equation 9) as  $102 \text{ cal/mol} \cdot \text{K}$ .

Stebbins *et al.* (1982a) measured the partial molar heat capacity of the anorthite component in stable liquids on the  $\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$  binary as  $113 \text{ cal/mol} \cdot \text{K}$ . This value is probably a good estimate of  $C_p$  of supercooled, pure anorthite liquid down to the lowest temperature at which measurements were made on  $\text{Ab}_{75}\text{An}_{25}$  liquid (about 1650 K). If this heat capacity is assumed to be constant down to the point at which the enthalpy of the glass and liquid are equal, however, the transition temperature is 300 K higher than that determined by dilatometry (Fig. 4). The difference in the heat of fusion calculated using the two values for the supercooled liquid  $C_p$  (102 vs. 113  $\text{cal/mol} \cdot \text{K}$ ) reaches 5 kcal/mol at the melting point of albite. An uncertainty of this magnitude has obvious importance in the calculation of plagioclase liquid-solid equilibria.

The drop data and the dilatometric  $T_g$  could be consistent if the  $C_p$  of supercooled anorthite liquid increases substantially with temperature. If we choose the simplest case and assume that  $dC_p/dT$  is constant, take  $T_g$  to be 1100 K (the mean of the values reported by Cukierman and Uhlmann, 1973 and by Arndt and Haberle 1973), and constrain  $C_p^L$  to be  $113 \text{ cal/mol} \cdot \text{K}$  at 1830 K, then

enthalpy points at 1830 K and 1100 K are fit by the equation (shown by the dashed curve in Fig. 4):

$$C_p = 57.43 + 3.04 \times 10^{-2} T \text{ cal/mol} \cdot \text{K} \quad (16)$$

The variation with  $T$  of  $C_p$  in this equation is large:  $dC_p/dT$  is 50% greater than that of the glass at 1100 K. Any variation of a silicate liquid heat capacity with temperature is speculative at this time, as direct enthalpy measurements on a given liquid can generally be fitted within experimental error by constant heat capacities. Curiously, though, the  $C_p$  predicted by the above equation at  $T_g$  (91  $\text{cal/mol} \cdot \text{K}$ ) is close to that of albite liquid. At stable liquid temperatures, of course, the anorthite liquid  $C_p$  is much higher than that of albite liquid. (For convenience in heat of fusion calculations, we have refit the enthalpy of crystalline anorthite predicted by the equation of Robie *et al.* (1979) with the simpler equation:  $H_T - H_{300} = 59.025 T + 8.5323 \times 10^{-3} T^2 - 20050 \text{ cal/mol}$ .)

There is probably a correlation between the change in heat capacity between a glass and a liquid and the increase in translational degrees of freedom associated with the glass transition (Navrotsky *et al.*, 1980). Since the heat capacities of albite and anorthite glasses are nearly identical (Stebbins *et al.*, 1982), a major difference between An and Ab liquids is that the former has more additional mechanisms for absorbing energy with increasing  $T$  than the latter. A similar pattern is also suggested by viscosity data for the two glasses and liquids (Cranmer and Uhlmann, 1981). Albite glass and liquid show Arrhenian behavior, with an activation energy that is constant from 800 to 1500 K. The viscosity of anorthite glass is actually greater than that of albite glass below 900 K, but

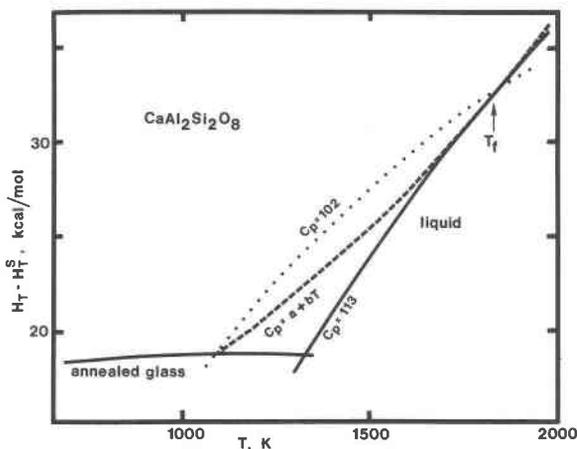


Fig. 4. The heats of vitrification and fusion of anorthite. Dotted curve for liquid is based on supercooled liquid  $C_p$  calculated from Equation 9 in text. Solid curve is derived using the  $C_p$  of the An component of liquids on the Ab-An binary. Dashed curve allows the supercooled liquid  $C_p$  to vary as a function of  $T$  to fit both the dilatometric  $T_g$  and the high temperature liquid data.

rapidly decreases until the viscosity at stable liquid temperatures is 400 times less than that of albite liquid, with a strong curvature in the plot of log viscosity vs.  $1/T$ . This behavior may be related to some sort of depolymerization process in anorthite liquid, but the microscopic nature of this process remains unknown.

The entropies of fusion of albite and anorthite at their melting points are 10.7 and 17.7 cal/mol · K, respectively. Part of this difference may be due to the fact that anorthite probably retains substantial Al–Si order up to its melting point. Complete disordering on melting might account for as much as 5.5 cal/mol · K in the entropy of fusion (Kerrick and Darken, 1975; Ulbrich and Waldbaum, 1876). Henry *et al.* (1982) combined heat of solution results in the Ab–An–Di ternary with liquid-plagioclase equilibrium data to estimate mixing entropies in the liquids. They concluded that aluminum avoidance and Al/Si order may not be maintained in anorthite-rich liquids.

The question of ordering in the plagioclase composition liquids can be further explored by calculating the entropies of the glasses at zero Kelvin ( $S_0^g$ ). We use the equations in Table 4 for the heat capacities of the glasses, data on  $S_{298} - S_0$  for solids and glasses from the adiabatic calorimetry of Openshaw *et al.* (1976) and Robie *et al.* (1978b), and the assumptions that anorthite is fully ordered and analbite fully disordered. We derive  $S_0^g$  for albite glass as 9.7 cal/mol · K, and  $S_0^g$  for anorthite glass as 8.5 cal/mol · K from the relation:

$$S_0^g = \Delta S_{f,T_i} + S_0^s - (S_{298}^g - S_0^g) + (S_{298}^s - S_0^s) - \int_{298}^{T_g} (C_P^g - C_P^s)/T dT - \int_{T_g}^{T_i} (C_P^l - C_P^s)/T dT \quad (17)$$

Here,  $T_g$  is the temperature of intersection of the enthalpy equations for liquid and solid. The lower estimates given by Robie *et al.* (1978b) are related to their lower estimates of the heats of fusion. Melting of disordered analbite probably produces a liquid with Al/Si disorder, which in turn quenches to a disordered glass. The similarity of the values for the two glasses therefore suggests that the degree of Al/Si disorder in anorthite glass and liquid is also high. If Al/Si disordering takes place only on tetrahedral sites, the maximum contribution to the zero point entropy will be  $-4R \ln(1/2) = 5.5$  cal/mol · K in An glass and  $-4RT(1/4 \ln(1/4) + 3/4 \ln(3/4)) = 4.5$  cal/mol · K in Ab glass. Other types of disorder must therefore also contribute to the entropies of the glass and the liquid.

The thermodynamic properties of sanidine liquid are quite similar to those of albite liquid: the heat capacity is 89 cal/mol · K, while the entropy of fusion is about 9.4 cal/mol · K. Such behavior is not surprising, as the heat capacities of the glasses are again very close, and the  $C_P$  and the transition behaviors of the solids are also similar. The viscosity of sanidine liquid is not very different, being about 2–3 times greater than that of albite liquid (Urbain *et al.*, 1982).

Nepheline and anorthite have analogous stoichiometry, with the same Al/Si ratio. The crystal structures are both tectosilicates, but are quite different in detail. Comparison of their fusion properties is complicated by uncertainties in the state of aluminum-silicon disorder in the synthetic nepheline used in solution calorimetry by Navrotsky *et al.* (1980). Analogy with synthetic feldspars suggest that the phase may have been highly disordered. Further uncertainties arise from lack of knowledge of the metastable melting point of  $\gamma$  nepheline. The range of values  $1750 \pm 50$  K leads to a range in  $\Delta S_f$  of  $6.7 \pm 0.2$  cal/mol · K or  $0.96 \pm 0.03$  cal/gram-atom · K. If it is assumed that anorthite is completely ordered at its melting point (as was assumed in the derivation of the heat of fusion in Weill *et al.*, 1980b), the entropy of fusion of the corresponding disordered phase can be estimated as 17.7–5.5 or 12.2 cal/mol · K, or 0.94 cal/gram-atom · K. The similarity of the per atom entropies of fusion of nepheline and of hypothetical disordered anorthite may suggest that the two liquids are similar in structure. Any quantitative interpretation awaits more data on carnegieite.

Liquids of pyroxene stoichiometry can also be compared with each other. Adamkovičová *et al.* (1980) report drop calorimetric measurements on  $\text{CaSiO}_3$ . Their data give  $C_P^l$  as 78.2 cal/mol · K for  $(\text{CaSiO}_3)_2$  which is about 8% less than that of  $\text{CaMgSi}_2\text{O}_6$  liquid. The heat capacities of the glasses differ by about the same amount, however, so that values of  $\Delta C_P$  through the glass transitions are similar. The viscosity of a liquid near to diopside in composition is about twice that of wollastonite liquid (Urbain *et al.*, 1982). The entropy of fusion for diopside ( $\Delta S_f$ ) is 20.2 cal/mol · K, but the value for  $(\text{CaSiO}_3)_2$  (pseudo-wollastonite on a six-oxygen basis) is only 15.1. Since the crystal structures are not strictly analogous, comparison of the fusion properties is complicated. However, about half of this difference could be due to the entropy of disordering of Ca and Mg in diopside liquid relative to the crystal. Such disorder is consistent with the two-lattice model of Weill *et al.*, (1980a), which was successfully used in calculation of the pyroxene saturation surface in the albite–anorthite–diopside system.

Heat of fusion data can also be applied to calculations of solid–liquid phase equilibria with varying composition and/or pressure. Comparison of high pressure fusion curves calculated from one bar thermodynamic data with those obtained directly is useful both to check the consistency of diverse measurements, and to observe changes in liquids induced by pressure. Non-aluminous liquids, including those of diopside, wollastonite, and fayalite composition, seem to behave predictably: the fusion curves agree with those calculated from one bar measurements and reasonable assumptions about changes in elastic compressibilities with pressure (Stebbins and Carmichael, 1981; Stebbins *et al.*, 1981). The  $P$ – $T$  slopes for both albite and anorthite, on the other hand, are much steeper than expected. Major structural changes in these liquids at pressures below ten kilobars are indicated. The

change in albite liquid has been modeled in terms of variations in liquid speciation (Boettcher *et al.*, 1982). The most obvious response to pressure in both albite and anorthite liquids is, however, a volume decrease much greater than that due to simple elastic compression (Stebbins *et al.*, 1981; Navrotsky *et al.*, 1982).

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