American Mineralogist, Volume 77, pages 53–61, 1992

Plagioclase feldspars: Activity-composition relations based upon Darken's quadratic formalism and Landau theory

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ABSTRACT

Activity-composition relations in plagioclase feldspars are modeled using both Darken's quadratic formalism (DQF) and Landau theory. In DQF, the thermodynamics of $C\bar{1}$ and $I\bar{1}$ solid solutions are treated separately, with imposed continuity constrained at the phase boundary. Three simple formulations of entropy of mixing are used, in conjunction with the cation exchange experiments in the literature, to generate predictive models for free energy of mixing over the range 500–1100 °C. All models yield solvi at low temperatures, which are in the position of the Bøggild miscibility gap. The predicted heats of mixing, compared with the calorimetrically determined enthalpies of solution, together with the calculated solvi and extrapolated activities are used to discriminate among five different mixing models for the plagioclase solid solution. The DQF approach appears most able to generate appropriate activity relations and calculated phase diagram features.

INTRODUCTION

Thermodynamic modeling of petrological equilibria and processes requires information from two major sources: thermodynamic data for stoichiometric mineral end-members and data for free energies of mixing in complex solid and fluid (including molten) phases. Whereas the data gained in recent years on the thermodynamic properties of end-members of silicate minerals have enabled quite sophisticated modeling of reaction equilibria, one of the major stumbling blocks to further progress is the poor understanding of mixing properties of solid solutions in common rock-forming minerals. Until such data become better constrained, the position for geological thermometry and barometry as well as for the calculation of petrogenetic grids cannot improve regardless of how much improvement is made in refining the end-member mineral properties. Currently, the poorly known activity-composition relations in plagioclase feldspars over wide ranges of pressure and temperature have severely hampered the use of common mineral barometers (Powell and Holland, 1988), and in this paper we attempt to find improved methods of describing and extrapolating the thermodynamics of mixing in plagioclase feldspar.

Past work has tended to rely upon the cation-exchange experiments of Orville (1972) in which the activities of the albite and anorthite components were derived at 700 °C. These data have been used extensively and sometimes uncritically over ranges of temperature and pressure considerably removed from the experimental conditions under which they were obtained. Orville's cation exchange experiments on the reaction

$$\underset{\text{plagioclase}}{2\mathrm{NaAlSi_3O_8}} + \underset{\text{fluid}}{\mathrm{CaCl_2}} = \underset{\text{plagioclase}}{\mathrm{CaAl_2Si_2O_8}} + \underset{\text{quartz}}{4\mathrm{SiO_2}} + \underset{\text{fluid}}{2\mathrm{NaCl}} \quad (1)$$

involved determining the equilibrium constant by measuring the compositions of coexisting feldspar and fluid, making the assumption that either the activity coefficients of the fluid species $CaCl_2$ and NaCl were unity (ideal solution) or that their ratio was constant. The justification for this lay in the experimental evidence that the distribution coefficient for Reaction 1, written as

$$K_d = \frac{X_{\mathrm{Ca(plag)}}\, m^2_{\mathrm{NaCl(f)}}}{X^2_{\mathrm{Na(plag)}}\, m_{\mathrm{CaCl_2(f)}}} \quad (2)$$

did not vary as a function of solution concentration, as would be required if the solution behaved in a nonideal fashion or if the ratio of activity coefficients of the fluid species did not remain constant. Using the Gibbs-Duhem equation, Orville obtained numerical values for the activities of anorthite and albite from his experimental data by a graphical technique.

Newton et al. (1980) synthesized plagioclases at high temperatures and measured the heats of mixing in disordered feldspars by solution calorimetry, which they then compared with Orville's activity data in an attempt to discriminate among various simple models for entropy of mixing that had been earlier proposed by Kerrick and Darken (1975). Newton et al. (1980) argued that their calorimetrically determined heats of mixing agreed well

0003–004X/92/0102–0053$02.00

with Orville's activity data only if they used the "Al-avoidance" (i.e., the 2T-disordered) model below for their activity expressions. In their calculations, they combined ideal activity expressions with activity coefficients derived from a subregular solution model. Carpenter et al. (1985) presented further measurements of enthalpies of solution on very carefully characterized plagioclase feldspars and reinterpreted the earlier calorimetric data of Newton et al. (1980) in terms of a structural break between $C\bar{1}$ and $I\bar{1}$ at around An_{70} for temperatures of annealing in the region of 1200 °C. Earlier, Carpenter and McConnell (1984) had determined experimentally the location of the $C\bar{1}$ to $I\bar{1}$ transition, which we can approximate by the straight line relationship (with X_b as the value of X_{An} at the transition):

$$X_b = 0.12 + 0.00038T\,(\mathrm{K}). \qquad (3)$$

The implications of the $C\bar{1}$ to $I\bar{1}$ transition for activity of anorthite in plagioclase feldspars has been discussed by Carpenter and Ferry (1984), who also noted that the significance of the phase transition had been fully realized by Orville in his original data reduction. However, the more recent experimental redeterminations of cation exchange (using Eq. 1) and their interpretation (Kotelnikov et al., 1981; Blencoe et al., 1982; Schliestedt and Johannes, 1990) have treated both the $C\bar{1}$ and $I\bar{1}$ regions as though they formed one continuous solid solution. In this paper, we wish to explore further the consequences of the $C\bar{1}$ to $I\bar{1}$ transition on the mixing properties in this feldspar system.

Two possible approaches have been suggested in the literature: Darken's quadratic formalism (DQF) (Powell, 1987) and Landau's theory of phase transitions (e.g., Carpenter, 1988). DQF is simply the division of a solution into two or more regions, each of which behaves according to a simple mixing model, and, in the context of plagioclase, it makes sense to treat the $C\bar{1}$ plagioclase and $I\bar{1}$ plagioclase as separate solid solutions. Landau theory has been applied successfully to the description of the activity-composition relations associated with order-disorder in omphacite (Holland, 1991); it should work reasonably well for plagioclase as the $C\bar{1}$ to $I\bar{1}$ transition in anorthite is thought to be nearly tricritical in character (Carpenter, 1988). In the next sections, we will take both approaches in order to test their relative merits in (1) fitting the known experimental and thermodynamic data on plagioclase and (2) extrapolating the mixing relations reliably to higher and lower temperature.

DARKEN'S QUADRATIC FORMALISM

As was recognized by Orville (1972), the plagioclase series is not a continuous solid solution but is composed of a $C\bar{1}$ region ranging in composition from albite to around An_{50} (at 700 °C) and a region of $I\bar{1}$ structure to more anorthitic compositions. The phase transition moves to more calcic compositions with increasing temperature, Equation 3, reaching around 2300 K at the pure anorthite composition (Carpenter and McConnell, 1984). In the $C\bar{1}$ region, the solid solution is characterized by a largely disordered distribution of Al and Si tetrahedra that become somewhat short-range ordered (on the albite ordering scheme) with decreasing temperature, whereas the $I\bar{1}$ structure is characterized by partial to high degrees of order based on the anorthite ordering scheme (Carpenter, 1988). In terms of the DQF approach, we will treat the $C\bar{1}$ region as having one real end-member, albite, which mixes with a fictive anorthite end-member having $C\bar{1}$ structure. Likewise, the $I\bar{1}$ region is characterized by a mixture of anorthite and a fictive albite end-member with $I\bar{1}$ structure. Thus the thermodynamic properties may be described if we assume for simplicity that each region behaves as a regular solution between the chosen end-members (e.g., Powell, 1987).

In the equations to follow, we use an X with a subscript of Ab or An to denote thermodynamic mole fraction (ideal mixing activity) of albite and anorthite in plagioclase and X without a subscript to denote mole fraction (proportion) of anorthite in plagioclase. For the $C\bar{1}$ structure (denoted by subscript c), the chemical potentials are

$$\mu_{Ab,c} = G_{Ab,c} + RT \ln X_{Ab} + W_c X^2$$

$$\mu_{An,c} = G_{An,c} + RT \ln X_{An} + W_c(1 - X)^2$$

$$= G_{An,i} + RT \ln X_{An} + W_c(1 - X)^2 + I_{An}$$

where I_{An} is the difference between the Gibbs energy for the anorthite composition of the real and fictive end-members, $G_{An,c} - G_{An,i}$. Thus, the activities are

$$RT \ln a_{An,c} = RT \ln X_{An} + W_c(1 - X)^2 + I_{An}$$

$$RT \ln a_{Ab,c} = RT \ln X_{Ab} + W_c X^2. \qquad (4a)$$

For the $I\bar{1}$ structure (denoted by subscript i), the chemical potentials are

$$\mu_{An,i} = G_{An,i} + RT \ln X_{An} + W_i(1 - X)^2$$

$$\mu_{Ab,i} = G_{Ab,i} + RT \ln X_{Ab} + W_i X^2$$

$$= G_{Ab,c} + RT \ln X_{Ab} + W_i X^2 + I_{Ab}$$

where $I_{Ab} = G_{Ab,i} - G_{Ab,c}$. Thus, the activities are

$$RT \ln a_{An,i} = RT \ln X_{An} + W_i(1 - X)^2$$

$$RT \ln a_{Ab,i} = RT \ln X_{Ab} + W_i X^2 + I_{Ab}. \qquad (4b)$$

We can substitute any ideal mixing activity model into the $RT \ln X_k$ terms above in order to calculate activities. We shall relate these activities to a standard state of the pure mineral end-members, albite and anorthite, in their stable structural states at the pressure and temperature of interest, i.e., $G_{Ab,c}$ and $G_{An,i}$.

In the DQF approach, we may further constrain the parameters by forcing the Gibbs free energy and the slope, $\partial G/\partial X$, to be the same at the boundary between the terminal regions. This amounts to treating the $C\bar{1} \rightarrow I\bar{1}$ boundary as higher than first order. The most practical way to do this is to equate the expressions for $RT \ln a$

for each end-member at the boundary; for example, this requires, for contiguity of the albite activity,

$$RT\ln X_{\mathrm{Ab,c}} + W_{\mathrm{c}}X_{\mathrm{b}}^2 = RT\ln X_{\mathrm{Ab,i}} + W_{\mathrm{i}}X_{\mathrm{b}}^2 + I_{\mathrm{Ab}} \quad (5a)$$

and, for the anorthite activity,

$$\begin{aligned} &RT\ln X_{\mathrm{An,c}} + W_{\mathrm{c}}(1 - X_{\mathrm{b}})^2 + I_{\mathrm{An}} \\ &\quad = RT\ln X_{\mathrm{An,i}} + W_{\mathrm{i}}(1 - X_{\mathrm{b}})^2 \end{aligned} \quad (5b)$$

where X_{b} is the plagioclase composition at the $C\overline{1} \rightarrow I\overline{1}$ boundary. Rearranging Equations 5a and 5b gives expressions for I_{Ab} and I_{An} in terms of the difference between the interaction parameters, $W_{\mathrm{c}} - W_{\mathrm{i}}$:

$$I_{\mathrm{Ab}} = RT\ln\frac{X_{\mathrm{Ab,c}}}{X_{\mathrm{Ab,i}}} + (W_{\mathrm{c}} - W_{\mathrm{i}})X_{\mathrm{b}}^2$$

and

$$I_{\mathrm{An}} = -RT\ln\frac{X_{\mathrm{An,c}}}{X_{\mathrm{An,i}}} - (W_{\mathrm{c}} - W_{\mathrm{i}})(1 - X_{\mathrm{b}})^2. \quad (6)$$

We have determined the parameters by taking the equilibrium constant for Reaction 1:

$$RT\ln K = RT\ln\left(\frac{a_{\mathrm{An(plag)}}m_{\mathrm{NaCl(f)}}^2}{a_{\mathrm{Ab(plag)}}^2 m_{\mathrm{CaCl_2(f)}}}\right)$$

and rearranging it to give

$$\begin{aligned} RT\ln K' &\equiv RT\ln\left(\frac{m_{\mathrm{NaCl(f)}}^2}{m_{\mathrm{CaCl_2(f)}}}\right) \\ &= RT\ln K - RT\ln\left(\frac{a_{\mathrm{An(plag)}}}{a_{\mathrm{Ab(plag)}}^2}\right). \end{aligned} \quad (7)$$

Into this, the activities of anorthite and albite are substituted, along with the substitutions for I_{An} and I_{Ab}, for example 6. The result is an equation in which the left hand side, the observed molalities, are expressed in terms of the observed composition of plagioclase and the unknowns, K, and the two interaction parameters, W_{c} and W_{i}. Equation 7 has been fitted to the experimental cation partitioning data of Orville (1972) and Schliestedt and Johannes (1990) by nonlinear least-squares regression. Within the errors on the data and given the small systematic inconsistencies between the sets of experiments at each temperature, all the models considered below fit the data equally well (see below).

In addition to the exchange data, excess enthalpies of mixing of plagioclase solid solutions have been measured by Newton et al. (1980) and Carpenter et al. (1985). We can use the DQF parameters estimated from the exchange data to calculate excess enthalpies of mixing to compare with these calorimetric measurements and, in principle, to distinguish between the models. However, because the plagioclase feldspars show complex ordering behavior as temperature changes, it is unlikely that the constant W terms and the resulting simple temperature-dependent I terms properly separate the Gibbs energy into its component enthalpy and entropy contributions even though they model the activity-composition relations well. Moreover, there are difficulties concerning the kinetics of ordering and the approach to equilibrium in the experiments. The calorimetric data were measured on high-temperature heat-treated plagioclase that is probably largely disordered (at least in the $C\overline{1}$ field), whereas the cation exchange experiments almost certainly involved partial ordering of unknown extent during the experiments, and the approach to equilibrium is unknown. Thus it is probably not wise to lay too much emphasis on the calorimetric data in constraining the activity models based upon the cation exchange experiments. However, the results from all models (see below) indicate that the $C\overline{1}$ solutions are adequately described by the parameters derived from the cation exchange. As a consequence, there is no degradation of the fit of the exchange data if the enthalpy measurements on the $C\overline{1}$ solutions are included. Thus the exchange data and the enthalpy data on the $C\overline{1}$ solutions are fitted together, whereas the enthalpy data for $I\overline{1}$ solutions are compared with the predicted enthalpies using the results of the regression. The enthalpy of solution data may be modeled by DQF using, for $C\overline{1}$ solutions,

$$\begin{aligned} \Delta H_{\mathrm{sol}} &= (1 - X)H_{\mathrm{Ab,sol}} + XH_{\mathrm{An,sol}} \\ &\quad - \left(I_{\mathrm{An}} - T\frac{\partial I_{\mathrm{An}}}{\partial T}\right)X - X(1 - X)W_{\mathrm{c}} \end{aligned} \quad (8a)$$

and, for $I\overline{1}$ solutions,

$$\begin{aligned} \Delta H_{\mathrm{sol}} &= (1 - X)H_{\mathrm{Ab,sol}} + XH_{\mathrm{An,sol}} \\ &\quad - \left(I_{\mathrm{Ab}} - T\frac{\partial I_{\mathrm{Ab}}}{\partial T}\right)(1 - X) \\ &\quad - X(1 - X)W_{\mathrm{i}}. \end{aligned} \quad (8b)$$

Although it would be advantageous to have physically realistic models with which to fit the data, in practice such models are not available, particularly with respect to modeling entropy of mixing for phases with anything but trivial nonideality (e.g., Powell, 1983). As a consequence, all models commonly used are, to a greater or lesser extent, empirical: we will use ideal mixing on sites to formulate thermodynamic mole fractions. We do have, however, some flexibility in the choice of the number of sites in the phase on which the elements mix. There are three obvious cases:

1. In the ordered model, mixing of Al and Si on the tetrahedral sites is not considered to contribute to the entropy of mixing and, therefore not to the thermodynamic mole fractions, so the thermodynamic mole fractions only reflect mixing of Ca and Na on the A site:

$$\begin{aligned} X_{\mathrm{An}} &= X \\ X_{\mathrm{Ab}} &= (1 - X). \end{aligned} \quad (9)$$

2. The 4T-disordered model involves random mixing

TABLE 1. Results of regressions for parameters and uncertainties ($\pm 2\sigma$) in models 1 to 5

Model	W_c	W_i	K	H_{Ab}	H_{An}
1	1.07	9.79	0.049	70.0	64.4
±	1.79	1.26	0.00395	1.39	2.31
2	5.61	13.7	0.049	70.4	65.7
±	1.80	1.26	0.00395	1.4	2.31
3	8.31	26.1	0.0544	70.8	70.9
±	2.43	1.9	0.00591	1.85	3.09
4	5.51	9.77	0.0489	70.4	66.3
±	1.79	1.25	0.00392	1.39	2.3
5	3.83	26.2	0.0539	70.6	64.7
±	2.37	1.87	0.00578	1.81	3.02
Correlation coefficients for model 4					
W_c	1.00	−0.528	0.591	0.1	−0.192
W_i	−0.528	1.00	−0.218	−0.046	0.293
K	0.591	−0.218	1.00	0.06	−0.089
H_{Ab}	0.1	−0.046	0.06	1.00	−0.66
H_{An}	−0.192	0.293	−0.089	−0.66	1.00

on the large cation site and the tetrahedral sites, with the four tetrahedral (4T) sites considered to be equivalent, with Al and Si distributed equally among them:

$$X_{An} = 16X_{Ca(A)}X^2_{Al(T)}X^2_{Si(T)}$$

$$= \frac{1}{16}X(1 - X)^2(3 - X)^2$$

$$X_{Ab} = \frac{256}{27}X_{Na(A)}X_{Al(T)}X^3_{Si(T)}$$

$$= \frac{1}{27}(1 - X)(1 + X)(3 - X)^3. \qquad (10)$$

3. The 2T-disordered model involves random mixing on the large cation site and the tetrahedral sites but with Al and Si distributed equally over only two of the tetrahedral (2T) sites, denoted TA, the other two tetrahedral sites involving only Si. The expressions are identical to those of the Al-avoidance model of Kerrick and Darken (1975):

$$X_{An} = X_{Ca(A)}X^2_{Al(TA)} = \frac{1}{4}X(1 + X)^2$$

$$X_{Ab} = 4X_{Na(A)}X_{Al(TA)}X_{Si(TA)} = (1 - X)^2(1 + X). \qquad (11)$$

In each of the models, the activity coefficients, in $a_i = x_i\gamma_i$, are represented by regular mixing; although the form of each will always be $\gamma_{An} = \exp[(W/RT)(1 - X)^2]$ and $\gamma_{Ab} = \exp[(W/RT)X^2]$ because the system of interest is binary, the meaning of the interaction parameter, W, will be different in each case if the W is envisaged as being the difference in energies of combinations of nearest neighbors. The models that we have applied to the experimental data involve the following combinations of the above activity models: (1) ordered in both regions, (2) 4T-disordered in both regions, (3) 2T-disordered in both regions, (4) 4T-disordered in the $C\bar{1}$ field and ordered in the $I\bar{1}$ field, and (5) 4T-disordered in the $C\bar{1}$ field and 2T-disordered in the $I\bar{1}$ field.

In the regressions, we used an algorithm from Mikhail (1976) coded in Mathematica (Wolfram, 1988). The data were weighted with $\sigma_X = 0.02$, $\sigma_{RT \ln K} = 2$ kJ, and $\sigma_{H(soln)} = 2$ kJ; the first has the important effect of accounting for the relatively large uncertainties on $\ln K_d$ as $X \rightarrow 0$ and $X \rightarrow 1$. The regressed values for the five models are presented in Table 1. Models 1–3 are computed for comparison with the earlier models of Newton et al. (1980). Models 4 and 5 are included to consider two possibilities involving different activity-composition relations in the two regions.

The results for models 1, 2, and 4 produce very similar activity-composition relations (and hence Gibbs energies of mixing) at all temperatures but yield different magnitudes for the W_c and W_i, Table 1. This is because these parameters can approximately counteract the effect of using different formulations of the thermodynamic mole fractions. Thus, W_c and W_i for model 1 are both about 4 kJ higher than for model 2. All three models predict enthalpies of solution that are too low for $I\bar{1}$ solutions. Figure 1 shows the correspondence between the experimental data and the model results and the predicted enthalpies of solution for $I\bar{1}$ solutions for model 4. Figure 2 shows the activity-composition relationships for model 4.

Model 3 is the only model that fits not only the exchange data and the $C\bar{1}$ enthalpy data but also predicts the form of the $I\bar{1}$ enthalpy data, Figure 3. However, at higher temperatures, the activity-composition relations show negative deviations from ideality, Figure 4. The main difference with models 1, 2, and 4 at lower temperatures is that in model 3 the positive deviations from nonideality are more pronounced. Model 5 shares this feature with model 3 but otherwise fits the $I\bar{1}$ enthalpy data less well than models 1, 2, and 4.

LANDAU MODEL FOR PLAGIOCLASE

A completely different approach to modeling feldspar thermodynamics, and one which has to date met with considerable success (Carpenter, 1988), is to apply Landau's theory of phase transitions to the $C\bar{1}$-$I\bar{1}$ transformation. For a good introduction to mineralogical applications of Landau theory, the reader is referred to Carpenter's (1988) review.

In the context of Landau theory, it is apparent that of the three possible phase transition descriptions (first order, second order, and tricritical) anorthite ordering appears to be very close to tricritical in character (Carpenter, 1988). The thermodynamics are dependent on the state of order as described by the macroscopic order parameter Q, which varies from $Q = 1$ (ordered) at $T = 0$ K to $Q = 0$ (disordered) at the critical temperature of the phase transition, T_c. For a tricritical transition, we may write the free energy of ordering as an expansion in Q:

$$G_{ord} = \frac{a}{2}(T - T_c)Q^2 + \frac{c}{6}Q^6 \qquad (12)$$

in which a and c are positive constants. As the temperature of the $C\bar{1}$ - $I\bar{1}$ transition depends linearly on X_{An},

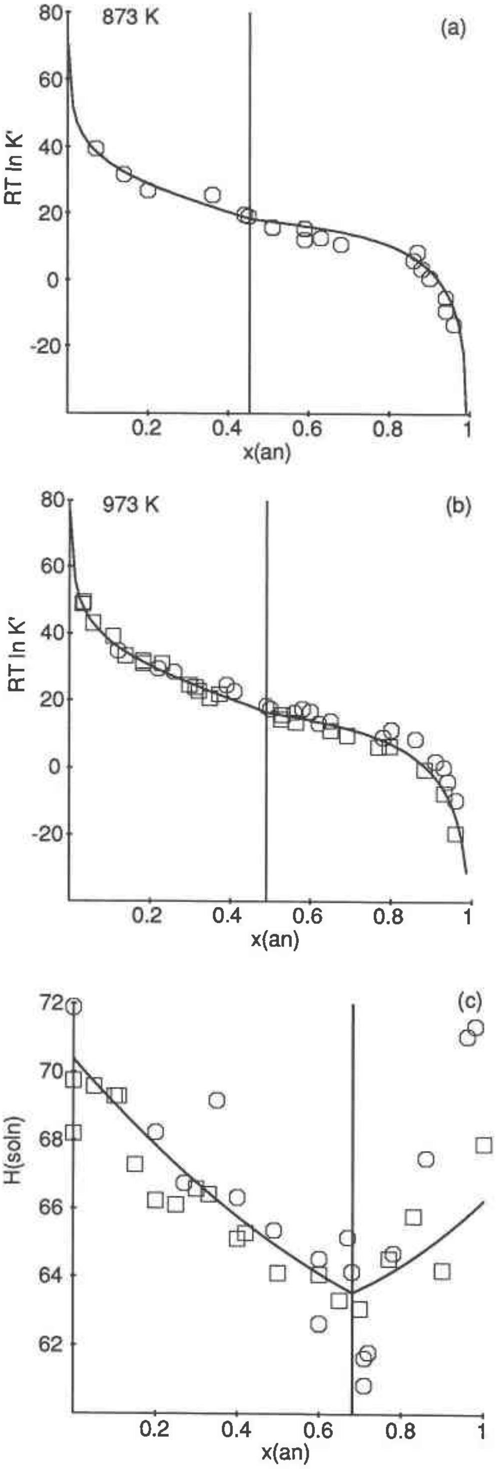

Fig. 1. Experimental data for the plagioclase-fluid exchange equilibria of Orville (1972) (square symbols) and Schliestedt and Johannes (1990) (hexagon symbols), (**a**) at 873 K and (**b**) at 973 K; in (**c**), the enthalpy of solution data of Newton et al. (1980) (square symbols) and Carpenter et al. (1985) (hexagon symbols). The trends through the data were calculated with the regression coefficients in Table 1 for model 4, involving 4T-disordered plagioclase in the $C\bar{1}$ field and ordered plagioclase in the $I\bar{1}$ field.

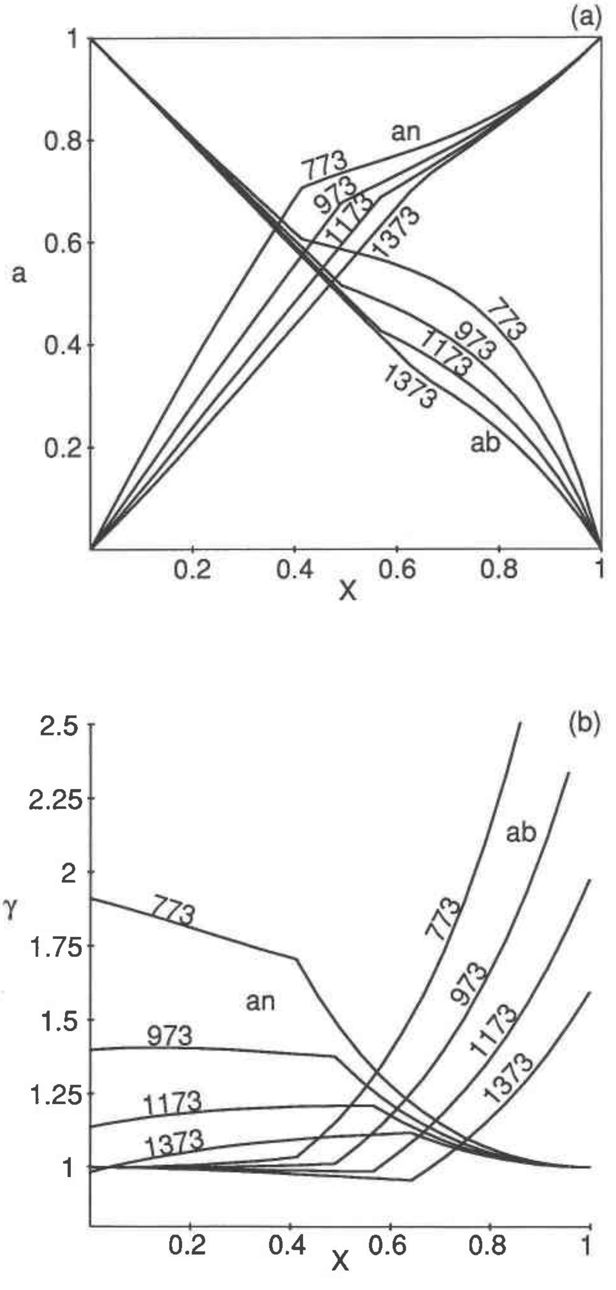

Fig. 2. The predicted activity-composition relationships (**a**) and activity coefficient–composition relationships (**b**) for model 4 using the regression coefficients from Table 1. Temperatures in kelvins.

then T_c can be written as $T_c = T_c^0 + m(1 - X)$, where T_c^0 is T_c at $X = 1$ and m for the $C\bar{1}$ - $I\bar{1}$ transition, from Equation 3, is $-1/0.00038 = -2630$. The equilibrium value of the order parameter Q at any temperature may be found from

$$\frac{\partial G_{\mathrm{ord}}}{\partial Q} = 0$$

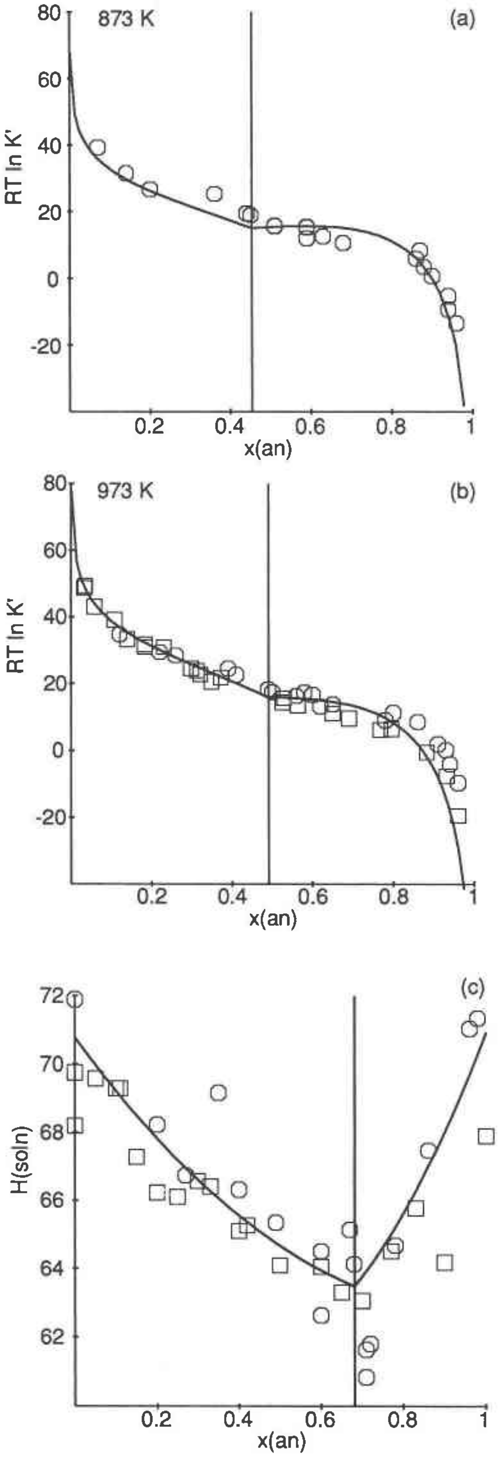

Fig. 3. The experimental data (see caption to Fig. 1 for details) and trends through the data calculated with the regression coefficients in Table 1 for model 3, involving 2T-disordered plagioclase in both the $C\bar{1}$ and $I\bar{1}$ fields.

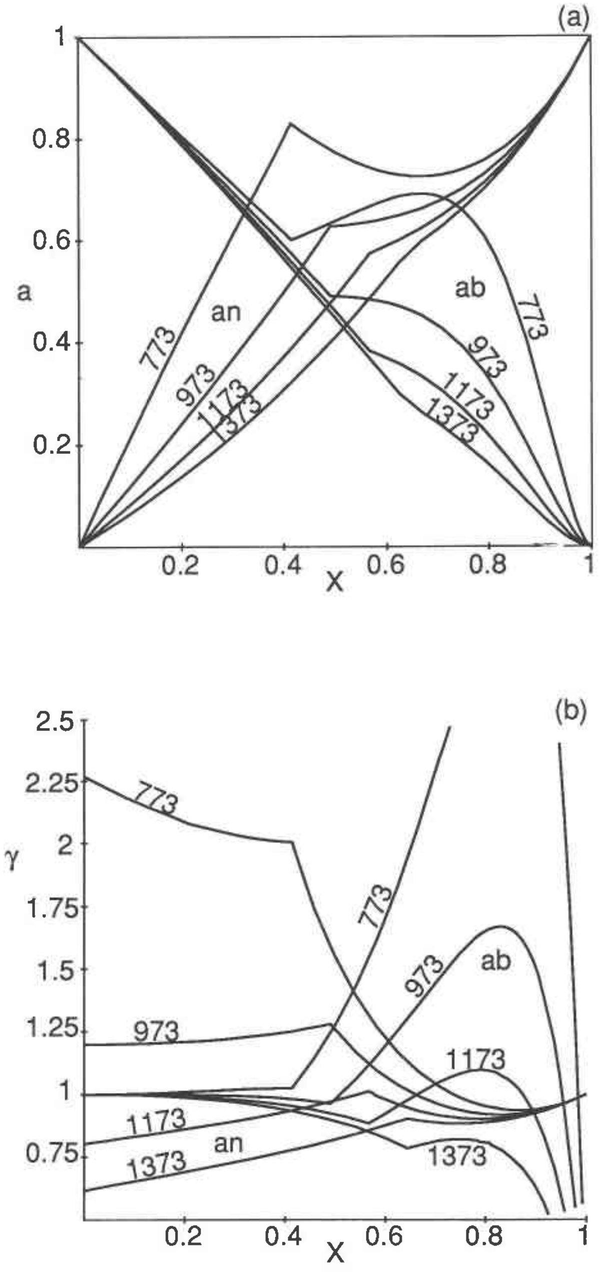

Fig. 4. The predicted activity-composition relationships (**a**) and activity coefficient–composition relationships (**b**) for model 3 using the regression coefficients from Table 1. Temperatures in kelvins.

giving, after rearrangement,

$$Q^4 = (T - T_c)\frac{a}{c}. \qquad (13)$$

Given that $Q = 1$ at $T = 0$, then $T_c^0 = c/a$ at $X = 1$, and c may be eliminated from Equation 13. Noting that the ordering entropy, S, is given by $-\partial G_{ord}/\partial T$ and that this is maximum at $T = 0$ where $Q = 1$, then $S^{max} = -a/2$ at $X = 1$, allowing a to be eliminated from Equation 13. Thus, combining Equations 12 and 13:

$$G_{ord} = S^{max}Q^6\left(T_c - \frac{T_c^0}{3}\right)$$
$$= S^{max}\sqrt{1 - \frac{T}{T_c}}\left(1 - \frac{T}{T_c}\right)\left(T_c - \frac{T_c^0}{3}\right). \quad (14)$$

To find the activities of albite and anorthite, we must differentiate with respect to X:

$$RT \ln \gamma_{An}^{ord} = G_{ord} + (1 - X)\frac{\partial G_{ord}}{\partial X}$$
$$RT \ln \gamma_{Ab}^{ord} = G_{ord} - X\frac{\partial G_{ord}}{\partial X} \quad (15)$$

where

$$\frac{\partial G_{ord}}{\partial X} = -mS^{max}\sqrt{1 - \frac{T}{T_c}}\left[1 + \frac{T}{2T_c}\left(1 - \frac{T_c^0}{T_c}\right)\right]. \quad (16)$$

These expressions refer to the activity coefficients for equilibrium-ordered plagioclase in the $I\bar{1}$ field relative to disordered end-members. Referring the activities to end-members in their equilibrium structural state we have for $C\bar{1}$:

$$RT \ln a_{An,c} = RT \ln X_{An} + W_c(1 - X)^2 - \frac{2}{3}S^{max}T_c^0Q^6$$
$$RT \ln a_{Ab,c} = RT \ln X_{Ab} + W_cX^2. \quad (17a)$$

The third term in $RT \ln a_{An,c}$ is the difference in Gibbs energy between anorthite in the $C\bar{1}$ structure and in the $I\bar{1}$ structure, which is just G^{ord} at $X = 1$. For $I\bar{1}$:

$$RT \ln a_{An,i} = RT \ln X_{An} + W_i(1 - X)^2 - \frac{2}{3}S^{max}T_c^0Q^6 + RT \ln \gamma_{An}^{ord}$$
$$RT \ln a_{Ab,i} = RT \ln X_{Ab} + W_iX^2 + RT \ln \gamma_{Ab}^{ord}. \quad (17b)$$

Using the 4T-disordered model as a base, the Landau terms can be added using an estimate of S^{max} of 11.5 kJ, from the configurational entropy of ordering (Carpenter, 1988), and using a minimum sensible value for W of zero. The results are shown on Figure 5 and the corresponding activity-composition relationships in Figure 6. The correspondence with the exchange data is disappointing, although regression delivers a closer fit but with a large negative W_c of −9 kJ that plays havoc with extrapolations. The calculated enthalpies of solution are also shown in Figure 5, using

$$\Delta H_{ord} = S^{max}\left(Q^6\frac{T_c^0}{3} - T_cQ^2\right) \quad (18)$$

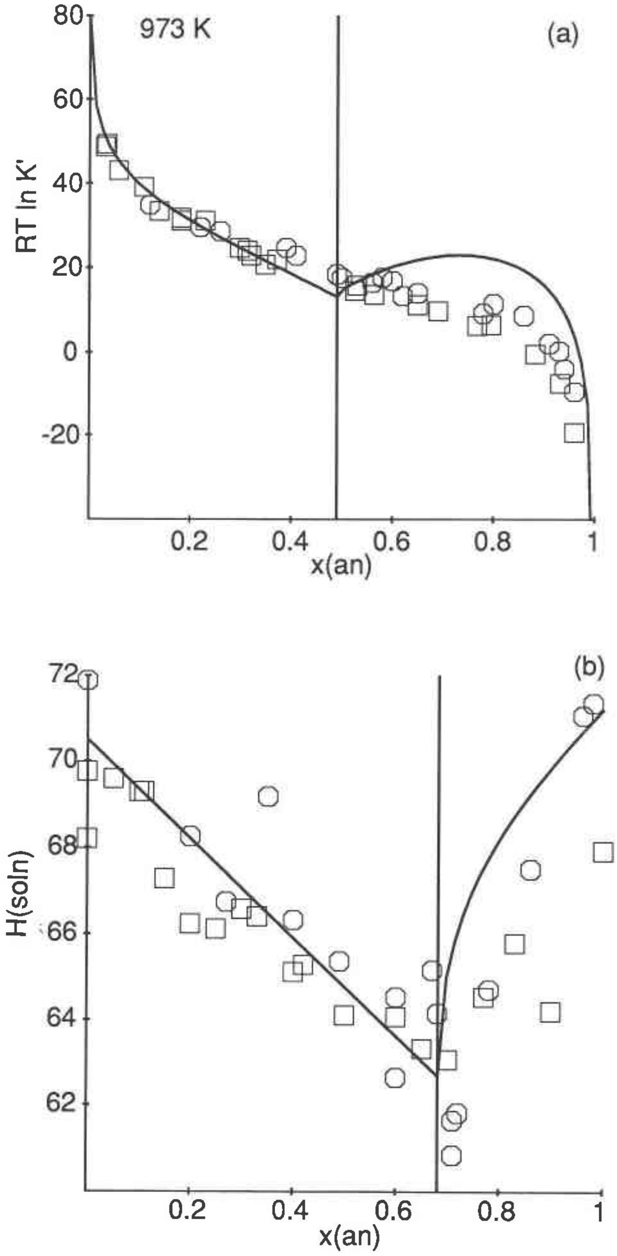

Fig. 5. The experimental data (see caption to Fig. 1 for details) and trends through the data using $W = 0$ for the Landau model.

where this contribution is added to the enthalpies only in the $I\bar{1}$ field. Whereas the form is not inappropriate, the curvature of the predicted enthalpies of solution in the $I\bar{1}$ field seems to be too strong.

DISCUSSION

All the models discussed above involve predicted solvi at lower temperatures, Figures 7a–7c. In the case of models 1, 2, and 4, the solvus peaks at a temperature of about

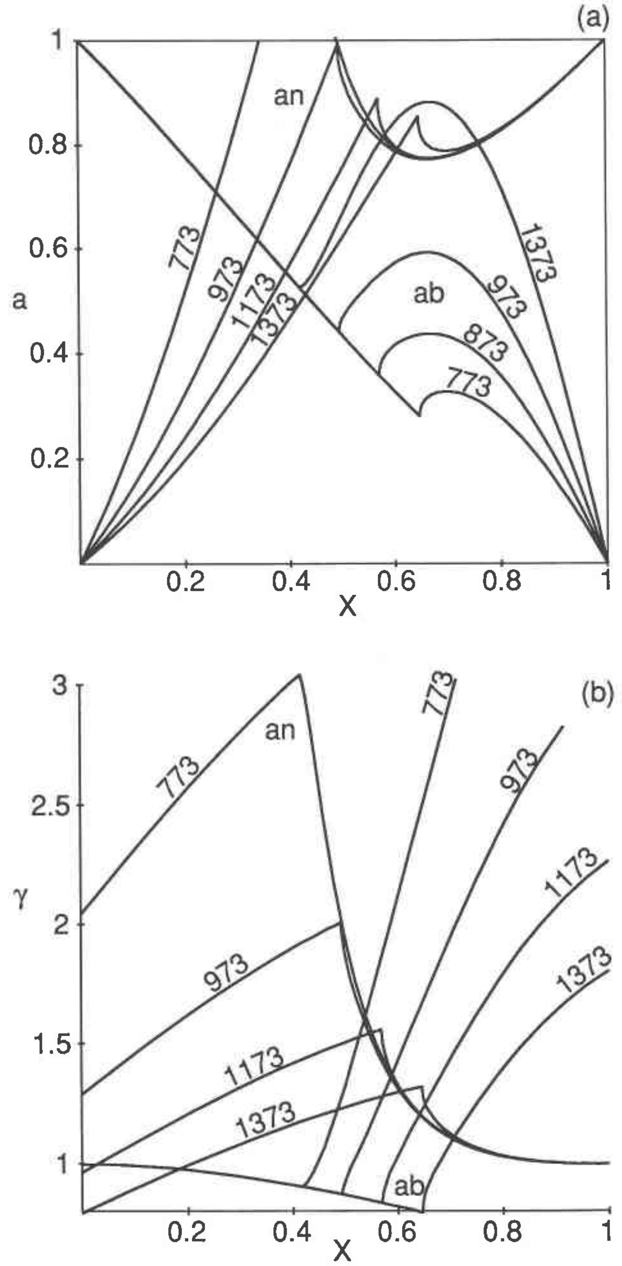

Fig. 6. The predicted activity-composition relationships (**a**) and activity coefficient–composition relationships (**b**) for the Landau model with $W = 0$. Temperatures in kelvins.

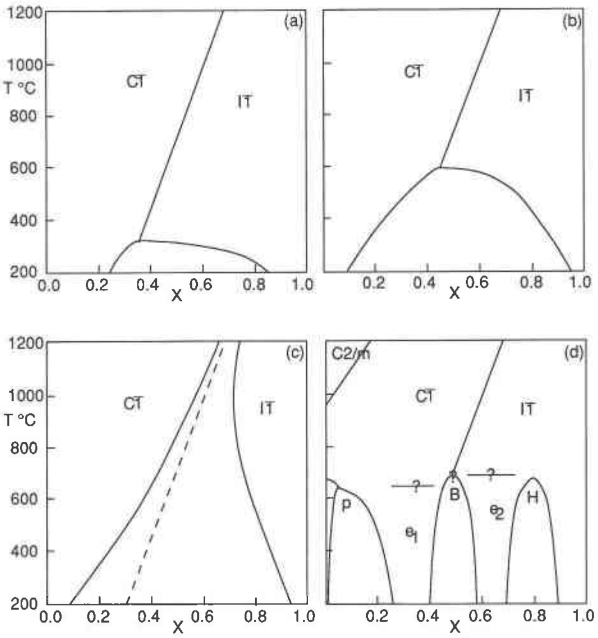

Fig. 7. The predicted phase diagrams for the regressions in Table 1 for (**a**) model 4, (**b**) model 3, and (**c**) the Landau model; in (**d**) are shown the relationships as suggested by Carpenter (1988). In **d**, p = peristerite, B = Bøggild, and H = Huttenlocher.

300 °C, whereas for models 3 and 5, the solvus peaks at a temperature of about 600 °C. In the case of the Landau model, the solvus continues right up to T_c^0, although the two phase field is very narrow at higher temperatures. However the solvus is already wide at 700 °C, extending from $X = 0.4$ to 0.75; it is primarily this that is causing the poor fit of the Landau model to the exchange data. It is interesting to note that DQF is more appropriate than Landau from the point of view of the form of the predicted phase diagram, although the Landau model is remarkably successful at accounting for the dependence on composition and temperature of most physical and chemical properties (see Carpenter, 1988). The solvus development in our DQF models is in the position of the Bøggild miscibility gap found in natural plagioclases in the intermediate composition range, but it would be dangerous to make too much of this correspondence.

It would be nice to suggest a particular model for activity-composition relations for plagioclase that we could advocate, with confidence, for thermodynamic calculations. However, the paucity of experimental data and the difficulty of appraising the approach to equilibrium in them make this task invidious. The various parameterizations, being based primarily on experimental data at 700 °C, should work well in the vicinity of that temperature. Away from that temperature, the activity-composition relations do vary, and this must be taken into account in appraising uncertainties on calculations of mineral equilibria. One way to proceed would be to use both models 3 and 4 and ascertain whether the differences between them make appreciable differences to the results of calculations. Additionally, the predicted activity-composition relations themselves are uncertain as a consequence of the uncertainties on the regressed parameters. Uncertainties on activity coefficients from this source are portrayed in Figure 8 for model 4, using the uncertainties and correlations in Table 1 and standard error propagation (e.g., Powell and Holland, 1988). These uncertainties are typical for all the models, and, moreover, they are representative of the uncertainties on activity coefficients derived directly from the experimental data. These are somewhat larger than sometimes assumed.

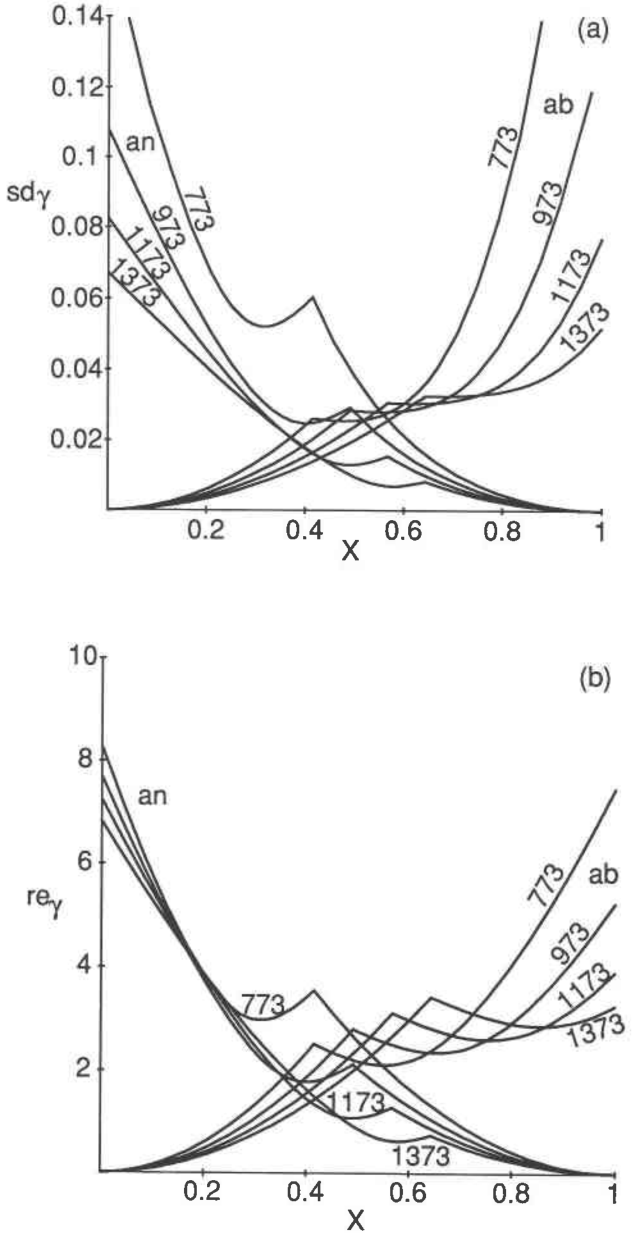

Fig. 8. The calculated uncertainties on the activity coefficients for model 4 using the uncertainty and correlations in Table 1, temperatures in kelvins: (**a**) gives $\sigma\gamma$ at the 1σ level; (**b**) gives the relative error, $\sigma\gamma/\gamma$, at the 1σ level.

The plagioclase feldspars exhibit a curious ordering behavior on cooling to temperatures below 700–800 °C, which has been the subject of intense study and which is not yet well understood (Carpenter, 1986). This ordering leads to the development of incommensurate structures ("e" plagioclase), which, through poor understanding, we have had to ignore. It may be that a Landau approach will provide the necessary framework to understand the thermodynamics of the $C\bar{1}$ to "e" and the $I\bar{1}$ to "e" transformations. However, the simple models used above may approximately apply to the thermodynamics of plagioclase down into the top end of the "e" fields. Likewise, the presence of the peristerite unmixing region at more albitic compositions will also seriously affect the validity of the simple activity models used above, and caution should be exercised in using them near the peristerite gap; certainly under no circumstances should they be used in the low-albite region, to the low X side of the peristerite gap, where γ_{An} must be much larger than predicted by the above models.

ACKNOWLEDGMENTS

We would like to acknowledge valuable discussions with Mike Carpenter and Thomas Will and generous reviews from M. Ghiorso and J.B. Thompson, Jr.

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MANUSCRIPT RECEIVED NOVEMBER 6, 1990
MANUSCRIPT ACCEPTED SEPTEMBER 11, 1991