

# Calculated activities for species in albite-water melts\*

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## Introduction

Both the stoichiometric and speciation approaches (Berman and Brown, 1987) have been employed to develop thermodynamic models for albite-water (*ab-w*) melts.<sup>1</sup> Significantly, in each of the speciation approaches (Burnham, 1981; Silver and Stolper, 1985, 1989; Burnham and Nekvasil, 1986; Wen and Nekvasil, 1994) it was assumed either that some, or all, of the species mix ideally. This is an unnecessary restriction that can hamper development of a rigorous quantitative description of the thermodynamic mixing properties of *ab-w* melts. An alternative approach, which permits species to mix nonideally, is described here, using the speciation scheme proposed by Silver and Stolper (1985, 1989).

## Discussion

Activity-composition relations for the stoichiometric components of *ab-w* melts and microscopic species in these melts — water molecules, OH groups and non-hydrogen-bonded oxygens (Silver and Stolper, 1985) — can be linked directly by (a) developing empirical equations for  $a_{ab}^L$  and  $a_w^L$  that yield accurate calculated heterogeneous phase relations for the *ab-w* system; and (b) applying these equations — along with spectroscopic data on  $X_{H_2O,mol}^L$  and  $X_{OH}^L$  in *ab-w* melts (Silver and Stolper, 1989) — to quantify  $a_{H_2O,mol}^L$  and  $a_{OH}^L$ , and  $a_O^L$ .

The presence of H<sub>2</sub>O molecules and OH groups in quenched *ab-w* melts (Stolper, 1982) implies that water dissolves in these melts according to the reaction

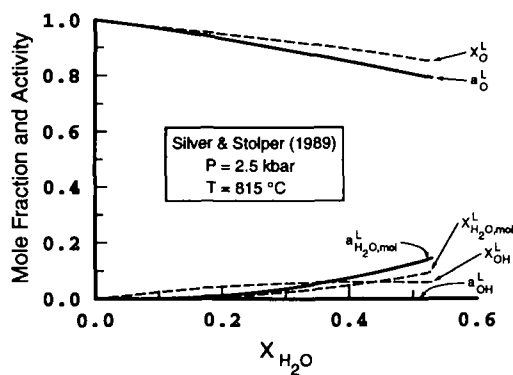
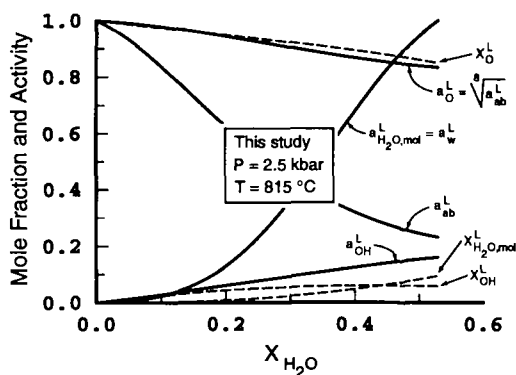
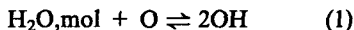


FIG. 1. Calculated activity-composition relations for *ab-w* melt species at 2.5 kbar, 815°C. (a) This study, (b) Silver and Stolper (1989).

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<sup>1</sup> Notation: *ab* = NaAlSi<sub>3</sub>O<sub>8</sub>; *w* = H<sub>2</sub>O; H<sub>2</sub>O,mol = water molecule; *O* = oxygen atom; *OH* = hydroxyl group; *L* = liquid (*ab-w* melt); *a* = activity;  $\gamma$  = activity coefficient; *X* = mole fraction.



for which we may write

$$K = \frac{(a_{\text{OH}}^L)^2}{(a_{\text{H}_2\text{O, mol}}^L)(a_{\text{O}}^L)} \quad (2)$$

A fixed value for  $K$  is given by Silver and Stolper (1985). Values for  $a_{\text{H}_2\text{O, mol}}^L$  and  $a_{\text{O}}^L$  can be obtained from the relations

$$a_{\text{H}_2\text{O, mol}}^L = a_w^L \quad (3)$$

and

$$a_{\text{O}}^L = \sqrt{a_{\text{ab}}^L} \quad (4)$$

(Silver and Stolper, 1985, 1989), using values for  $a_w^L$  and  $a_{\text{ab}}^L$  obtained from the two-parameter Margules equations for  $a_w^L$  and  $a_{\text{ab}}^L$  developed by Blencoe (1992). With values for  $K$ ,  $a_{\text{H}_2\text{O, mol}}^L$  and  $a_{\text{O}}^L$ , equation (2) can be used to evaluate  $a_{\text{OH}}^L$ .

The foregoing thermodynamic theory was applied to calculate  $a$ - $X$  relations for  $ab$ - $w$  melt species at 2.5 kbar. Results obtained for 815°C are illustrated in Fig. 1a. Fig. 1b shows corresponding results obtained from the thermodynamic model developed by Silver and Stolper (1985, 1989). It is evident from these two figures that the two models yield markedly different results. The most obvious difference concerns  $a$ - $X$  relations for water molecules. In the model described here,  $a_{\text{H}_2\text{O, mol}}^L$  increases from 0 at  $X_w^L = 0$  to  $\cong 1$  at  $X_w^L \cong 0.53$ , the latter value representing the bulk composition of the  $ab$ - $w$  melt that is saturated with  $\text{H}_2\text{O}$  at 2.5 kbar, 815°C. By contrast, with the Silver and Stolper model,  $a_{\text{H}_2\text{O, mol}}^L$  increases from 0 at  $X_w^L = 0$  to only  $\cong 0.16$  at  $X_w^L \cong 0.53$ . This difference results from the different standard states for water molecules in the two models (a Raoultian standard state for this species in the present model, a Henrian standard state in the Silver and Stolper model). It is also evident from Figs. 1a and 1b that the two models yield significantly different calculated  $a_{\text{OH}}^L$ - $X_w^L$  relations. Using the model described here,  $a_{\text{OH}}^L$  increases from 0 at  $X_w^L = 0$  to  $\cong 0.17$  at  $X_w^L \cong 0.53$ . In marked contrast, the Silver and Stolper model yields  $a_{\text{OH}}^L < 0.01$  for  $0 < X_w^L \leq 0.53$ .

The observations above indicate that the thermodynamic approach described here has two advantages over the approach taken by Silver and

Stolper. First, it is both conventional and logical to adopt a Raoultian standard state for water molecules. Second, the values for  $a_{\text{OH}}^L$  obtained from the new model are more rational than those obtained from the Silver and Stolper model. In the new model, values for  $\gamma_{\text{OH}}^L$  are slightly greater than one over the entire range of melt compositions. By contrast, in the Silver and Stolper model,  $\gamma_{\text{OH}}^L \ll 1$  over this range.

### Conclusions

Speciation models for  $ab$ - $w$  melts should be accordant with all accurate phase equilibrium, thermodynamic and spectroscopic data for high temperature phases of the  $ab$ - $w$  system. To achieve this consistency, it may be necessary to employ modeling methods that permit nonideal mixing of species. Models based on ideal mixing of species are unlikely to be completely satisfactory formalisms for representing the thermodynamic mixing properties of albite-water melts.

### References

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