

Short communication

Exsolution enthalpy of water from silicate liquids

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Abstract

Because water dissolves in silicate melts as at least two species, H₂O molecules and OH groups, the exsolution (evaporation) enthalpy of the H₂O component from a silicate melt depends on species proportions, which in turn depends on H₂O pressure. In this short communication, a formal analysis of the exsolution enthalpy of water from a silicate melt is presented, taking into account of the role of speciation. The exsolution enthalpy from a rhyolitic melt at 850°C is found to increase with pressure at ≤ 100 bar and this increase is mostly caused by the speciation reaction. Sahagian and Proussevitch [Sahagian, D.L., Proussevitch, A.A., 1996. Thermal effects of magma degassing. *J. Volcanol. Geotherm. Res.* 74, 19–38] also found an increase of the exsolution enthalpy with pressure up to 20 bar for an albitic melt. However, the rate of increase determined from this work is an order of magnitude less than that determined by Sahagian and Proussevitch. It is concluded that the strong pressure dependence of the exsolution enthalpy at low pressures they inferred is probably an artifact of their treatment. The method presented here is general and can be applied to other multi-species components. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: heat of evaporation; exsolution enthalpy; speciation; multi-species components

1. Introduction

The purpose of this short communication is to outline a formal analysis for the estimation of the exsolution enthalpy (i.e., heat of evaporation) of the H₂O component from a silicate melt taking into account the presence of two species (Stolper, 1982), molecular H₂O (referred to as H₂O_m) and OH groups (referred to as OH). The exsolution enthalpy is important for evaluating the thermal effect of magma degassing and explosive volcanic eruption (Sahagian and Proussevitch, 1996), and for estimating and extrapolating how the solubility of water changes with temperature. In addition, the method presented below

can also be used to investigate the variation of the exsolution enthalpy or other thermodynamic properties of other multi-species components.

For a volatile component A that can dissolve in a liquid, the usual expression for the enthalpy of exsolution from the liquid is:

$$\Delta \bar{H}_{\text{ex}}(T, P) = \bar{H}_{\text{A}}^{\text{g}}(T, P) - \bar{H}_{\text{A}}^{\text{l}}(T, P, X_{\text{A}}^{\text{l}}), \quad (\text{a})$$

where the system pressure P is assumed to be the same as the pressure of component A in the gas phase (i.e., the gas phase consists of only component A), X_{A}^{l} is the molar fraction of A in the liquid in equilibrium with the gas phase, $\bar{H}_{\text{A}}^{\text{g}}$ is the molar enthalpy of component A in the gas phase, and $\bar{H}_{\text{A}}^{\text{l}}$ is the partial molar enthalpy of the dissolved component A in the liquid. Because X_{A}^{l} at equilibrium is a function of T and P , the exsolution enthalpy is a

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function of T and P only. For an ideal solution, \bar{H}_A^1 is independent of X_A^1 . The pressure derivative of \bar{H}_A^1 is $\bar{V}_A^1(1 - \alpha_A^1 T)$ where \bar{V}_A^1 is the partial molar volume of component A in the liquid and α_A^1 is the thermal expansivity. Since \bar{V}_A^1 is typically small (2.2 J mol⁻¹ bar⁻¹ for H₂O in magma at 850°C and 1 bar, Ochs and Lange, 1997), \bar{H}_A^1 does not change significantly from 1 to 2 bars. If this small pressure dependence is ignored, and if the gas is ideal (hence, enthalpy of the gas is independent of pressure) and the liquid phase is an ideal mixture (hence, no mixing enthalpy), the above equation can be simplified as:

$$\Delta \bar{H}_{\text{ex}}(T, P, X_A^1) \approx \bar{H}_A^{\text{g},0}(T) - \bar{H}_A^{1,0}(T) = \Delta \bar{H}_{\text{ex}}^0(T), \quad (\text{b})$$

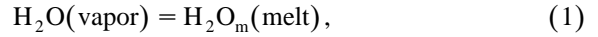
where $\Delta \bar{H}_{\text{ex}}^0(T)$ is the standard state exsolution enthalpy that is independent of pressure and liquid composition. Therefore, at low pressures (and hence, low dissolved concentration of A), the exsolution enthalpy of a volatile component is roughly independent of pressure for an ideal gas and ideal mixture. However, Sahagian and Proussevitch (1996) evaluated the exsolution enthalpy of the H₂O component in the albitic melt and concluded that it varied strongly even at low pressures (e.g., an increase of 1500 J mol⁻¹ from 1 to 2 bars at 850°C). Since H₂O in the vapor phase is roughly ideal at such low pressures and 850°C, the large variation with pressure, if real, must be owing to the speciation effect of dissolved H₂O in silicate melts. It is thus of interest to examine $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$ by explicitly incorporating the effect of the two species, H₂O_m and OH, and to understand whether such large variation in $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$ is possible. Since the speciation of dissolved H₂O is best understood in hydrous rhyolitic systems, this work concentrates on hydrous rhyolitic melts.

2. Exsolution enthalpy of H₂O from a silicate melt

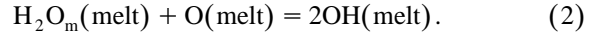
2.1. The dissolution and speciation of water in silicate melts

By explicitly incorporating the effect of the two species, H₂O_m and OH, the dissolution of H₂O

component into magma can be treated as a two-step reaction:



and



The standard state enthalpy changes (ΔH) and the equilibrium constants (K) for Reactions (1) and (2) will be referred to as:

$$\Delta H_{r1}^0 = \bar{H}_{\text{H}_2\text{O}_m}^{\text{melt},0}(T, P) - \bar{H}_{\text{H}_2\text{O}}^{\text{vapor},0}(T), \quad (3)$$

$$\begin{aligned} \Delta H_{r2}^0 &= 2\bar{H}_{\text{OH}}^{\text{melt},0} - \bar{H}_{\text{O}}^{\text{melt},0} - \bar{H}_{\text{H}_2\text{O}_m}^{\text{melt},0} \\ &\equiv \bar{H}_{2\text{OH}-\text{O}}^{\text{melt},0}(T, P) - \bar{H}_{\text{H}_2\text{O}_m}^{\text{melt},0}(T, P), \end{aligned} \quad (4)$$

$$K_1 = \frac{a_{\text{H}_2\text{O}_m}^{\text{melt}}}{f_{\text{H}_2\text{O}}^{\text{vapor}}} \approx K_{1\infty} \exp\left[-\Delta H_{r1}^0/(RT)\right], \quad (5)$$

and

$$K_2 = \frac{(a_{\text{OH}}^{\text{melt}})^2}{a_{\text{H}_2\text{O}_m}^{\text{melt}} a_{\text{O}}^{\text{melt}}} \approx K_{2\infty} \exp\left[-\Delta H_{r2}^0/(RT)\right], \quad (6)$$

where $K_{1\infty}$ and $K_{2\infty}$ depend on pressure as

$$K_{1\infty} = A_1 \exp\left[-\int_1^P \bar{V}_{\text{H}_2\text{O}_m}^{\text{melt}} dP/(RT)\right], \quad (7)$$

$$K_{2\infty} = A_2 \exp\left[-P\Delta V_{r2}^0/(RT)\right], \quad (8)$$

where A_1 and A_2 are two constants, and the subscript 2OH–O means two OH groups minus an oxygen (i.e., 2OH–O means part of the H₂O component that is in the form of OH). In the above expressions, the standard state is indicated with the superscript 0. The standard state for H₂O in the vapor phase is the hypothetical ideal gas at 1 bar (very close to the real gas at 1 bar) and T . The standard state for each species in the melt at P and T is the nonexistent hypothetical ideal end member melt at the activity of 1. If $K_{1\infty}$ (or $K_{2\infty}$) and ΔH_{r1}^0 (or ΔH_{r2}^0) are independent of T at a given P (equivalent to small ΔC_p), then $\ln K_1$ (or $\ln K_2$) vs. $1/T$ is a straight line. Conversely, if $\ln K_1$ (or $\ln K_2$) vs. $1/T$ follows a straight line, ΔC_p cannot be obtained from such data, and $K_{1\infty}$ (or $K_{2\infty}$) and ΔH_{r1}^0 (or ΔH_{r2}^0) can be viewed as independent of T . Note that the standard state of H₂O in the vapor phase is at 1 bar and the standard states for dissolved H₂O species are at T and P . This will bear on later derivation of

exsolution enthalpy since the exsolution enthalpy is the enthalpy change for H₂O in the melt at *T* and *P* to exsolve to H₂O in vapor at *T* and *P*.

Recent experimental work on both speciation and solubility provides main constraints on the equilibrium constants and thermodynamic functions of the above two reactions. The variations of *K*₁, *K*₂, Δ*H*_{r1}⁰, and Δ*H*_{r2}⁰ are summarized below.

(i) *K*₁ and Δ*H*_{r1}⁰. Since it takes heat for a component in a liquid to vaporize, −Δ*H*_{r1}⁰ is expected to be positive at not too high a pressure and *K*₁ decreases with increasing *T* (Eq. (5)). Because $\bar{V}_{\text{H}_2\text{O}_m}^{\text{melt}} > 0$, *K*₁ decreases with increasing *P* (Eq. (7)). The temperature dependence of Δ*H*_{r1}⁰ cannot be evaluated at this time by ∫*C*_p*dT* because *C*_p of H₂O_m in a silicate melt is not well-known. The pressure dependence of Δ*H*_{r1}⁰ can be estimated from that of $\bar{H}_{\text{H}_2\text{O}_m}^{\text{melt}}$ because by definition $\bar{H}_{\text{H}_2\text{O}}^{\text{vapor},0}$ is independent of *P*. At 850°C and < 100 bars, $(\partial\bar{H}_{\text{H}_2\text{O}_m}^{\text{melt}}/\partial P)_{T,X} = \bar{V}_{\text{H}_2\text{O}_m}^{\text{melt}}(1 - \alpha_{\text{H}_2\text{O}_m}^{\text{melt}}T)$. Because $\bar{V}_{\text{H}_2\text{O}_m}^{\text{melt}} \approx \bar{V}_{\text{H}_2\text{O}_t}^{\text{melt}} = 2.2 \text{ J mol}^{-1} \text{ bar}^{-1}$ (Ochs and Lange, 1997) and $(1 - \alpha_{\text{H}_2\text{O}_m}^{\text{melt}}T) < 1$, $(\partial\bar{H}_{\text{H}_2\text{O}_m}^{\text{melt}}/\partial P)_T$ is a small term in any case. Therefore, at low pressures, the pressure dependence of −Δ*H*_{r1}⁰ is small.

(ii) *K*₂ and Δ*H*_{r2}⁰. Experimental speciation data show that *K*₂ increases with increasing *T* (Zhang et al., 1991; Nowak and Behrens, 1995; Romano et al., 1995; Shen and Keppler, 1995; Zhang et al., 1995, 1997) and decreases only slowly with increasing *P* at *P* < 10 kbar. Hence, Δ*H*_{r2}⁰ is positive (Eq. (6)) and Δ*V*_{r2}⁰ is small at *P* < 10 kbar. The experimental speciation data do not show any dependence of Δ*H*_{r2}⁰ on *T*, hence, the dependence is ignored. Zhang et al. (1991, 1995, 1997) investigated the equilibrium in rhyolitic glasses/melts by measuring glasses quenched from 400–600°C. From these data, the experimental speciation data at H₂O_t ≤ 2.4% can be expressed as (Zhang et al., 1997):

$$K_2 = 6.53\exp(-3110/T), \tag{9}$$

with Δ*H*_{r2}⁰ = 25.9 kJ. Two experimental investigations of the speciation equilibrium by measuring infrared band intensities in situ at high temperature and assuming that extinction coefficients are independent of temperature (Nowak and Behrens, 1995; Shen and Keppler, 1995) reported *K*₂ expressions and Δ*H*_{r2}⁰ values different from those above. However, if one assumes that the infrared band intensity

changes at ≤ 300°C in the work of Nowak and Behrens (1995) represent mainly the dependence of molar absorptivities on temperature, and calculates molar absorptivities at higher *T* by extrapolation (Fig. 2a), the in situ data for the haplogranitic melt (Nowak and Behrens, 1995) and the quench data for rhyolitic glasses (Zhang et al., 1991, 1995, 1997) are in agreement (Fig. 1b). This interpretation is supported by recent work of Behrens et al. (1998) and Zhang and Behrens (1998) who found that extinction coefficients depends on measurement temperature and that infrared band intensity changes at ≤ 300°C

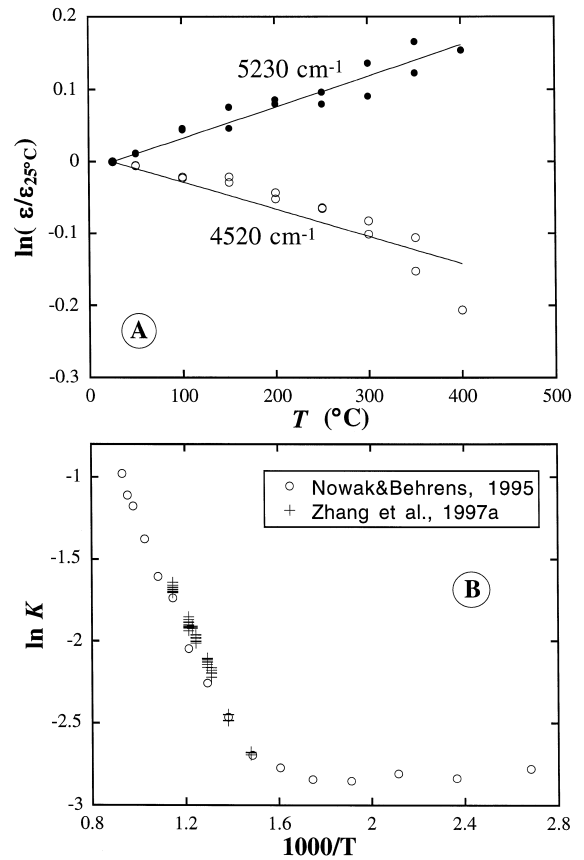


Fig. 1. Reinterpretation of the in situ speciation data (Nowak and Behrens, 1995) and comparison with the quench speciation data of Zhang et al. (1997). (a) Molar absorptivity (obtained by assuming that species concentrations do not change in the glass state) divided by that at 25°C vs. *T* for the 5230 cm⁻¹ and 4520 cm⁻¹ bands. (b) ln *K* (*K* means *K*₂) vs. 1/*T* where species contents from Nowak and Behrens (1995) are recalculated using extinction coefficients in (a). See the work of Zhang (1998) for details.

represent mainly the dependence of molar absorptivities on temperature. Hence, the discussion below uses the speciation model of Eq. (9). The accuracy of Eq. (9) to $H_2O_t > 2.4\%$ is not known. Nevertheless, using Eq. (9) to approximate speciation at high H_2O_t is better than assuming all dissolved water dissociates into OH (as implicitly assumed in the work of Sahagian and Proussevitch (1996)), or completely ignoring speciation.

For hyrous albite glasses and melts, speciation data are limited and reported data show large discrepancies (Romano et al., 1995; Zhang et al., 1995). Hence, these data will not be used.

2.2. The solubility of the H_2O component in a silicate melt

The solubility of the H_2O component in a melt is related to the species concentrations as:

$$X_{H_2O_t}^{\text{melt}} = X_{H_2O_m}^{\text{melt}} + X_{2OH-O}^{\text{melt}} = X_{H_2O_m}^{\text{melt}} + 0.5X_{OH}^{\text{melt}} \quad (10)$$

where X is the molar fraction on a single oxygen basis (Stolper, 1982), and $X_{2OH-O}^{\text{melt}} = 0.5X_{OH}^{\text{melt}}$. Using the equilibrium constants defined above, the solubility of H_2O component can be written as:

$$X_{H_2O_t}^{\text{melt}} = K_1 f + 0.5(K_2 K_1 f X_O^{\text{melt}})^{1/2} \quad (11)$$

where f is the fugacity of H_2O . At low f (below 30 bars), $X_O^{\text{melt}} \approx 1$ and $X_{H_2O_m}^{\text{melt}} \ll X_{H_2O_t}^{\text{melt}}$, leading to

$$X_{H_2O_t}^{\text{melt}} \approx 0.5(K_1 K_2 P)^{1/2}. \quad (12)$$

The more general expression of the solubility is obtained by eliminating X_O^{melt} in Eq. (11):

$$X_{H_2O_t}^{\text{melt}} = K_1 f + 0.25 \times \left[\sqrt{(K_1 K_2 f)^2 + 4K_1 K_2 f(1 - K_1 f)} - K_1 K_2 f \right]. \quad (13)$$

2.3. The exsolution enthalpy of the H_2O component

The enthalpy of the H_2O_t component in the melt is:

$$\begin{aligned} \bar{H}_{H_2O_t}^{\text{melt}}(T, P, X) &= \frac{X_{H_2O_m}^{\text{melt}}}{X_{H_2O_t}^{\text{melt}}} \bar{H}_{H_2O_m}^{\text{melt}}(T, P, X) \\ &+ \frac{X_{2OH-O}^{\text{melt}}}{X_{H_2O_t}^{\text{melt}}} \bar{H}_{2OH-O}^{\text{melt}}(T, P, X). \end{aligned} \quad (14)$$

Ignoring the variation of \bar{H} of each species with X by assuming roughly ideal mixing (at least up to 2.4% H_2O_t , Zhang et al., 1997), and combining with Eqs. (4) and (10), the above equation can be rearranged as:

$$\begin{aligned} \bar{H}_{H_2O_t}^{\text{melt},0}(T, P) &= \bar{H}_{H_2O_m}^{\text{melt},0}(T, P) \\ &+ \left(1 - \frac{X_{H_2O_m}^{\text{melt}}}{X_{H_2O_t}^{\text{melt}}} \right) \Delta H_{r2}^0(T, P). \end{aligned} \quad (15)$$

Therefore, the exsolution enthalpy can be written as:

$$\begin{aligned} \Delta \bar{H}_{\text{ex}, H_2O_t}(T, P) &= \bar{H}_{H_2O}^{\text{vapor}}(T, P) - \bar{H}_{H_2O_t}^{\text{melt},0}(T, P) \\ &= \bar{H}_{H_2O}^{\text{vapor}}(T, P) - \bar{H}_{H_2O}^{\text{vapor},0}(T) \\ &\quad + \bar{H}_{H_2O}^{\text{vapor},0}(T) - \bar{H}_{H_2O_t}^{\text{melt},0}(T, P) \\ &= \left[\bar{H}_{H_2O}^{\text{vapor}}(T, P) - \bar{H}_{H_2O}^{\text{vapor},0}(T) \right] \\ &\quad - \Delta H_{r1}^0(T, P) - \left(1 - \frac{X_{H_2O_m}^{\text{melt}}}{X_{H_2O_t}^{\text{melt}}} \right) \\ &\quad \times \Delta H_{r2}^0(T, P) \end{aligned} \quad (16)$$

where $\Delta H_{r1}^0(T, P)$ is negative and $\Delta H_{r2}^0(T, P)$ is positive. It is necessary to include the term $[\bar{H}_{H_2O}^{\text{vapor}}(T, P) - \bar{H}_{H_2O}^{\text{vapor},0}(T)]$ because the standard state of H_2O in vapor is at T and 1 bar. The term $[\bar{H}_{H_2O}^{\text{vapor}}(T, P) - \bar{H}_{H_2O}^{\text{vapor},0}(T)]$ can be found from steam tables (Haar et al., 1984) and changes roughly by $-7.6 \text{ J mol}^{-1} \text{ bar}^{-1}$ at $P \leq 600$ bar. The last term in Eq. (16) can be evaluated from speciation data with $\Delta H_{r2}^0 = 25.9 \text{ kJ}$. Hence, as long as ΔH_{r1}^0 is known as a function of T and P , the exsolution enthalpy can be calculated.

At low pressures (≤ 10 bars), Eq. (16) can be simplified to reveal how the exsolution enthalpy depends on P . From Eqs. (5), (6) and (12), $X_{\text{H}_2\text{O}_m}^{\text{melt}}/X_{\text{H}_2\text{O}_i}^{\text{melt}} \approx 4X_{\text{H}_2\text{O}_i}^{\text{melt}}/K_2 \approx 2(K_1P/K_2)^{1/2}$, leading to

$$\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i} \approx \bar{H}_{\text{H}_2\text{O}}^{\text{vapor}}(T, P) - \bar{H}_{\text{H}_2\text{O}}^{\text{vapor},0}(T) - \Delta H_{\text{r1}}^0 - \Delta H_{\text{r2}}^0 + 4(\Delta H_{\text{r2}}^0)X_{\text{H}_2\text{O}_i}^{\text{melt}}/K_2. \quad (17)$$

The last term in Eq. (17) can also be expressed as $4(\Delta H_{\text{r2}}^0)X_{\text{H}_2\text{O}_i}^{\text{melt}}|_{P=1}\sqrt{P}/K_2$ where P is in bar and is owing to the speciation effect. In a small pressure range (0–10 bars), the variation of ΔH_{r1}^0 with P is expected to be small, and $[\bar{H}_{\text{H}_2\text{O}}^{\text{vapor}}(T, P) - \bar{H}_{\text{H}_2\text{O}}^{\text{vapor},0}(T)]$ is also small. Hence, the dependence of the exsolution enthalpy on pressure is mostly reflected in the last term in Eq. (17) with $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$ being roughly proportional to $P^{1/2}$. Therefore, the pressure dependence of $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$ at low pressures is well-characterizable, and almost independent of the values of ΔH_{r1}^0 and $[\bar{H}_{\text{H}_2\text{O}}^{\text{vapor}}(T, P) - \bar{H}_{\text{H}_2\text{O}}^{\text{vapor},0}(T)]$.

2.4. The relation between constant-pressure solubility and exsolution enthalpy

Experimental solubility data at constant pressure and variable temperatures can be used to constrain $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$. At 1 bar, from Eq. (12), $X_{\text{H}_2\text{O}_i}^{\text{melt}} \approx (0.25 K_1 K_2 P)^{1/2}$, leading to $\ln X_{\text{H}_2\text{O}_i}^{\text{melt}} = 0.5 \ln(0.25 P) + 0.5 \ln(K_1 K_2) = 0.5 \ln A - 0.5(\Delta H_{\text{r1}}^0 + \Delta H_{\text{r2}}^0)/(RT) \approx 0.5 \ln A + 0.5 \Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}/(RT)$, where A (including $0.25P$ and $K_{1\infty}$ and $K_{2\infty}$) is independent of temperature. Hence, using the standard thermodynamic approach, the slope in $\ln X_{\text{H}_2\text{O}_i}^{\text{melt}}$ vs. $1/T$ diagram at a given low P (close to 1 bar) gives $0.5 \Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}/R$. That is, at 1 bar, $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$ can be directly obtained from constant-pressure solubility data at variable T .

At high pressures, however, no such simple relation exists because of the complex expression of $X_{\text{H}_2\text{O}_i}^{\text{melt}}$ in Eq. (13). Given a speciation model (that is, given K_2 as a function of T and P) and assuming ideal mixing, $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$ can be inferred using the following procedure.

(i) From T and $P_{\text{H}_2\text{O}}, f_{\text{H}_2\text{O}}$ can be calculated from the equation of state of H_2O (Pitzer and Sterner, 1994).

(ii) From measured H_2O_i at a given T , $X_{\text{H}_2\text{O}_m}$ can be solved from H_2O_i and K_2 value (Eq. (9)) by combining $K_2 = [\text{OH}]^2/([\text{H}_2\text{O}_m][\text{O}])$, $[\text{H}_2\text{O}_m] +$

$0.5[\text{OH}] = [\text{H}_2\text{O}_i] = X$, and $[\text{H}_2\text{O}_m] + [\text{OH}] + [\text{O}] = 1$, leading to

$$X_{\text{H}_2\text{O}_m} = \frac{8X^2}{8X + K_2(1-2X) + \sqrt{\{K_2(1-2X)\}^2 + 16K_2X(1-X)}}. \quad (18)$$

(iii) K_1 ($= X_{\text{H}_2\text{O}_m}/f_{\text{H}_2\text{O}}$, assuming ideal mixing) can then be calculated at each T .

(iv) By plotting $\ln K_1$ vs. $1/T$ at constant P , ΔH_{r1}^0 at P can be obtained from the slope (see Eq. (5)). This ΔH_{r1}^0 depends on the assumed speciation model and hence, on ΔH_{r2}^0 .

(v) $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$ at P as a function of T can then be obtained using Eq. (16). This $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$ turns out to be roughly independent of the assumed speciation model and hence, on ΔH_{r2}^0 .

The above discussion shows that obtaining $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_i}$ using high-pressure solubility data is complicated and somewhat model-dependent, whereas low-pressure solubility data are especially useful in directly constraining H_2O exsolution enthalpy from a melt. Because low-pressure (such as 1, 10 or 100 bars) solubility data as a function of temperature are not available, and because obtaining ΔH_{r1}^0 at high P may introduce uncertainties, the absolute values of ΔH_{r1}^0 from high-pressure solubility data are not used in the following discussion. Only the relative variations of the evaporation enthalpy with pressure will be considered.

2.5. Other thermodynamic properties of a multi-species component

Other thermodynamic properties can be treated in a fashion similar to that of \bar{H} . For example, the chemical potential (μ) and partial molar volume (\bar{V}) of the H_2O component at (T, P, X) can be written as:

$$\mu_{\text{H}_2\text{O}}^{\text{melt}} \equiv \mu_{\text{H}_2\text{O}_i}^{\text{melt}} = \frac{X_{\text{H}_2\text{O}_m}^{\text{melt}}}{X_{\text{H}_2\text{O}_i}^{\text{melt}}} \mu_{\text{H}_2\text{O}_m}^{\text{melt}} + \frac{X_{2\text{OH}-\text{O}}^{\text{melt}}}{X_{\text{H}_2\text{O}_i}^{\text{melt}}} \mu_{2\text{OH}-\text{O}}^{\text{melt}}, \quad (19)$$

$$\bar{V}_{\text{H}_2\text{O}}^{\text{melt}} \equiv \bar{V}_{\text{H}_2\text{O}_i}^{\text{melt}} = \frac{X_{\text{H}_2\text{O}_m}^{\text{melt}}}{X_{\text{H}_2\text{O}_i}^{\text{melt}}} \bar{V}_{\text{H}_2\text{O}_m}^{\text{melt}} + \frac{X_{2\text{OH}-\text{O}}^{\text{melt}}}{X_{\text{H}_2\text{O}_i}^{\text{melt}}} \bar{V}_{2\text{OH}-\text{O}}^{\text{melt}}. \quad (20)$$

At equilibrium, ΔG for Reaction (2) is zero, meaning $\mu_{2\text{OH}-\text{O}}^{\text{melt}} \equiv 2\mu_{\text{OH}}^{\text{melt}} - \mu_{\text{O}}^{\text{melt}} = \mu_{\text{H}_2\text{O}_m}^{\text{melt}}$, leading to

$$\mu_{\text{H}_2\text{O}}^{\text{melt}} \equiv \mu_{\text{H}_2\text{O}_t}^{\text{melt}} = \mu_{\text{H}_2\text{O}_m}^{\text{melt}} = \mu_{2\text{OH}-\text{O}}^{\text{melt}}. \quad (21)$$

Hence, for chemical potential, the result is very simple. If ΔV for Reaction (2) is small (at $P \leq 10$ kbar), then an equation similar to Eq. (21) holds for the partial molar volumes. At higher pressures, however, this may no longer be true (Zhang, 1994).

3. Comparison with the results of Sahagian and Proussevitch

Fig. 2 compares the shape of the exsolution enthalpy as a function of pressure for rhyolitic melts from this work with that for albitic melt obtained by Sahagian and Proussevitch (1996). Because ΔH_{r1}^0 is not accurately known, the solid curve in Fig. 2 may be moved up or down, but the shape stays the same. The $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_t}$ increase with pressure (solid curve) can be identified to be mostly caused by the speciation reaction (the last term in Eq. (16) or Eq. (17)). Compared with the dashed curve (result of Sahagian and Proussevitch, 1996), both reveals that $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_t}$ increases with P at low P . However, the rate of increase of $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_t}$ with increasing P is much

smaller in my treatment than that obtained by Sahagian and Proussevitch (1996). For example, from 1 bar to 2 bars, they obtained that $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_t}$ of hydrous albitic melt increases by 1500 J mol^{-1} , whereas my results show that $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_t}$ of hydrous rhyolitic melt increases by 170 J mol^{-1} , a factor of nine less.

Sahagian and Proussevitch (1996) tried different ways to estimate the exsolution enthalpy of water from an albitic melt but found that most methods they came up with did not work. They settled for using the estimated ΔS as a function of temperature at 2 kbar by Burnham and Davis (1974) and then estimating how this ΔS changes with P and H_2O_t , also using results in Burnham and Davis (1974). This approach of Sahagian and Proussevitch (1996) suffers from several possible problems: (i) the compositional dependence of the partial molar entropy is clearly not well-known and they had to arbitrarily adjust the numbers to make their relations (30a) and (30b) self-consistent; (ii) the partial molar entropy equation implicitly assumes that all H_2O_t is dissolved as OH (no H_2O_m), which is clearly an oversimplification. Use of Eq. (9) as the speciation model, although still not perfect especially at high H_2O_t , is expected to yield more reliable results; (iii) the very complicated expression of partial molar volume of H_2O_t in albitic melt by Burnham and Davis (1974) has been shown to be inaccurate (Ochs and Lange, 1997); and (iv) they relied heavily on the ΔS estimate as a function of temperature at 2 kbar by Burnham and Davis (1974). The need for revision of the ΔS and ΔV results of Burnham and Davis (1974) (even though some of the original experimental data are of high quality) is not surprising since progresses in the field in the last 20+ years are major. Furthermore, in my opinion, in deriving how the exsolution or evaporation enthalpy depends on pressure, it is much easier to work with the partial molar enthalpy itself (as in this work) rather than to detour from partial molar entropy (as in the work of Sahagian and Proussevitch (1996)) because the partial molar enthalpy does not depend on the molar fraction of the component in the solution for an ideal solution and does not depend on the pressure of the gas for an ideal gas, whereas the partial molar entropy for ideal (and nonideal) solutions (or gases) depends on these. That is, use of gas-solution entropy difference to obtain the enthalpy difference at

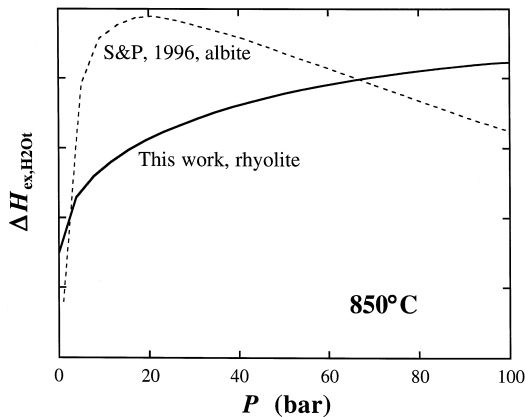


Fig. 2. $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_t}$ vs. $(P_{\text{H}_2\text{O}})^{1/2}$. The dashed curve is from the work of Sahagian and Proussevitch (1996) for albitic melt. The solid curve is from this work for $\Delta \bar{H}_{\text{ex},\text{H}_2\text{O}_t}$ for rhyolitic melts. Each division in the vertical axis represents 1 kJ. Because of an uncertain constant for the solid curve, absolute exsolution enthalpy values are not shown on the vertical axis and the solid curve can be moved up or down without changing its shape.

two different pressures depends on how well the small difference between two large numbers (the large entropy changes in the gas and solution states from one pressure to another) can be determined.

The formal approach in this work does not have such uncertainties. Although ΔH_{r1}^0 is difficult to obtain, the dependence of $\Delta \bar{H}_{\text{ex}, \text{H}_2\text{O}_t}$ on P is well-characterizable (Eqs. (16) and (17)). Therefore, for rhyolitic melts, the exsolution enthalpy does not increase with pressure as rapidly as that in the work of Sahagian and Proussevitch (1996). It is possible that the large difference between this study and that of Sahagian and Proussevitch (1996) is owing to difference between albitic and rhyolitic melts. More likely, however, the discrepancy suggests that the results of Sahagian and Proussevitch (1996) are incorrect because of the several complications discussed above. Whichever is the explanation, their results cannot be used to infer thermal effects of H_2O exsolution from a rhyolitic magma at low pressures.

In conclusion, the formal analysis presented in this work shows how to treat thermodynamic properties of a multi-species component. This study also reveals that the increase of $\Delta \bar{H}_{\text{ex}, \text{H}_2\text{O}_t}$ with P at low P is mostly owing to the effect of speciation of H_2O component and the rate of increase in a rhyolitic melt is a factor of nine less than that of Sahagian and Proussevitch (1996) for hydrous albitic melt. Hence, thermal effect during gas-driven volcanic eruptions needs to be re-evaluated. More experimental effort, especially at lower pressures, is necessary to further constrain the exsolution enthalpy of water from silicate melts.

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References

- Behrens, H., Withers, A., Zhang, Y., 1998. In situ IR spectroscopy on hydrous albitic and rhyolitic glasses and its implications for water speciation and water reactions in silicate glasses and melts. Goldschmidt Conference, Toulouse. *Min. Mag.* 62A, 139–140.
- Burnham, C.W., Davis, N.F., 1974. The role of H_2O in silicate melts: II. Thermodynamic and phase relations in the system $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O}$ to 10 kbar, 700 to 1100°C. *Am. J. Sci.* 274, 902–904.
- Haar, L., Gallagher, J.S., Kell, G.S., 1984. NBS/NRC Steam Tables: Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units. Hemisphere, Washington, DC, 320 pp.
- Nowak, M., Behrens, H., 1995. The speciation of water in haplogranitic glasses and melts determined by in situ near infrared spectroscopy. *Geochim. Cosmochim. Acta* 59, 3445–3450.
- Ochs, F.A., Lange, R.A., 1997. The partial molar volume, thermal expansivity, and compressibility of H_2O in silicate melts. *Contrib. Mineral. Petrol.* 129, 155–165.
- Pitzer, K.S., Sterner, S.M., 1994. Equation of state valid continuously from zero to extreme pressures for H_2O and CO_2 . *J. Chem. Phys.* 101, 3111–3116.
- Romano et al., 1995.
- Sahagian, D.L., Proussevitch, A.A., 1996. Thermal effects of magma degassing. *J. Volcanol. Geotherm. Res.* 74, 19–38.
- Shen, A., Keppler, H., 1995. Infrared spectroscopy of hydrous silicate melts to 1000°C and 10 kbar: direct observation of H_2O speciation in a diamond-anvil cell. *Am. Mineral.* 80, 1335–1338.
- Stolper, E.M., 1982. Water in silicate glasses: an infrared spectroscopic study. *Contrib. Mineral. Petrol.* 81, 1–17.
- Zhang, Y., 1994. Temperature and pressure dependence of the speciation of water in rhyolitic glasses. *EOS* 75, 54.
- Zhang, Y., 1998. H_2O in rhyolitic glasses and melts: measurement, speciation, solubility, and diffusion. *Rev. Geophys.*, submitted.
- Zhang, Y., Behrens, H., 1998. Resolving the controversy between quenched and in situ H_2O speciation in silicate melts and glasses. *EOS* 79, W123–W124.
- Zhang, Y., Stolper, E.M., Wasserburg, G.J., 1991. Diffusion of water in rhyolitic glasses. *Geochim. Cosmochim. Acta* 55, 441–456.
- Zhang, Y., Stolper, E.M., Ihinger, P.D., 1995. Kinetics of reaction $\text{H}_2\text{O} + \text{O} = 2\text{OH}$ in rhyolitic glasses: preliminary results. *Am. Mineral.* 80, 593–612.
- Zhang, Y., Belcher, R., Ihinger, P.D., Wang, L., Xu, Z., Newman, S., 1997. New calibration of infrared measurement of water in rhyolitic glasses. *Geochim. Cosmochim. Acta* 61, 3089–3100.