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Solubility Behavior of Quartz and Corundum in Supercritical
Water - A Quantitative Thermodynamic Interpretation

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ABSTRACT

Dissolution reaction equilibria for α -quartz (SiO_2) and corundum ($\alpha\text{-Al}_2\text{O}_3$) in pure, supercritical water are quantified using a density-dependent thermodynamic model. The database of existing solubility literature for α -quartz (0.2-10 kb, 200-575°C) is shown to be consistent with the presence of two hydrolyzed Si(IV) ion forms: $\text{Si(OH)}_4(\text{aq})$ and $\text{Si}_2\text{O(OH)}_6(\text{aq})$; the corundum database (1-20 kb, 400-700°C) is consistent with $\text{Al(OH)}_3(\text{aq})$ and Al(OH)_4^- . A third Si(IV) ion hydroxocomplex, $\text{Si}_2\text{O}_2(\text{OH})_5^-$, is indicated at lower pressures (0.03-0.10 kb). The characteristic sigmoidal nature of the solubility isobars is explained by dimerization of $\text{Si(OH)}_4(\text{aq})$ (at high densities) or the formation of anionic hydrolysis products, $\text{Si}_2\text{O}_2(\text{OH})_5^-$ and Al(OH)_4^- , in the low density region ($\rho < 0.01 \text{ gm/cc}$). By means of the evaluated equilibria, thermochemical properties of $\text{Si}_2\text{O(OH)}_6(\text{aq})$ and $\text{Si}_2\text{O}_2(\text{OH})_5^-$ are made available for the first time.

KEY WORDS: Silicon(IV) oxide, quartz, aluminum(III) oxide, corundum, aqueous solutions, thermodynamics, equilibrium constant, corrosion, supercritical water, hydrothermal solutions, pressurized water.

SOLUBILITY BEHAVIOR OF QUARTZ AND CORUNDUM IN SUPERCRITICAL WATER - A QUANTITATIVE THERMODYNAMIC INTERPRETATION

INTRODUCTION

Fundamental knowledge of metal oxide-water binary systems is necessary for a quantitative understanding of many hydro- and geothermal processes. For example, the solubility behavior of many common metal oxides is predictable in dilute, subcritical, aqueous solutions as a function of temperature and pH through suitable application of thermodynamic properties of mononuclear metal ion hydroxocomplexes, Ziemniak (1992). Although models are available to estimate thermodynamic properties for metal ion hydroxocomplexes in supercritical solutions, there exists a certain reluctance to apply these concepts to predict metal oxide solubility behavior in supercritical water. Such reluctance is due in part to the characteristic sigmoidal shape exhibited by the solubility isobars of many metal oxides. The usual explanation given for the second upturn in the isobaric solubility curves is formation of new metal ion (hydroxo)complexes that are present in undetectable concentrations in subcritical solutions.

Recently, a pressure-dependent thermodynamic model was developed and applied to interpret CuO solubility behavior in supercritical water, Ziemniak (1992). In this case, the second upturn in the Cu(II) ion solubility isobars correlated well with the formation of the $\text{Cu}(\text{OH})_3^-$ hydroxocomplex, rather than the formation of a polynuclear Cu(II) ion complex.

This study demonstrates a broader applicability of the pressure-dependent thermodynamic model by providing a new interpretation of the existing solubility databases for Si(IV) and Al(III) oxides in pure, supercritical water. This oxide pair was selected on the basis of their neighboring locations in the Periodic Table. Note that the Si^{4+} and Al^{3+} ions possess identical electron configurations which are similar to atomic neon; both have lost their 3s and 3p electrons.

THE PRESSURE-DEPENDENT MODEL

The equilibrium for any metal oxide dissolution reaction in water is quantified via

$$\Delta G(T, P) = A - BT - CT \ln T - DRT \ln \rho \quad (1)$$

where ρ is the water density (in gm/cc) and A, B, C and D are constants. All water densities can be evaluated at temperature and pressure via application of a computer code given in the NBS/NRC Steam Tables, Haar et al. (1984). An additional degree of modeling freedom, suggested by Marshall (1972), allows for a weak temperature dependency of D, although D is expected to be independent of pressure.

QUARTZ (SiO_2) SOLUBILITY DATABASE

The solubility behavior of silicon(IV) oxide (i.e., quartz and its polymorphs cristobalite and amorphous silica) has been studied extensively in pure water at temperatures up to 900°C

and at pressures up to 10 kb, cf., the data summary provided by Fournier and Potter (1982).

An empirically-derived correlation of the form

$$\log m = a + b \log V + c(\log V)^2 \quad (2)$$

where m is the molal concentration of soluble silicon, V is the specific volume of pure water, and a , b , and c are polynomial functions of temperature, has been found to approximate the solubility of α -quartz in water quite well for water densities >0.01 gm/cc, Fournier and Potter (1982). Note that, if Eq. (2) represents the solubility behavior of quartz in equilibrium with a single type of neutral Si(IV) ion hydroxocomplex, then $\log K \equiv -\Delta G/2.303RT = \log m$, and Eq. (2) may be recast as

$$\Delta G(T, P) = a' + b' RT \ln p [1 - c' \ln p] \quad (2a)$$

where a' , b' and c' are functions of temperature only.

While general agreement exists that the neutral Si(IV) ion hydroxocomplex, $\text{Si}(\text{OH})_4(\text{aq})$, is the predominant soluble species present in pure, subcritical water, only qualitative explanations have been offered to describe the additional Si(IV) ion speciation that occurs in supercritical water. Due to the relatively high saturation solubility levels, additional SiO_2 dissolution reactions have been proposed based on the concepts of polymerization and solvation:

where x is the degree of polymerization and n is the degree of solvation. For example, when

the logarithms of the Si(IV) solubility isotherms are constructed and plotted versus logarithms of water density, two approximately linear regions are observed: I ($\rho > 0.3$ gm/cc) and II ($\rho < 0.2$ gm/cc). Regions II and I are associated with the preferred stability of the respective $\text{Si(OH)}_4(\text{aq})$ species and its dimer, $\text{Si}_2\text{O(OH)}_6(\text{aq})$. This prescription is necessary to ensure that $\text{Si(OH)}_4(\text{aq})$ transitions as the dominant species in subcritical solutions. The applicable SiO_2 dissolution reactions are

A least-squares analysis of the SiO_2 -pure water solubility database for pressures as low as 0.15 kb (i.e., $\rho > 0.05$ gm/cc) was performed to quantify the Eqs. (4, 5) equilibria using Eq. (1). Table I summarizes the fitted thermodynamic parameters. The use of temperature-dependent D parameters was found to significantly improve the fit. Typical solubility isotherms and isobars, as shown in Figs. 1 and 2, demonstrate excellent agreement with the experimental data ($\sigma = \pm 5\%$) as typified by the Fournier-Potter empirical correlation. Note that our analysis has been restricted to temperatures $< 575^\circ\text{C}$ to avoid a confounding thermodynamic effect due to the α - β quartz solid phase transition. Quartz solubilities calculated via the Table I parameters deviated by less than 9% from Eq. (2) for the stated ranges of temperature and pressure. Application to lower density solutions led to Si(IV) solubility underpredictions which progressively worsened as densities decreased.

Walther and Helgeson (1977) previously fitted the quartz solubility database in pure water

to the dissolution reaction

and found that

$$\Delta G(T), \text{ J/mol} = 28970 - 20.59T \quad (7)$$

was approached in the pressure-independent region. This result deviates by as much as 2.5 kJ/mol in the temperature interval 25-300°C relative to that presently fitted for the Eq. (4) equilibrium in Table I (when density effects are neglected). Although the difference is greater than the expected accuracy of our fit ($\sigma = \pm 1$ kJ/mol), our fit accounts for speciation of the neutral Si(IV) ion hydroxocomplexes, while Eq. (6) represents the total contribution of all (uncharged) Si(IV) ion hydrolysis products. Since the $\text{Si}_2\text{O}(\text{OH})_6(\text{aq})$ species contributes about 25% of the total dissolved silicon at 300°C (for saturation pressure), see Figure 3, the difference is more apparent than real. Therefore, Table I is expected to provide accurate thermodynamic properties for $\text{Si}(\text{OH})_4(\text{aq})$ and $\text{Si}_2\text{O}(\text{OH})_6(\text{aq})$.

QUARTZ SOLUBILITY BEHAVIOR IN REGION III

Previous attempts to interpret SiO_2 solubility behavior in the region of lowest density ($\rho < 0.01$ gm/cc) via Eq. (3) have invoked the presence of higher order polymers of $\text{Si}(\text{OH})_4(\text{aq})$, including the trimer or the hexacyclic species $(\text{SiO}(\text{OH})_2)_3(\text{aq})$, Heitmann (1965). Note that, at these solution densities, the Fournier-Potter correlation is no longer valid. However, when it is recognized that the ionization equilibrium for water in supercritical solutions is also represented by Eq. (1), appreciable shifts in the neutral pH of pure water are

generated at low pressures. These changes increase the likelihood of forming significant concentrations of anionic hydrolytic products in pure water at supercritical temperatures. The most likely anionic hydrolytic product can be inferred by comparison with known hydrolytic behavior of the neighboring P^{5+} ion under subcritical conditions. Such a comparison is appropriate because of the similar electron configurations of the P^{5+} , Si^{4+} and Al^{3+} ions.

A comparison of free energy changes for the first stepwise hydrolysis reaction of the two phosphate ion neutral oxohydroxocomplexes, based on tabulated thermodynamic properties, Mesmer and Baes (1974) and Wagman et al. (1982), is given in Fig. 4. It is seen that hydrolysis of the pyrophosphate form (i.e., the dimer) occurs at lower pH values than its monomeric analog. Therefore, the most likely quartz dissolution reaction in this region is

Inclusion of this reaction in the analysis requires that the actual hydronium ion concentration be determined via an ion electroneutrality balance. It is found that

$$[H^+] = \sqrt{K_w + K_8} \quad (9)$$

where K_w is the ionization constant for water and K_8 is the equilibrium constant for Eq. (8), i.e., $[Si_2O_2(OH)_5^-][H^+]$. Presently, a correlation for K_w is available for use in the supercritical region, Marshall and Franck (1981). Therefore, a second least-squares fit was obtained by: (a) including Heitmann's (1965) quartz solubility data for pressures as low as 31 bars, (b) accounting for the presence of the $Si_2O_2(OH)_5^-$ species in the manner described above, and (c)

constraining Eqs. (4, 5) to their Table I values. It is noted that the present calculations extend the density range of validity from 0.05 down to 0.008 gm/cc. Included in Table I are the fitted parameters for Eq (8).

Subtraction of the free energy changes for Eq. (5) from Eq. (8) yields ΔG values for hydrolysis of the dimer

The above equilibrium (for $P = P_{\text{sat}}$) is compared to that expected for hydrolysis of the monomer

based on the summary of Fleming and Crerar (1982). As shown in Fig. 4, hydrolysis of the dimer is favored over that of the monomer, in agreement with the phosphate ion analogy presented earlier.

Because a caveat has been placed on applicability of the Marshall-Franck equation at $\rho < 0.4$ gm/cc, Lindsay (1989), our fit should be regarded as a "best effort" approximation. If one is willing to accept the validity of the Marshall-Franck equation at very low densities, then the available quartz solubility database (for pressures < 31 bars), Heitmann (1965), suggests that additional, higher order anionic hydrolytic species may need to be included. Their expected order of appearance at ever-decreasing densities is: $\text{SiO}(\text{OH})_3^-$, $\text{Si}_2\text{O}_3(\text{OH})_4^-$ and $\text{SiO}_2(\text{OH})_2^-$. It is noted that additional analyses, beyond the scope of the

present paper, are now possible using the quartz solubility database in basic fluids, cf. Laudise and Ballman (1961), to determine thermochemical properties for the anionic complexes at high densities where the validity of the Marshall-Franck equation is not in question.

CORUNDUM (α - Al_2O_3) SOLUBILITY DATABASE

Although an extensive aluminum(III) oxide solubility database exists, cf. review by Pokrovskii and Helgeson (1992), most of the database relates to hydrous oxide forms that are stable in subcritical water, i.e., gibbsite ($\text{Al}(\text{OH})_3$) and boehmite ($\text{AlO}(\text{OH})$). Anhydrous aluminum(III) oxide is stable only at supercritical conditions, and a recent review of this portion of the database by Ragnarsdottir and Walther (1985) revealed considerable scatter. It was reported that a consistent set of data is comprised of the corundum solubility measurements reported by Morey (1957), Becker et al. (1983), and Ragnarsdottir and Walther (1985).

It is generally accepted that the preferred corundum dissolution reaction in pure, supercritical water is

The additional Al(III) ion speciation that occurs at higher pressures (and which may contribute to the second upturn in the solubility isobars) has not yet been established.

Although Anderson et al. (1985) rule out the possibility of a charged Al(III) complex, Baes and Mesmer (1976) indicate that the equilibrium for the hydrolytic reaction

occurs in room temperature solutions under neutral pH conditions. Previously, we had demonstrated the importance of the Cu(II) ion anionic hydroxocomplex, Cu(OH)_3^- , in contributing to CuO solubility behavior in pure, supercritical water. Since Al_2O_3 and CuO saturation solubilities differ by approximately a factor of 10 in this region, and Al(III) hydrolyses more readily to Al(OH)_4^- than does Cu(II) to Cu(OH)_3^- , we conclude that the second preferred corundum dissolution reaction is

Furthermore, dimerization of $\text{Al(OH)}_3(\text{aq})$ to $\text{Al}_2\text{O(OH)}_4(\text{aq})$ does not appear likely because of the extremely low saturation solubility limits for aluminum(III), i.e., the solubility of corundum is lower by a factor of 300 compared to quartz.

A least-squares analysis of the aforementioned Al_2O_3 -pure water solubility database was performed to quantify the Eqs. (12, 14) equilibria using Eq. (1). The fitted thermodynamic parameters are given in Table II. Due to the somewhat restricted temperature range of the corundum solubility database ($t > 400^\circ\text{C}$), the asymptotic behavior of the Eq. (14) equilibrium (i.e., for $\rho = 1 \text{ gm/cc}$) was constrained to a $\Delta G(T)$ dependency based on tabulated thermodynamic properties of corundum and Al(OH)_4^- ; see Table III. The resulting solubility isotherms and isobars are plotted in Figs. 5 and 6. Again, agreement between data and fit ($\sigma = \pm 20\%$) is excellent. The somewhat higher degree of data scatter is caused by lower Al solubilities, i.e., $< 0.1 \text{ mm}$. It is encouraging to note the excellent agreement between our $\Delta G(T)$ correlation for Eq. (12) compared with results of Bourcier et al. (1993), who

experimentally determined thermodynamic properties for $\text{Al}(\text{OH})_3(\text{aq})$. Their results suggest that the equilibrium for Eq. (12) should extrapolate to

$$\Delta G(T), \text{ J/mol} = 34220 + 18.52T \quad (15)$$

over the temperature interval 150-250°C. The above parameters are within the 1σ limits of the A and B parameters fitted for Eq. (12) in Table II.

CONCLUSIONS

The solubility behavior exhibited by oxides of two neighboring Period 3 elements in pure, supercritical water is due mainly to the presence of the metal ion neutral hydroxocomplex. The high solubility levels of quartz led to significant dimerization of the neutral hydroxocomplex to $\text{Si}_2\text{O}(\text{OH})_6(\text{aq})$ at high pressures, and its hydrolysis to $\text{Si}_2\text{O}_2(\text{OH})_5$ at low pressures. On the other hand, the lower solubility levels of corundum did not allow dimerization at high pressures; but low pressures allowed significant hydrolysis of the neutral hydroxocomplex to $\text{Al}(\text{OH})_4$. The thermodynamic equilibria for the five applicable metal oxide dissolution reactions, Eqs. (4, 5, 8, 12 and 14), were readily quantified via least-squares fits using a pressure-dependent thermodynamic model together with the existing quartz and corundum solubility databases in supercritical water. The existence of these anionic (oxo) hydroxocomplexes, together with the new thermodynamic model, successfully explained the sigmoidal nature of the isobaric solubility curves when $\rho < 0.05 \text{ gm/cc}$.

The solubility behavior of three metal oxides - CuO , $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-SiO}_2$ - has now been

described by the pressure-dependent thermodynamic model. Although additional discussion concerning the validity of the Marshall-Franck equation to describe the ionization of water in the low density supercritical region is needed, inclusion of solubility measurements in basic supercritical fluids is suggested to allow thermochemical properties for these anionic complexes to be determined at (high) densities where the ionization of water is not in question.

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Table I
Fitted Solubility Behavior of Quartz in Pure, Supercritical
Water via $\Delta G(T, P) = A - BT - DRT \ln p$

<u>Dissolution Reaction</u>	<u>A(kJ/mol)</u>	<u>B(J/mol-K)</u>	<u>D</u>
($p > 0.05$ gm/cc)*			
Eq. (4)	24.79 $\pm$ 1.15	8.79 $\pm$ 2.93	-0.024 + 1123/T
Eq. (5)	42.74 $\pm$ 2.53	30.88 $\pm$ 2.89	-1.177 + 3115/T
(0.008 < p , gm/cc < 0.05)			
Eq. (8)	76.08 $\pm$ 5.35	-52.97 $\pm$ 11.72	0.675 $\pm$ 0.196

*Quartz solubility database represented by Kennedy (1950), Morey et al. (1962), Weill and Fyfe (1964), Anderson and Burnham (1965), Heitmann (1965), and Hemley et al. (1980).

Table II

Fitted Solubility Behavior of Corundum in Pure Supercritical
Water via $\Delta G(T, P) = A - BT - CT \ln T - DRT \ln p$ ($p > 0.3$ gm/cc)*

<u>Dissolution Reaction</u>	A <u>kJ/mol</u>	B <u>J/mol-K</u>	C <u>J/mol-K</u>	D <u></u>
Eq. (12)	31.63 $\pm$ 3.26	-21.99 $\pm$ 3.70	-	4.03 $\pm$ 0.25
Eq. (14)	90.42**	790.86**	-131.38**	1.51 $\pm$ 0.31

* Range of database: 400-700°C, 1-20 kb. ** Values constrained per Table III.

Table III

Thermodynamic Properties of Aluminum(III) Oxide
and its Anionic Hydroxocomplex at Room Temperature*

<u>Species</u>	<u>C_p[°] J/mol-K</u>	<u>S[°] J/mol-K</u>	<u>ΔH_f[°] kJ/mol</u>	<u>ΔG_f[°] kJ/mol</u>	<u>Ref.</u>
Al ₂ O ₃ (s)	79.04	50.92	-1675.7	-1582.3	Wagman et al.(1982)
H ₂ O(l)	75.35	69.95	-285.83	-237.14	Wagman et al.(1982)
Al(OH) ₄ ⁻	96.5	111.3	-1500.84	-1305.6	Hovey et al.(1988)

* Conventional properties of H⁺(aq) taken to be zero.

Fig. 1 Solubility isotherms for quartz in supercritical water at 400° (a) and 500°C (b). Solid curves based on fit of Eqs. (4,5); Fournier-Potter correlation shown as dashed line.

Fig. 2 Isobaric solubility curves for quartz in water at 0.2, 0.3, 0.5, 1 and 2 kb. Data taken from Kennedy (1950) (◆) and Heitmann (1965) (○). Solid curves based on fit of Eqs. (4, 5). Dashed line is 'isobar' for $P = P_{\text{sat}}$.

Fig. 3 Contribution of $\text{Si}_2\text{O}(\text{OH})_6(\text{aq})$ oxohydroxocomplex to quartz solubility in pure water.

Fig. 4 Comparison of free energy changes for first stepwise hydrolysis reaction of phosphate and silicate ion neutral (oxo) hydroxocomplexes. Labelled curves for Eq. (10) are for pressures of 0.05 kb (a), 0.10kb (b), 0.20 kb (c), P_{sat} (d) and at $\rho = 1 \text{ gm/cc}$ (e).

Fig. 5 Corundum solubility isotherm at 700°C. Data taken from Becker et al. (1983) (♦) and Ragnarsdottir and Walther (1985) (+). Solid curve based on fit of Eqs. (12, 14).

Fig. 6 Isobaric solubility curves for corundum in water at 0.5, 1(+), 2(●) and 3(♦) kb. Data taken from Ragnarisdottir and Walther (1985). Solid curves based on fit of Eqs. (12, 14); dashed line is "isobar" for $P = P_{\text{sat}}$.