Calculation of the effect of $KAl(OH)_4^0$ formation on the solubility of corundum at high pressures and temperatures

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Introduction

Experimental solubilities over limited ranges of temperature, pressure, and solution composition of gibbsite and corundum in KOH solutions taken from the literature were regressed to generate the standard partial molal properties and revised HKF equations of state coefficients (Tanger and Helgeson 1988; Shock *et al.*, 1989) for $KAl(OH)_4$. The values of log$K$ for KOH used in the calculations were computed from equations of state coefficients generated by regression of low-temperature activity coefficient data and values of log$K$ for KOH at high pressures and temperatures reported by Franck (1956) and Lukashev *et al.* (1975). The purpose of the present communication is to make available the computed dissociation constants for $KAl(OH)_4$ to 1000°C and 5 kbars and to report calculated solubilities of corundum as a function of KOH concentration at pressures and temperatures for which no experimental data are available.

Calculation of equilibrium constants

Values of the logarithm of the equilibrium constant for

$$KAl(OH)_4 \rightleftharpoons K^+ + Al(OH)_4^- \qquad (1)$$

at temperatures to 1000°C and pressures to 5 kbars are given in Table 1. The values shown in this table were computed with the aid of SUPCRT92 (Johnson *et al.*, 1991) by combining the standard molal thermodynamic properties and HKF equations of state coefficients for $Al(OH)_4^-$ (Pokrovskii and Helgeson 1994a) with those for K^+ taken from Tanger and Helgeson (1988).

Solubility of corundum

Logarithms of computed corundum solubilities as a function of the logarithm of the molality of KOH (m_{KOH}) at 400°C and 500°C and 1 kbar are depicted in figure 1. The solubilities shown in this figure were generated with the aid of the GIBBS computer code (Shvarov, 1976) using thermodynamic properties of corundum and aqueous species other than KOH and $KAl(OH)_4$ taken from Pokrovskii and Helgeson (1994a). The activity coefficients of charged and neutral aqueous species used in the calculations were computed from the Hückel and Setchénow equations (Helgeson *et al.*, 1981), respectively, using extended-term parameters taken from Helgeson *et al.* (1981) and Pokrovskii and Helgeson (1994a).

It can be seen in figure 1 that the logarithm of the solubility of corundum at supercritical temperatures and pressures increases in a $\sim$ 1:1 fashion with $\log m_{KOH}$. However, it is virtually independent of temperature. For example, increasing temperature from 400°C to 500°C increases the solubility by only $\sim 0.02 - 0.05$ log units. Note that $Al(OH)_4^-$ predominates over $KAl(OH)_4$ only if $\log m_{KOH} <\sim -1.5$ at 400°C and $\log m_{KOH} <\sim -2.5$ at 500°C. At 400°C, $KAl(OH)_4$ forms 7.5% and 32.1% of the total dissolved aluminum in 0.001 m and 0.01 m KOH solutions, respectively. However, at 500°C these percents increase to 31.3% and 64.6% of the total aluminum concentration, respectively. Despite the fact that the relative concentrations of $KAl(OH)_4$ and $Al(OH)_4^-$ change substantially with temperature, the solubility curves are essentially unaffected by the difference in temperature.

The solubility behavior observed in figure 1 is consistent with experimental observations by Barns *et al.* (1963), Anderson and Burnham (1967), and Pascal and Anderson (1989), who demonstrated that the solubility of corundum is virtually independent of pressure and temperature in supercritical KOH solutions. Further details of the calculations described above can be found in Pokrovskii and Helgeson (1994b).

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TABLE 1. Equilibrium constants for reaction (1)

		log K Pressure, kbar					
T°C	CSAT†	0.5	1	2	3	4	5
25	1.34	1.44	1.51	1.62	1.68	1.71	1.72
50	0.92	1.00	1.07	1.16	1.21	1.24	1.25
100	0.22	0.31	0.37	0.46	0.52	0.55	0.57
150	–0.34	–0.23	–0.16	–0.05	0.03	0.07	0.10
200	–0.83	–0.69	–0.58	–0.44	–0.34	–0.28	–0.24
250	–1.33	–1.11	–0.96	–0.76	–0.63	–0.54	–0.48
300	–1.92	–1.55	–1.31	–1.04	–0.87	–0.75	–0.66
350	–2.83	–2.08	–1.66	–1.29	–1.07	–0.91	–0.80
400		–2.54	–2.03	–1.53	–1.25	–1.05	–0.91
450			–2.44	–1.77	–1.41	–1.18	–1.01
500			–2.94	–2.02	–1.57	–1.29	–1.09
550			–3.53	–2.28	–1.74	–1.40	–1.16
600				–2.55	–1.91	–1.51	–1.24
700				–3.11	–2.26	–1.75	–1.40
800				–3.62	–2.64	–2.01	–1.60
900					–2.99	–2.28	–1.83
1000					–3.29	–2.53	–2.08

† SAT represents pressures corresponding to liquid–vapour equilibrium for the system H_2O, except at temperatures < 100°C where it refers to the reference pressure of one bar.

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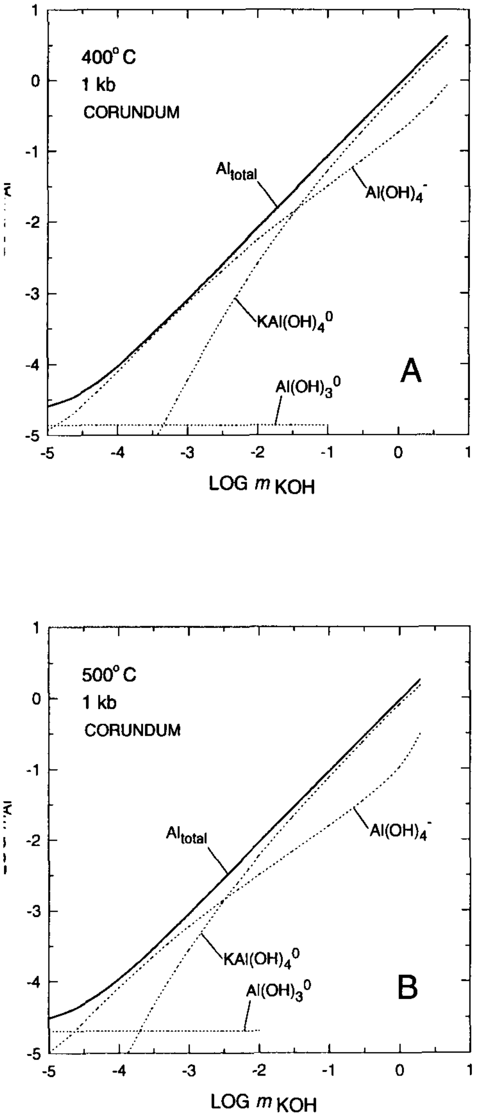

FIG. 1. Logarithm of corundum solubility in KOH solutions at a pressure of 1 kbar and various temperatures: (A) 400°C, (B) 500°C. The solid curves represent total dissolved aluminum, but the dotted curves refer to the molalities of individual species. The curves shown in above were generated from thermodynamic calculations described in the text.