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THERMODYNAMIC PROPERTIES OF AQUEOUS SPECIES AND THE SOLUBILITIES OF MINERALS AT HIGH PRESSURES AND TEMPERATURES: THE SYSTEM Al_2O_3-H_2O-NaCl

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ABSTRACT. The revised Helgeson-Kirkham-Flowers (HKF) equations of state (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock, Helgeson, and Sverjensky, 1989) were used together with the Hückel (1925) and Setchénow (1892) equations for activity coefficients of aqueous species (Helgeson, Kirkham, and Flowers, 1981) and selected potentiometric data to interpret experimental solubilities reported in the literature for gibbsite, boehmite, diaspore, and corundum. The study resulted in an internally consistent set of thermodynamic data for Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, and $Al(OH)_4^-$[1] which permits calculation of the standard partial molal properties of these species at temperatures to 1000°C and pressures to 5 kb. Standard partial molal Gibbs free energies of formation of boehmite and diaspore were retrieved from experimental solubilities of these minerals in NaOH solutions at P_{SAT}[2] by regressing solubility data reported in the literature using the Hückel extended-term parameters for aqueous NaOH, together with Setchénow coefficients and dissociation constants for $NaOH^0$ generated in the present study. The results of these calculations indicate that appreciable concentrations of $NaAl(OH)_4^0$ are present in NaOH solutions saturated with gibbsite, boehmite, and diaspore (see footnote 1). Dissociation constants for $NaAl(OH)_4^0$ were retrieved from the solubility data for temperatures ranging from 40° to 350°C at P_{SAT}. These equilibrium constants were then used to calculate the standard partial molal thermodynamic properties and HKF equations of state coefficients for the species. Where comparisons can be made, the results of the calculations yield predicted solubilities of gibbsite in concentrated NaCl + NaOH solutions that are within ± 0.05 log units

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[1] $Al(OH)_3^0$, $Al(OH)_4^-$, and $NaAl(OH)_4^0$ are used in the present communication to refer to both the hydrated and dehydrated species in accord with the convention that the standard molal thermodynamic properties of

$$HAlO_2^0 + H_2O \rightleftharpoons Al(OH)_3^0$$

and

$$AlO_2^- + 2H_2O \rightleftharpoons Al(OH)_4^-$$

are taken to be zero (Wagman and others, 1982). Hence the designations $Al(OH)_3^0$, $Al(OH)_4^-$, and $NaAl(OH)_4^0$ are not necessarily indicative of the actual extent to which these species are dehydrated in aqueous solution.

[2] P_{SAT} represents pressures corresponding to liquid-vapor equilibrium for the system H_2O, except at temperatures <100°C where it refers to the reference pressure of 1 bar.

of their experimental counterparts at temperatures as low as 6.4°C and independently those of corundum in NaOH solutions within the same uncertainty limits at temperatures to 700°C and pressures to 2.5 kb. The calculations indicate that the concentration of $NaAl(OH)_4^0$ in supercritical NaOH solutions saturated with corundum is comparable to, or even greater than, that of $Al(OH)_4^-$. In supercritical H_2O, the species $Al(OH)_3^0$ and $Al(OH)_4^-$ predominate in the presence of corundum. The thermodynamic properties of $Al(OH)_3^0$ were calculated by taking explicit account of the formation of $Al(OH)_4^-$ in these solutions. Calculated solubilities of boehmite as a function of pH generated in the present study are consistent with the bulk of the experimental data reported for alkaline solutions by Kuyunko, Malinin, and Khodakovsky (1983), Bourcier, Knauss, and Jackson (1993), and Castet and others (1993). In neutral and acid solutions, the computed solubilities are in close agreement with their experimental counterparts at 150° and 200°C. However, at higher temperatures, the calculated solubilities are systematically higher than those measured by Castet and others (1993) but agree well with the experimental data reported by Kuyunko, Malinin, and Khodakovsky (1983) and Bourcier, Knauss, and Jackson (1993). It appears from the results of the present study that the discrepancy between the sets of experimental data cannot be resolved without additional experiments to better constrain the relative stabilities of $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3^0$ at temperatures >200°C and pressures exceeding P_{SAT}. Additional experimental data are also required further to substantiate or contradict the conclusion drawn below that aluminum chloride complexing does not contribute to a substantial degree to the solubilities of aluminum-bearing minerals in concentrated alkali chloride solutions at temperatures ≤300°C and pressures ≤1 kb.

INTRODUCTION

Prediction of the aqueous solubilities of rock- and ore-forming minerals at temperatures and pressures obtaining in the Earth's crust is a prerequisite for accurate interpretation of phase relations in hydrothermal systems. The present communication and those in the series to follow represent a step in this direction based on critical evaluation of experimental solubility data for minerals reported in the literature using the revised Helgeson-Kirkham-Flowers (HKF) equations of state for the standard and excess partial molal thermodynamic properties of aqueous species and electrolytes (Helgeson, Kirkham, and Flowers, 1981; Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock, Helgeson, and Sverjensky, 1989; Oelkers and Helgeson, 1990; Shock and others, 1992). Because this approach affords accurate calculation and prediction of the thermodynamic behavior of aqueous species at high pressures and temperatures, it provides a sound basis for identifying and calculating the thermodynamic properties of aqueous complexes that contribute substantially to mineral solubilities in supercritical electrolyte solutions but may be present in undetectable concentrations at low temperatures and pressures. The purpose of the present communication is to summarize

the results of a comprehensive critical analysis of the solubilities of gibbsite, boehmite, diaspore, and corundum in the system Al_2O_3–H_2O–NaCl–NaOH and tabulating an internally-consistent set of standard partial molal thermodynamic properties and revised HKF equations of state parameters for Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$, and $NaAl(OH)_4^0$ (see footnote 1).

Thermodynamic properties of minerals derived solely from calorimetric and/or high pressure-temperature phase equilibrium data rarely yield predicted mineral solubilities consistent with experimental solubility data (Helgeson and others, 1978; Sverjensky, Hemley, and D'Angelo, 1991). Such discrepancies can be reduced by carrying out simultaneous regression of experimental solubility and phase equilibrium data reported in the literature. Regression calculations of this kind can be used to assess the accuracy of the standard partial molal thermodynamic properties of minerals derived solely from calorimetric and/or phase equilibrium data such as those reported by Helgeson and others (1978), Robie, Hemingway, and Fisher (1978), Berman (1989), and Holland and Powell (1990). They also permit calculation of the hydrothermal solubilities of aluminum hydroxides and corundum at temperatures, pressures, and solution pHs for which no experimental data are available.

REVIEW OF PREVIOUS WORK

Mineral solubilities and the thermodynamic properties of minerals and aqueous species in the system Al_2O_3–H_2O–NaCl have been studied extensively since the turn of the century. For example, a plethora of papers has been published on the solubilities of aluminum hydroxides and oxyhydroxides at temperatures and pressures corresponding to vapor-liquid equilibrium over a wide range of pH and solution composition. In addition, the solubility of corundum has been investigated experimentally at supercritical pressures and temperatures. These various solubility studies are summarized in table 1. In addition to these, many other experimental investigations were instrumental in accomplishing the thermodynamic analysis carried out in the present study. These include calorimetric and density measurements for aqueous aluminum-bearing solutions (Calvet and others, 1950, 1951; Couture and Laidler, 1956; Vydrevich and Zaitseva, 1961; Ikkatai and Okada, 1962; Sakamoto, 1962; Dibrov, Matveeva, and Mashovets, 1964; Baron, Baranova, and Matveeva, 1965; Mal'tsev and Mashovets, 1965; Mashovets and others, 1967, 1969, 1971; Babakulov and Latysheva, 1974; Puchkov and Chakhal'yan, 1971, 1976a; Barta and Hepler, 1986; Hovey and Tremaine, 1986; Hovey, ms; Hovey, Hepler, and Tremaine, 1988; Caiani and others, 1989; Chen, Xu, and Hepler, 1991; Conti, Gianni, and Matteoli, 1992; Conti and others, 1992), potentiometric titration and complexing measurements (Ley, 1899; Bjerrum, 1907; Denham, 1908; Kullgren, 1913; Heyrovský, 1920a–c; Brönsted and Volquvartz, 1928; Hartford, 1942; Lacroix, 1949; Brosset, 1952; Ito and Yui, 1953; Brosset, Biedermann, and Sillén, 1954; Faucherre, 1954; Schofield and Taylor,

TABLE 1

Summary of experimental studies of the equilibrium solubilities of minerals in the system Al_2O_3–H_2O [a]

Mineral	Temperature, Pressure	Initial Solution	Reference
gibbsite?	25°C, 1 bar	H_2O + NaOH	Wood (1908)
gibbsite?	18°C, 1 bar	H_2O + NaOH	Slade (1911)
gibbsite	20°, 30°C, 1 bar	H_2O + NH_4OH, H_2O + NH_4NO_3 + NH_4OH, H_2O + KNO_3 + NH_4OH	Archibald and Habasian (1917)
gibbsite?	25°C, 1 bar	H_2O + $AlCl_3$	Heyrovský (1920a)
gibbsite?	15°C, 1 bar	H_2O + $KAl(SO_4)_2$ + NaOH	Kolthoff (1920)
gibbsite	30°C, 1 bar	H_2O + NaOH	Goudriaan (1922)
gibbsite?	18°C, 1 bar	H_2O	Remy and Kuhlmann (1924)
gibbsite?	18°C, 1 bar	H_2O	Remy (1925)
gibbsite	18°C, 1 bar	H_2O + $AlCl_3$ + NaOH	Fricke (1929)
gibbsite	30°, 60°C, 1 bar	H_2O + NaOH, H_2O + KOH	Fricke and Jucaitis (1930)
gibbsite	25°C, 1 bar	H_2O + NaOH	Kittle (ms, 1931)
pseudoboehmite, bayerite	18°C, 1 bar	H_2O + $AlCl_3$ + NaOH	Fricke and Meyering (1933)
gibbsite	40°–100°C, 1 bar	H_2O + NaOH	Tosterud (1934) [b]
gibbsite	95°C, 1 bar	H_2O + NaOH	Tsirlina (1936)
gibbsite	74°–100°C, 1 bar	H_2O + NaOH	Baurmeister (1938) [b]
boehmite	150°, 200°C, P_{SAT}	H_2O + NaOH	Magarshak (1938)
gibbsite	25°C, 1 bar	H_2O + NaOH	Sprauer and Pearce (1940)
boehmite	150°–200°C, P_{SAT}	H_2O + NaOH	Baurmeister and Fulda (1943) [b]
gibbsite	60°C, 1 bar	H_2O + NaOH + CO_2	Elmore, Mason, and Hatfield (1945)
gibbsite	18°C, 1 bar	H_2O + $AlCl_3$ + NaOH, H_2O + $Al_2(SO_4)_3$ + NaOH, H_2O + $Al(ClO_4)_3$ + NaOH	Lacroix (1949)
gibbsite	18°C, 1 bar	H_2O + $Al_2(SO_4)_3$	Akselrud and Fialkov (1950)
gibbsite	74°–100°C, 1 bar	H_2O + NaOH	Fulda and Ginsberg (1951)
boehmite	125°–200°C, P_{SAT}	H_2O + NaOH	Fulda and Ginsberg (1951)
pseudoboehmite?, bayerite?	40°C, 1 bar	H_2O + $Al(ClO_4)_3$ + $NaClO_4$ + NaOH	Brosset (1952)
gibbsite	25°–140°C, P_{SAT}	H_2O + NaOH	Kuznetsov (1952)
gibbsite	30°–100°C, 1 bar	H_2O + NaOH	Herrmann (1953)
gibbsite	30°–70°C, 1 bar	H_2O + NaOH	Sato (1954)
gibbsite	45°–90°C, 1 bar	H_2O + NaOH	Dachselt (1955)
diaspore	200°C, P_{SAT}	H_2O + NaOH	Druzhinina (1955)
gibbsite	50°C, 1 bar	H_2O + NaOH	Pearson (1955)
gibbsite, boehmite, bayerite	40°–170°C, P_{SAT}	H_2O + NaOH	Russell, Edwards, and Taylor (1955)
gibbsite?	20°, 30°C, 1 bar	H_2O + K_2SO_4, H_2O + H_2SO_4, H_2O + NaOH	Szabó, Csányi, and Kávai (1955)
gibbsite	25°C, 1 bar	H_2O + $HClO_4$, H_2O + NaOH	Thompson (ms, 1955)
gibbsite	30°–130°C, P_{SAT}	H_2O + NaOH	Volf and Kuznetsov (1955)
corundum	500°C, 1.034 kb	H_2O	Morey (1957)
bayerite?	25°C, 1 bar	H_2O + NaOH, H_2O + $HClO_4$	Gayer, Thompson, and Zajicek (1958)
gibbsite	30°C, 1 bar	H_2O + NaOH	Vrbaški, Iveković, and Pavlović (1958)
corundum	380°–420°C, 0.25–0.49 kb	H_2O, H_2O + NaOH	Yalman, Show, and Corwin (1960)
boehmite	250°–300°C, P_{SAT}	H_2O + NaOH + $NaAlO_2$	Bernshtein and Matsenok (1961)
gibbsite	25°C, 1 bar	H_2O + $AlCl_3$, H_2O + HCl, H_2O + $AlCl_3$ + HCl, H_2O + $AlCl_3$ + NaOH	Frink and Peech (1962)
gibbsite?	110°–358°C, P_{SAT}	Not specified	Martynova, Reznikov, and Volosnikova (1962)
gibbsite	40°–130°C, P_{SAT}	H_2O + NaOH	Ikkatai and Okada (1962)

TABLE 1

(continued)

Mineral	Temperature, Pressure	Initial Solution	Reference
corundum	400°–450°C, 0.51–1.52 kb	$H_2O + NaOH$	Yamaguchi, Yanagida, and Soejima (1962)
corundum	400°–600°C, 0.31–2.8 kb	$H_2O + NaOH$, $H_2O + KOH$, $H_2O + NaCl$, $H_2O + KCl$, $H_2O + HCl$, $H_2O + CsOH$, $H_2O + Na_2CO_3$, $H_2O + K_2CO_3$, $H_2O + Cs_2CO_3$, $H_2O + NH_4OH$	Barns, Laudise, and Shields (1963)
gibbsite, boehmite + bayerite, diaspore	20°C, 1 bar	$H_2O + K_2SO_4 + HCl$, $H_2O + K_2SO_4 + KOH$	Raupach (1963a)
gibbsite, gibbsite + bayerite	20°, 50°C, 1 bar	$H_2O + K_2SO_4 + HCl$	Raupach (1963b)
bayerite	20°C, 1 bar	$H_2O + NaAlO_2 + NaOH$	Chistyakova (1964)
gibbsite, gibbsite + bayerite	30°–70°C, 1 bar	$H_2O + NaAlO_2$, $H_2O + NaOH$, $H_2O + NaOH + NaAlO_2$	Lundquist and Leitch (1964)
gibbsite	60°, 95°C, 1 bar	$H_2O + NaOH$, $H_2O + NaOH + NaCl$, $H_2O + NaOH + Na_2CO_3$	Lyapunov, Khodakova, and Galkina (1964)
diaspore	250°–300°C, P_{SAT}	$H_2O + NaOH + NaAlO_2$	Bernshtein and Matsenok (1965)
corundum	328°–515°C, 0.34–1.93 kb	$H_2O + Na_2B_4O_7$	Levinson, Douglas, and Johnson (1965)
gibbsite	25°C, 1 bar	$H_2O + AlCl_3 + Ca(OH)_2$	Turner and Brydon (1965)
gibbsite	25°C, 1 bar	$H_2O + HCl$, $H_2O + NaOH$	Kittrick (1966)
corundum	700°–900°C, 2–6.75 kb	H_2O, $H_2O + NaCl$, $H_2O + KCl$, $H_2O + KOH$, $H_2O + NaOH$	Anderson and Burnham (1967)
gibbsite, bayerite, pseudoboehmite	25°C, 1 bar	$H_2O + Al(ClO_4)_3 + NaClO_4 + HClO_4 + NaOH$	Hem and Roberson (1967)
gibbsite, boehmite, diaspore, diaspore + corundum	60°–350°C, P_{SAT}	$H_2O + NaOH$	Wefers (1967) [c]
gibbsite, boehmite, diaspore	25°C, 1 bar	H_2O	Reesman and Keller (1968)
gibbsite	25°C, 1 bar	$H_2O + AlCl_3 + Ca(OH)_2$, $H_2O + Al(NO_3)_3 + Ca(OH)_2$	Turner (1968)
gibbsite	24°–90°C, 1 bar	$H_2O + NaOH$	Apps (1970) [c]
boehmite	50°–255°C, P_{SAT}	$H_2O + NaOH$	Apps (1970) [c]
diaspore	25°–260°C, P_{SAT}	$H_2O + NaOH$	Apps (1970) [c]
gibbsite	25°–60°C, 1 bar	$H_2O + NaOH$	Berecz and Szita (1970)
corundum	460°–500°C, 0.507–2.065 kb	$H_2O + NaOH$, $H_2O + Na_2CO_3$, $H_2O + NaHCO_3$	Ganeev, Menkovskii, and Rumyantsev (1970)
gibbsite?	20°C, 1 bar	$H_2O + AlCl_3 + NaOH + NaCl$	Deželić, Bilinski, and Wolf (1971)
corundum	285°C, 0.45 kb	$H_2O + HCl$	Ostapenko and Arapova (1971)
gibbsite	25°C, 1 bar	$H_2O + Al(ClO_4)_3 + NaClO_4 + NaOH$	Smith and Hem (1972)
corundum	500°–800°C, 6 kbar	H_2O	Burnham, Ryzhenko, and Schitel (1973)
corundum	350°–500°C, 0.2–1.96 kb	H_2O	Ganeev and Rumyantsev (1974)

TABLE 1

(continued)

Mineral	Temperature, Pressure	Initial Solution	Reference
gibbsite, bayerite, nordstrandite	25°C, 1 bar	$H_2O + Al(NO_3)_3 + HNO_3 + NaOH$	Hayden and Rubin (1974)
gibbsite	15°–35°C, 1 bar	$H_2O + AlCl_3 + HCl$, $H_2O + AlCl_3 + NaOH$	Singh (1974)
gibbsite	25°C, 1 bar	$H_2O + NaNO_3 + CH_3COOH + CH_3COONa$, $H_2O + NaNO_3 +$ Bistris, $H_2O + NaNO_3 +$ Tris	May, Helmke, and Jackson (1979)
gibbsite	20°–80°C, 1 bar	$H_2O + NaOH$	Packter (1979)
diaspore	250°–325°C, P_{SAT}	$H_2O + NaOH$	Chang, Pak, and Li (1979)
gibbsite	35°–90°C, 1 bar	$H_2O + NaCl + NaOH$, $H_2O + NaCl + HCl$	Hitch and others (1980)
gibbsite	25°C, 1 bar	$H_2O + HCl$	Kittrick (1980)
gibbsite	22°C, 1 bar	$H_2O + HCl$, $H_2O + AlCl_3 + HCl$, $H_2O + KNO_3 + AlCl_3 + HCl$	Bloom and Weaver (1982)
corundum	670°–700°C, 2.5–6 kb	H_2O	Becker, Cemič, and Langer (1983)
boehmite	150°–250°C, P_{SAT}	$H_2O + NaClO_4 + HClO_4$, $H_2O + NaClO_4 + NaOH$	Kuyunko, Malinin, and Khodakovsky (1983)
corundum	400°–700°C, 1–3 kb	H_2O	Ragnarsdóttir and Walther (1985)
corundum	450°–700°C, 1–2 kb	$H_2O + HCl$, $H_2O + NaCl$, $H_2O + KCl$, $H_2O + AlCl_3$	Korzhinskii (1987)
gibbsite, bayerite?	50°C, 1 bar	$H_2O + CH_3COOH + CH_3COONH_4$ (+ NaF), $H_2O + CH_3COONH_4 + NH_4OH$ (+ NaF)	Sanjuan and Michard (1987a)
gibbsite, bayerite?	80°C, 1 bar	$H_2O + CH_3COOH + CH_3COONH_4$, $H_2O + CH_3COONH_4 + NH_4OH$	Sanjuan and Michard (1987b)
bayerite	25°C, 1 bar	$H_2O + NaOH$	Verdes and Gout (1987)
gibbsite, boehmite, diaspore, corundum	25°C, 1 bar	$H_2O + HCl$, $H_2O + AlCl_3 + HCl$ (+ NaCl or KCl)	Peryea and Kittrick (1988)
diaspore	300°C, 1 kbar	$H_2O + NaCl + AlCl_3 + HCl$, $H_2O + AlCl_3 + HCl$	Red'kin and Chevychelova (1988)
corundum	600°C, 2 kb	$H_2O + HCl$	Baumgartner and Eugster (1988)
corundum	500°–700°C, 1.86–2.65 kb	$H_2O + NaOH$, $H_2O + KOH$	Pascal and Anderson (1989)
corundum	600°C, 2 kb	$H_2O + NaCl$, $H_2O + KCl$	Pascal, Puaya, and Roux (1989)
diaspore	25°–350°C, P_{SAT}	$H_2O + NaCl$, $H_2O + NaOH$, $H_2O + NaCl + NaOH$	Apps, Neil, and Jun (1989)
bayerite	21°–65°C, 1 bar	$H_2O + NaCl + NaOH$, $H_2O + NH_4Cl + NH_4OH$, $H_2O + HClO_4 + NaClO_4$	Verdes (ms, 1990) [d]; Verdes, Gout, and Castet (1992)
gibbsite	21°–70°C, 1 bar	$H_2O + NH_4Cl + NH_4OH$	Verdes (ms, 1990) [d]; Verdes, Gout, and Castet (1992)
boehmite	70°–300°C, P_{SAT}	$H_2O + HClO_4 + NaClO_4$, $H_2O + CH_3COOH + CH_3COONa$, $H_2O + NH_4Cl + NH_4OH$, $H_2O + NaCl + NaOH$, $H_2O + NaOH$	Verdes (ms, 1990) [d]; Verdes, Gout, and Castet (1992)
gibbsite	80°C, 1 bar	$H_2O + CH_3COOH + CH_3COONa$	Fein (1991)
diaspore	296°C, 1 kb	H_2O, $H_2O + HCl$	Red'kin and Chevychelova (1991)
boehmite	170°, 200°C, P_{SAT}	$H_2O + NaCl + HCl +$	Castet and others (1992)

TABLE 1

(continued)

Mineral	Temperature, Pressure	Initial Solution	Reference
		$CH_3COOH + CH_3COONa$	
boehmite	300°C, P_{SAT}	$H_2O + NaCl + NaOH$	Castet and others (1992)
diaspore	130°–300°C, P_{SAT}	$H_2O + NH_4Cl + NH_4OH$, $H_2O + NaCl + NaOH$	Verdes, Gout, and Castet (1992)
gibbsite	80°C, 1 bar	$H_2O + HClO_4$, $H_2O + NaCl + HCl$	Nagy and Lasaga (1992)
gibbsite	30°–70°C, 1 bar	$H_2O + NaCl + AlCl_3 + HCl$	Palmer and Wesolowski (1992)
gibbsite	6.4°–80°C, 1 bar	$H_2O + NaOH + NaCl$, $H_2O + KOH$	Wesolowski (1992)
boehmite	150°–250°C, P_{SAT}	$H_2O + KCl + HCl$, $H_2O + CH_3COOH + CH_3COONa$, $H_2O + B(OH)_3 + K_2B_4O_7$	Bourcier, Knauss, and Jackson (1993)
boehmite	90°–350°C, P_{SAT}	H_2O +$NaCl + HCl$, $H_2O + NH_4Cl + NH_4OH$, $H_2O + NaCl + NaOH$, $H_2O + CH_3COOH + CH_3COONa$	Castet and others (1993)
gibbsite	80°C, 1 bar	$H_2O + NaCl + HCl$	Nagy and Lasaga (1993)
gibbsite, boehmite	25°C, 1 bar	$H_2O + NaCl + AlCl_3 + HCl$	Su and Harsh (1994)
gibbsite	50°C, 1 bar	$H_2O + NaCl + HCl + CH_3COOH$, $H_2O + NaCl + HCl$ + Bistris, $H_2O + NaCl + NaOH$ + Tris	Wesolowski and Palmer (1994)

[a] The mineral names shown in this table refer to $Al(OH)_3$ (gibbsite, bayerite, and nordstrandite), AlO(OH) (boehmite and diaspore), and Al_2O_3 (corundum). Pseudoboehmite connotes synthetic cryptocrystalline boehmite (Brown, 1980). A question mark after the name indicates uncertainty with respect to which polymorph was actually synthesized or used in the experiments. Mineral names separated by a plus sign indicate that both minerals were present in the experimental charges, but those with a comma in between were studied separately. [b] Quoted by Misra (1970). [c] Quoted by Apps, Neil, and Jun (1989). [d] Quoted by Castet (ms, 1991).

1954; Kenttämaa, 1955; Kubota, ms; Matijević and others, 1961; Frink and Peech, 1963; Aveston, 1965; Sannikov, Krylov, and Vinogradov, 1967; Holmes, Cole, and Eyring, 1968; Grunwald and Fong, 1969; Nazarenko and Nevskaya, 1969; Nikolaeva and Tolpygina, 1969; Mesmer and Baes, 1971; Volokhov and others, 1971; Stefanowicz and Kiciak, 1972; MacDonald, Butler, and Owen, 1973; Hayden and Rubin, 1974; Baes and Mesmer, 1976; Öhman and Forsling, 1981; Couturier, Michard, and Sarazin, 1984; Brown and others, 1985; Sjöberg and Öhman, 1985; Konshin and Chernyshov, 1990; Palmer, Wesolowski, and Drummond, 1990; Wesolowski, Palmer, and Begun, 1990; Milić, Bugarčić, and Djurdjević, 1991; Milić, Bugarčić, and Niketić, 1991; Palmer and Wesolowski, 1993; Palmer and Bell, 1994), spectroscopic observations (Lippincott, Psellos, and Tobin, 1952; Connick and Fiat, 1963; Fratiello and others, 1967, 1968, 1992; Akitt, Greenwood, and Lester, 1969; Haraguchi and Fujiwara, 1969; Mironov and others, 1969; Pavlov and others,

1969; Moolenaar, Evans, and McKeever, 1970; Akitt and others, 1972; Eremin, Volokhov, and Mironov, 1974; Serna, White, and Hem, 1977; Akitt and Farthing, 1978, 1981a–d; Bottero and others, 1980; Akitt and Milić, 1984; Akitt and Elders, 1985; Hugi-Clearly, Helm, and Merbach, 1985; Bertsch, Layton, and Barnhisel, 1986; Bertsch, Thomas, and Barnhisel, 1986; Denney and Hsu, 1986; Bertram and others, 1990; Herdman and Salmon, 1991; Brooker and Tremaine, 1992), and studies of the mechanisms and kinetics of aqueous polymerization and the dissolution and precipitation of aluminum hydroxides in different aquatic media (Herrmann, 1953; Bye and Robinson, 1964; Hsu, 1966, 1967, 1977, 1988; Hsu and Bates, 1964; Barnhisel and Rich, 1965; Black and Chen, 1967; Hem and Roberson, 1967, 1990; Turner, 1968, 1976a,b; Glastonbury, 1968; Schoen and Roberson, 1970; Turner and Ross, 1970; Ross and Turner, 1971; Scotford and Glastonbury, 1971; Smith, 1971; Scotford, 1972; Smith and Hem, 1972; Elderfield and Hem, 1973; Nail, White, and Hem, 1975; Stol, Van Helden, and De Bruyn, 1976; Bersillon and others, 1978; Kodama and Schitzer, 1980; Hem, 1983, 1986; Tsai and Hsu, 1984, 1985; Snodgrass, Clark, and O'Melia, 1984; Van Straten and De Bruyn, 1984; Van Straten, Holtcamp, and De Bruyn, 1984; Van Straten, Schoonen, and De Bruyn, 1985; Van Straten and others, 1985; Bottero and others, 1987, 1988; Bertsch, 1987, 1989; Verdes and Gout, 1987; Davis and Hem, 1989; Hille and others, 1989a,b; Nesterov and Teslya, 1989; Buining and others, 1990; Nagy and Lasaga, 1992, 1993).

Numerous efforts have been made in recent years to calculate accurate values of the thermodynamic properties of various minerals and aqueous species in the system Al_2O_3–H_2O by combining solubility and/or phase equilibrium data with the results of potentiometric and calorimetric measurements (Deltombe and Pourbaix, 1958; Reesman, Pickett, and Keller, 1969; Parks, 1972; MacDonald and Butler, 1973; Hemingway and Robie, 1977b; Sokolova and Khodakovsky, 1977; Hemingway, Robie, and Kittrick, 1978; Khodakovsky, Katorcha, and Kuyunko, 1980; Chang, 1981a,b, 1982a,b; Arnórsson, Sigurdsson, and Svavarsson, 1982; Hemingway, 1982; Kuyunko, Malinin, and Khodakovsky, 1983; Pokrovskii and Ivanov, 1983; Couturier, Michard, and Sarazin, 1984; Reed and Spycher, 1984; Ragnarsdóttir and Walther, 1985; Apps, Neil, and Jun, 1989; Nordstrom and May, 1989; Pascal and Anderson, 1989; Nordstrom and others, 1990; Verdes, ms; Anderson and others, 1991; Castet, ms; Hemingway, Robie, and Apps, 1991; Verdes, Gout, and Castet, 1992; Castet and others, 1993; Wesolowski and Palmer, 1994; and others). The standard partial molal enthalpies and Gibbs free energies of formation and entropies of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, and $Al(OH)_4^-$ at elevated temperatures were estimated in a number of these studies directly from experimentally derived equilibrium constants, which in most cases were extrapolated using empirical equations to represent the properties as a function of temperature or, in some cases, temperature and the density of the solvent. However, few of the empirical relations used for this purpose are compatible with experimental measure-

ments of the standard partial molal heat capacities and volumes of aqueous species as a function of pressure and temperature. In contrast, the revised HKF equations of state (Tanger and Helgeson, 1988) are consistent with these experimental data, as well as with electrostatic theory and the volumetric and calorimetric consequences of short- and long-range interaction in electrolyte solutions, which facilitates accurate calculation of the standard partial molal thermodynamic properties of aqueous species at both low and high temperatures and pressures.

Hovey (ms) and Tremaine (1990) used the original HKF equations of state (Helgeson, Kirkham, and Flowers, 1981) to fit the experimental values of the standard partial molal volumes and heat capacities of the aluminum and aluminate ions reported by Hovey and Tremaine (1986), Barta and Hepler (1986), and Hovey, Hepler, and Tremaine (1988). In the process, they generated equations of state parameters they then used to estimate corresponding properties for $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3^0$ by linear interpolation of those for Al^{3+} and $Al(OH)_4^-$. This approach led to close description of the experimental solubilities of boehmite over a wide range of pH at temperatures from 150° to 250°C reported by Kuyunko, Malinin, and Khodakovsky (1983). Using the revised HKF equations of state (Tanger and Helgeson, 1988), Shock and Helgeson (1988) calculated revised standard partial molal volumes and heat capacities of the aluminum and aluminate ions from the experimental data reported by Hovey and Tremaine (1986), Barta and Hepler (1986), and Hovey, Hepler, and Tremaine (1988). Shock and Helgeson (1988) report values of the standard partial molal thermodynamic properties for the aluminate ion (expressed as AlO_2^-) which are closely consistent with the experimental solubilities of aluminum hydroxides and oxyhydroxides in alkaline solutions compiled by Apps and Neil (1989) and Apps, Neil, and Jun (1989) at temperatures to 350°C at P_{SAT}. However, those given by Shock and Helgeson (1988) for Al^{3+} are not consistent with recent calorimetric and solubility data (see below).

Despite the wealth of experimental data for the system Al_2O_3–H_2O–NaCl–NaOH that has accrued over the years, no reliable and internally consistent comprehensive set of thermodynamic data and equations of state parameters is available for the system which is consistent with both the experimental solubility behavior of aluminum-bearing minerals over wide ranges of pressure and temperature and potentiometric and high temperature-pressure phase equilibrium data. As noted above, the present study constitutes an attempt to generate such a set of thermodynamic data using the revised HKF equations of state (Tanger and Helgeson, 1988), correlations among various thermodynamic properties and parameters in the revised equations of state (Shock and Helgeson, 1988; Shock, Helgeson, and Sverjensky, 1989), and equations describing the concentration dependence of the apparent and partial molal properties and activity coefficients of aqueous species and electrolytes given by Helgeson, Kirkham, and Flowers (1981) and Oelkers and Helgeson (1990). These equations of state for aqueous species are summarized in app. A

TABLE 2

Standard partial molal thermodynamic properties at 298.15 K and 1 bar, and Maier-Kelley heat capacity power function coefficients for minerals in the system Al_2O_3–H_2O

Mineral	$\Delta\overline{G}^{\circ}_{f,T_r,P_r}$ [a]	$\overline{S}^{\circ}_{T_r,P_r}$ [b]	$\Delta\overline{H}^{\circ}_{f,T_r,P_r}$ [a]	$\overline{V}^{\circ}$ [c,j]	a [b]	$b \cdot 10^{-3}$ [d]	$c \cdot 10^{-5}$ [e]	T [f]
Corundum, Al_2O_3	−378,167 [g] ± 311	12.17 [h] ± 0.02	−400,500 [h] ± 310	25.575 ± 0.007	23.197 [i,h] 29.321 [i,h]	9.326 [i,h] 1.644 [i,h]	−6.300 [i,h] −12.007 [i,h]	500 1200
Gibbsite, $Al(OH)_3$	−276,025 [j] ± 290	16.36 [j] ± 0.03	−309,065 [j] ± 285	31.956 ± 0.015	13.073 [k]	40.696 [k]	−2.920 [k]	600
Boehmite, AlO(OH)	−219,599 [l] ± 340	8.89 [m] ± 0.02	−238,240 [n] ± 340	19.535 ± 0.026	12.902 [o]	12.421 [o]	−3.228 [o]	900
Diaspore, AlO(OH)	−220,150 [l] ± 300	8.446 [p] ± 0.02	−238,924 [n] ± 300	17.760 ± 0.026	12.273 [q]	13.070 [q]	−2.903 [q]	900

[a] cal mol^{-1}. [b] cal K^{-1} mol^{-1}. [c] cm^3 mol^{-1}. [d] cal K^{-2} mol^{-1}. [e] cal K mol^{-1}. [f] The upper temperature limit in K for reliable use of the heat capacity power function coefficients for the mineral. [g] Computed from the values of $\Delta\overline{H}^{\circ}_{f,T_r,P_r}$ and $\overline{S}^{\circ}_{T_r,P_r}$ given above for corundum using the standard molal entropies for $Al_{(c)}$, $O_{2(g)}$, and $H_{2(g)}$ (6.764, 49.033, and 31.233 cal K^{-1} mol^{-1}, respectively) adopted by Cox, Wagman, and Medvedev (1989). [h] Cox, Wagman, and Medvedev (1989). [i] Gurvich and others (1981). [j] Robie, Hemingway, and Fisher (1978). [k] Computed from experimental heat capacity data reported by Hemingway and others (1977). [l] Present study (see text). [m] Hemingway, Robie, and Apps (1991). [n] Computed from the values of $\Delta\overline{G}^{\circ}_{f,T_r,P_r}$ and $\overline{S}^{\circ}_{T_r,P_r}$ given above for boehmite and diaspore using the standard partial molal entropies of the elements adopted by Cox, Wagman, and Medvedev (1989). [o] Computed from experimental heat capacity data reported by Hemingway, Robie, and Apps (1991). [p] Perkins and others (1979). [q] Computed from experimental heat capacity data reported by Perkins and others (1979).

and B. The thermodynamic and electrostatic properties of H_2O used in the calculations were generated from equations and parameters reported by Johnson and Norton (1991), which have been incorporated into the SUPCRT92 software package (Johnson, Oelkers, and Helgeson, 1992). The standard partial molal thermodynamic properties of minerals, aqueous species, and reactions at high temperatures and pressures were calculated with the aid of SUPCRT92 using the standard partial molal properties of the species at 25°C and 1 bar and parameters given in tables 2 and 3. The solubility and speciation calculations described below were carried out by taking explicit account of the activity coefficients of neutral ion pairs using the approach adopted by Helgeson, Kirkham, and Flowers (1981), Oelkers and Helgeson (1991), and Pokrovskii and Helgeson (1995a).

CALCULATION OF THE THERMODYNAMIC PROPERTIES OF AQUEOUS ALUMINUM SPECIES IN THE SYSTEM Al_2O_3–H_2O–NaCl

Aluminum is present in dilute aqueous solutions in this system primarily as Al^{3+}, $Al(OH)^{2+}$, $Al(OH)^{+}_{2}$, $Al(OH)^{0}_{3}$, and $Al(OH)^{-}_{4}$. In contrast,

TABLE 3

Standard partial molal thermodynamic properties of aqueous species at 25°C and 1 bar and equations of state parameters required to calculate corresponding properties at high temperatures and pressures[a]

Species	$\Delta\overline{G}^{\circ}_{f,T_r,P_r}$ [b]	$\overline{S}^{\circ}_{T_r,P_r}$ [c]	$\Delta\overline{H}^{\circ}_{f,T_r,P_r}$ [b]	a_1 [d] × 10	a_2 [b] × 10^{-2}	a_3 [e]	a_4 [f] × 10^{-4}	c_1 [c]	c_2 [f] × 10^{-4}	ω_{T_r,P_r} [b] × 10^{-5}
H^+ [g]	0	0	0	0	0	0	0	0	0	0
Na^+ [g]	−62,591	13.96	−57,433	1.8390	−2.2850	3.2560	−2.726	18.18	−2.981	0.3306
Cl^- [g]	−31,379	13.56	−39,933	4.0320	4.8010	5.5630	−2.847	−4.40	−5.714	1.4560
OH^- [g]	−37,595	−2.56	−54,977	1.2527	0.0738	1.8423	−2.7821	4.15	−10.346	1.7246
Al^{3+}	−116,543	−80.80	−128,681 [h]	−3.3404 [g]	−17.1108 [g]	14.9917 [g]	−2.0716 [g]	10.70 [g]	−8.06 [g]	2.8711 [g]
$Al(OH)^{2+}$	−166,468	−46.82	−185,096	0.2580	−9.6965	9.6000	−2.5767	38.00	−2.60	1.7666
$Al(OH)_2^+$	−215,465	−17.00	−241,825	3.5000	−2.4600	6.3000	−2.8100	46.70	−1.50	0.8089
$HAlO_2^0$	−207,500	−6.50	−230,730	3.6808	1.2058	5.2761	−2.8288	39.00	2.50	0.3000
AlO_2^-	−198,700	−7.00	−222,079	3.7280 [g]	3.9800 [g]	−1.5170 [g]	−2.9435 [g]	19.10 [g]	−6.20 [g]	1.7595 [g]
$NaAlO_2^0$	−260,277	11.10	−277,259	4.7640	0.4850	12.6690	−4.8975	32.43	3.80	−0.1000
$NaOH^0$	−99,095	6.00	−112,927	1.4675	−4.1982	7.4001	−2.6054	22.00	3.00	−0.7200
$NaCl^0$ [i]	−92,910	28.00	−96,160	5.0363	4.7365	3.4154	−2.9748	10.80	−1.30	−0.0380

[a] All the values of these properties and parameters were generated in the present study, unless indicated otherwise. A discussion of the uncertainties associated with calculation of HKF equations of state coefficients can be found in Shock and Helgeson (1988). [b] cal mol^{-1}. [c] cal K^{-1} mol^{-1}. [d] cal bar^{-1} mol^{-1}. [e] cal K bar^{-1} mol^{-1}. [f] cal K mol^{-1}. [g] Shock and Helgeson (1988). [h] Cox, Wagman, and Medvedev (1989). [i] Shock and others (1992).

a number of polynuclear aluminum complexes such as $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al_6(OH)_{12}^{6+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_2O(OH)_6^{2-}$, and probably others may form and exist indefinitely at room temperature in solutions supersaturated with respect to gibbsite (Hem, 1968; Akitt and others, 1972; Eremin, Volokhov, and Mironov, 1974; Baes and Mesmer, 1976; Bottero and others, 1980; Brown and others, 1985; Bertsch, 1989; Hem and Roberson, 1990; and others). However, because these polynuclear species are metastable, they were omitted from consideration in the present study. The aluminum ion (Al^{3+}) and its aluminate counterpart ($Al(OH)_4^-$) are the only aqueous aluminum species for which standard partial molal heat capacities and volumes have been determined experimentally from those of aqueous aluminum chloride and sodium aluminate (Hovey and Tremaine, 1986; Barta and Hepler, 1986; Hovey, Hepler, and Tremaine, 1988; Sanjuan and Michard, 1988; Caiani and others, 1989; Conti, Gianni, and Matteoli, 1992). The standard partial molal heat capacities and volumes of aqueous aluminum chloride and sodium aluminate are shown as a function of temperature at P_{SAT} in figure 1. The curves in this figure were generated using equations of state coefficients for the ions taken from table 3. It can be seen in figure 1 that the calculated values of $\overline{V}^o$ for $AlCl_{3(aq)}$ are ~ 2 cm^3 mol^{-1} lower than the experimental data represented by the symbols. This discrepancy is somewhat surprising because the a_1, a_2, a_3, and a_4 equations of state parameters (see app. A) for Al^{3+} were generated by Shock and Helgeson (1988) from experimental values of $\overline{V}^o$ for $AlCl_{3(aq)}$ reported by Barta and Hepler (1986) and Hovey and Tremaine (1986). As shown in figure 6 in Shock and Helgeson (1988), their regression curve is closely consistent with the experimental data. Upon further examination, it appears that the discrepancies between the curve and symbols for $\overline{V}^o_{AlCl_3}$ in figure 1 are due to differences in the values of the Q Born coefficient (eq A-8 in app. A) used in the regression calculations carried out by Tanger and Helgeson (1988) and Shock and Helgeson (1988) and the revised values generated from equations incorporated into SUPCRT92 (Shock and others, 1992). The value of $\overline{V}^o$ for the aluminum ion at 25°C and 1 bar generated from SUPCRT92 (-45.3 cm^3 mol^{-1}) is in excellent agreement with the values adopted by Barta and Hepler (1986) and Hovey and Tremaine (1986); that is, -45.04 ± 0.27 and -45.30 cm^3 mol^{-1}, respectively. For the same reason, the value of $\overline{V}^o$ for Cl^- given by Tanger and Helgeson (1988) which was adopted by Shock and Helgeson (1988) (17.8 cm^3 mol^{-1}) is 0.5 cm^3 mol^{-1} larger than that calculated from SUPCRT92. It is also slightly smaller than the values of $\overline{V}^o_{Cl^-}$ adopted by Barta and Hepler (1986) and Hovey and Tremaine (1986), who chose 17.95 ± 0.06 and 18.1 cm^3 mol^{-1}, respectively. It should perhaps be emphasized that these various discrepancies are within the overall experimental uncertainties in the values of $\overline{V}^o_{Cl^-}$ and $\overline{V}^o_{Al^{3+}}$ given by Tanger and Helgeson (1988) and Shock and Helgeson (1988).

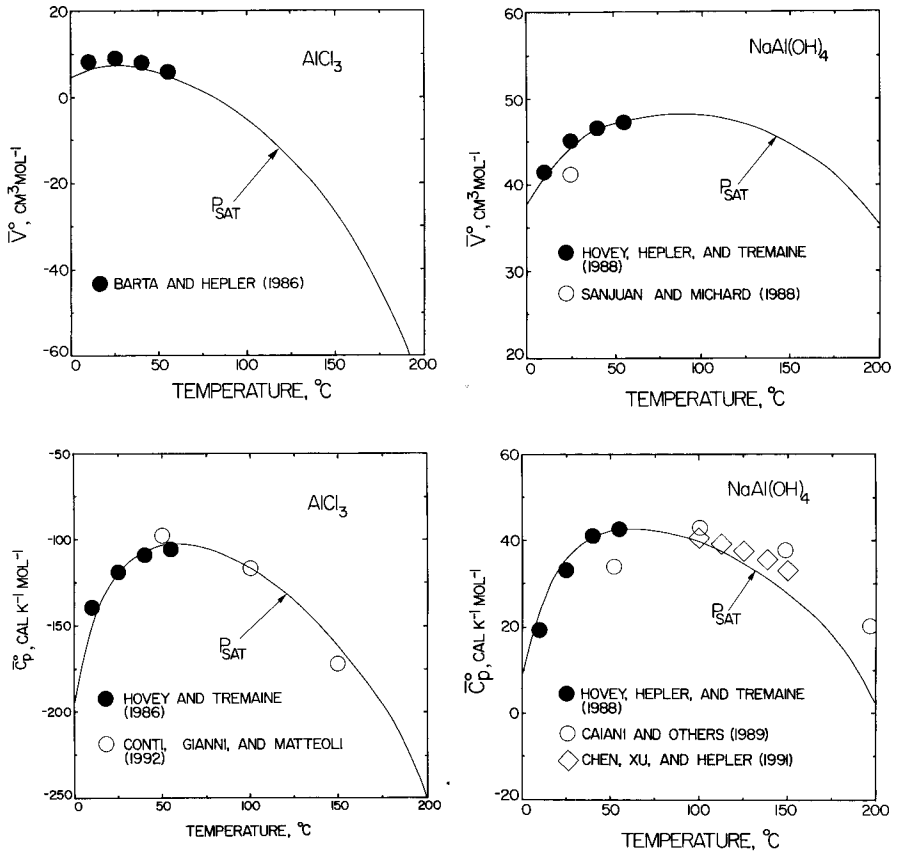

Fig. 1. Standard partial molal heat capacity and volume of aqueous $AlCl_3$ and $NaAl(OH)_4$ as a function of temperature at P_{SAT}. The symbols represent experimental values taken from the literature, but the curves were generated using equations of state parameters given in table 3.

It can be seen in figure 1 that the calculated values of $\overline{C}_P^\circ$ for the aqueous electrolyte $NaAl(OH)_4$ at temperatures $\geq$ 100°C are systematically lower than their experimental counterparts. These discrepancies may arise from the fact that Caiani and others (1989) and Chen, Xu, and Hepler (1991) interpreted their experimental results by assuming the concentrated $NaAl(OH)_4$–$NaOH$–H_2O solutions used in their experiments to be completely dissociated. However, speciation calculations carried out in the present study using Hückel extended-term parameters for $NaOH_{(aq)}$ and Setchénow coefficients and dissociation constants for $NaOH^0$ given in app. B, together with dissociation constants for $NaAl(OH)_4^0$ generated independently in the present study (see below), indicate that substantial concentrations of ion pairs may have been

present in the experimental solutions. Even in the solution with the lowest concentration of $NaAl(OH)_4$ and NaOH used by Caiani and others (1989) in their experiment at 100.5°C and 20 bar (0.0953 *m* $NaAl(OH)_4$ + 0.2229 *m* NaOH), the speciation calculations indicate that $NaAl(OH)_4^0$ and $NaOH^0$ may have constituted as much as ~6.7 and ~2 mole percent of the total Al and Na in solution, respectively. The calculations for the aqueous solution used by Caiani and others (1989) at 196.64°C and 30 bar (0.4956 *m* $NaAl(OH)_4$ + 1.2140 *m* NaOH) indicate that ~43 and ~13.8 mole percent of the total aluminum and sodium in solution were present as $NaAl(OH)_4^0$ and $Na(OH)^0$, respectively. Caiani and others (1989) used sodium aluminate solutions which were supersaturated with respect to gibbsite. Although they observed no precipitate, it remains unclear to what extent the formation of polynuclear and/or polymeric species such as $Al_2O(OH)_6^{2-}$ occurred in their experimental solutions. The latter observation also applies to the experimental data reported by Chen, Xu, and Hepler (1991), who generated supersaturated sodium aluminate solutions in the process of measuring heats of solution of gibbsite in NaOH solutions with starting concentrations ranging from 1 to 5 molal. Speciation calculations indicate that in a final solution containing 0.695 *m* NaOH and 0.305 *m* $NaAl(OH)_4$ at 100.1°C, which was the lowest temperature considered in their study, ~14.1 and ~4.4 mole percent of the total aluminum and sodium may have been present as $NaAl(OH)_4^0$ and $NaOH^0$, respectively. It thus appears that ion association may have contributed appreciably to the magnitude of the calorimetric heat capacities and heats of solution reported by Caiani and others (1989) and Chen, Xu, and Hepler (1991).

Al^{3+}

Numerous studies have been devoted to estimating the thermodynamic properties of the aluminum ion. Nevertheless, no consensus has been reached in the literature regarding the standard state properties of this ion. For example, Couturier, Michard, and Sarazin (1984) calculated the standard partial molal Gibbs free energy of formation of Al^{3+} from the elements at 25°C and 1 bar ($\Delta\bar{G}_f^\circ$) to be −115,600 cal mol^{-1} from the results of their potentiometric measurements. This value was adopted by Anderson and others (1991) in their analysis of mineral solubilities in the system Al_2O_3–H_2O. However, in the final report of the CODATA Task Group in Key Values for Thermodynamics (Cox, Wagman, and Medvedev, 1989), the standard partial molal enthalpy of formation from the elements (ΔH_f°) and the standard partial molal entropy ($\bar{S}^\circ$) of Al^{3+} are given as −128,681 ± 360 cal mol^{-1} and −77.68 ± 2.4 cal K^{-1} mol^{-1} respectively, which yield $\Delta\bar{G}_f^\circ$ of the aluminum ion equal to −117,473 ± 800 cal mol^{-1}. Combining the latter value with that of gibbsite given by Robie, Hemingway, and Fisher (1978), which was derived solely from calorimetric data (Hemingway and Robie, 1977a; Hemingway and others, 1977), and the value of $\Delta\bar{G}_f^\circ$ of H_2O adopted by Cox, Wagman, and Medvedev (1989) (−56,678 ± 10 cal mol^{-1}) yields a value of the loga-

rithm of the equilibrium constant (K) for the reaction

$$\underset{\text{(gibbsite)}}{Al(OH)_3} + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O \qquad (1)$$

of 8.416 ± 0.624 at 25°C and 1 bar, which is in close agreement with the experimental value of 8.5 reported by Frink and Peech (1962). However, this value is substantially higher than those measured by Kittrick (1966), Turner (1968), Singh (1974), and May, Helmke, and Jackson (1979), who report 7.97, 8.20, 8.03, and 8.11, respectively. The value of log K reported by May, Helmke, and Jackson (1979) is consistent with −117,055 cal mol^{-1} for $\Delta\overline{G}^{\circ}_{f}$ of the aqueous aluminum ion.

Bloom and Weaver (1982) carried out reversed gibbsite solubility measurements with various synthetic gibbsite samples, including those used by Frink and Peech (1962) and Kittrick (1966). In their investigation, Bloom and Weaver (1982) discovered that the grains of synthetic gibbsite used in the previous solubility studies were covered with reactive globular material which was enriched with Na. Removing the surface material (presumably cryptocrystalline gibbsite) by strong acid treatment (0.1 *m* HCl for 14 days) decreased the measured gibbsite solubility, which then approached a level consistent with log K = 7.71 ± 0.055 for reaction (1). This value corresponds to the average log K for 3 different samples at 22°C, which according to Bloom and Weaver (1982) is consistent with log K = 7.55 ± 0.055 at 25°C and 1 bar. Their measured solubility of an untreated gibbsite sample agrees well with those reported by Kittrick (1966), Singh (1974), and May, Helmke, and Jackson (1979). Although little is still known about the structure and reactivity of acid pre-treated gibbsite surfaces, the study by Bloom and Weaver (1982) in which equilibrium was attained from both under- and supersaturation indicates that the solubility of coarsely crystalline gibbsite may be substantially lower than those reported in previous studies, all of which were carried out using untreated natural and synthetic gibbsite samples with different grain size, crystallinity, and density of structural defects. The equilibrium constant for reaction (1) at 25°C and 1 bar adopted by Bloom and Weaver (1982) is consistent with $\overline{G}^{\circ}_{f,Al^{3+}}$ = −116,260 ± 300 cal mol^{-1}.

Since publication of Bloom and Weaver's (1982) paper, new measurements of gibbsite solubilities in acid solutions have been reported for temperatures from 25° to 80°C by Peryea and Kittrick (1988), Nagy and Lasaga (1992, 1993), and Palmer and Wesolowski (1992). The same acid treatment of synthetic gibbsite samples recommended by Bloom and Weaver (1982) was used in these studies. The equilibrium solubilities of gibbsite at 25°C and 1 bar obtained by Peryea and Kittrick (1988) and Palmer and Wesolowski (1992) lead to a value of log K for reaction (1) of 7.735 ± 0.06. This value is consistent with $\Delta\overline{G}^{\circ}_{f,Al^{3+}}$ = −116,543 ± 300 cal mol^{-1}, which falls within the uncertainty of Bloom and Weaver's (1982) value. However, because it is based on a more extensive set of experiments carried out independently in two separate laboratories, the value of −116,543 ± 300 cal mol^{-1} for $\Delta\overline{G}^{\circ}_{f,Al^{3+}}$ was adopted in the present

study together with the experimental value of $\Delta\overline{H}^{\circ}_{f}$ of Al^{3+} given in table 3 (see below), which was used to calculate the standard partial molal entropy of Al^{3+} at 25°C and 1 bar shown in the table.

Khodakovsky, Katorcha, and Kuyunko (1980) calculated $\Delta\overline{H}^{\circ}_{f,Al^{3+}}$ to be $-128{,}520 \pm 250$ cal mol^{-1} at 25°C and 1 bar from calorimetric heats of solution of crystalline $AlCl_3 \cdot 6H_2O$ and $AlCl_3$ ion in water and aqueous HCl solutions reported by Coughlin (1958), Smith and Bass (1963), and Krivtsov, Rossolovskii, and Shirokova (1971), together with heats of dilution of aqueous $AlCl_3$ solutions measured by Lange and Meiderer (1957). In the 1989 CODATA report, Cox, Wagman, and Medvedev (1989) give a value for $\Delta\overline{H}^{\circ}_{f,Al^{3+}}$ at 25°C and 1 bar of $-128{,}681 \pm 360$ cal mol^{-1}. Efimov, Furkalyuk, and Medvedev (1988) report $\Delta\overline{H}^{\circ}_{f,Al^{3+}} = -128{,}413$ cal mol^{-1} at 25°C and 1 bar, based on their own calorimetric measurements. Recently, Zeng (ms) and Zeng, Chen, and Chen (1994b) reported a value of $\Delta\overline{H}^{\circ}_{f,Al^{3+}} = -128{,}645 \pm 240$ cal mol^{-1} which is in close agreement with that adopted by Cox, Wagman, and Medvedev (1989). All these values differ appreciably from the value of $-126{,}912 \pm 960$ cal mol^{-1} given in the NBS Tables (Wagman and others, 1968, 1982) which was adopted by Hemingway and Robie (1977b) in their analysis of the thermodynamic properties of Al^{3+}. It has been suggested (Khodakovsky, Katorcha, and Kuyunko, 1980; Cox, Wagman, and Medvedev, 1989) that the differences in the values of $\Delta\overline{H}^{\circ}_{f}$ of Al^{3+} given in the NBS Tables and those generated from the sources adduced above can be attributed to underestimation by Wagman and others (1968, 1982) of the enthalpy change associated with the hydrolysis of the aluminum ion represented by

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^{+}. \qquad (2)$$

Combining the value of $\Delta\overline{H}^{\circ}_{f,Al^{3+}} = -128{,}681 \pm 360$ cal mol^{-1} reported by Cox, Wagman, and Medvedev (1989) with $\Delta\overline{G}^{\circ}_{f,Al^{3+}} = -116{,}543 \pm 300$ cal mol^{-1} computed from the solubility data obtained by Peryea and Kittrick (1988) and Palmer and Wesolowski (1992) leads to a value of $\overline{S}^{\circ}_{Al^{3+}}$ of -80.8 ± 1.6 cal K^{-1} mol^{-1}, which differs substantially from the value of -73.6 ± 3.6 cal K^{-1} mol^{-1} for $\overline{S}^{\circ}_{Al^{3+}}$ at 25°C and 1 bar adopted by Hemingway and Robie (1977b) and Robie, Hemingway, and Fisher (1978). However, it is in reasonably close agreement with the values of -78.2 ± 1.0 and -77.6 ± 2.4 cal K^{-1} mol^{-1} for $\overline{S}^{\circ}_{Al^{3+}}$ at 25°C and 1 bar given by Khodakovsky, Katorcha, and Kuyunko (1980) and Cox, Wagman, and Medvedev (1989), respectively. The latter values represent averages of standard molal entropies generated from different reaction schemes, which include reaction (1). However, the equilibrium constants for reaction (1) used by Khodakovsky, Katorcha, and Kuyunko (1980) and Cox, Wagman, and Medvedev (1989) are consistent with the solubilities of untreated gibbsite samples, which apparently do not represent the solubility of coarsely crystalline gibbsite (see above).

In attempts to resolve the discrepancies discussed in the preceding paragraph, Hemingway (1982) and Hemingway, Robie, and Apps (1991) reviewed the factors affecting the rates and mechanisms of precipitation and dissolution of $Al(OH)_3$ polymorphs and concluded that the presence of Cl^- in solution may have some poorly understood effect on the results of solubility measurements, presumably due to adsorption of Cl^- and/or formation of aluminum oxychloride complexes on reactant grain surfaces. To illustrate the basis for their conclusion, they cite the study by Frink and Peech (1962), who measured the solubility of synthetic gibbsite at 25°C and 1 bar in both supersaturated H_2O + $AlCl_3$ solutions and undersaturated H_2O + $AlCl_3$ + HCl and H_2O + HCl solutions. Hemingway (1982) and Hemingway, Robie, and Apps (1991) argue that addition of Cl^- in the form of HCl was responsible for the low solubilities measured by Frink and Peech (1962). However, Frink and Peech (1962) note that addition of HCl caused the solution to become highly undersaturated. They report that "dissolution of gibbsite in undersaturated solutions . . . was extremely slow; virtually none had dissolved in most of the solutions during [the] 1- to 3-month equilibration period." This observation can be attributed to the large volume of solution and the high solution to grain surface ratios in their experimental charges, which would be expected to increase substantially the time required to achieve equilibrium in their experiments.

Frink and Peech (1962) calculated the equilibrium constant for reaction (1) from the solubilities they obtained by precipitation of gibbsite from supersaturated $AlCl_3$ solutions which most likely represent the properties of a cryptocrystalline form of gibbsite. Note in this regard that the equilibrium quotients reported by Frink and Peech (1962) for their experiments in which undersaturated $AlCl_3$ + HCl solutions were used with starting values of $m_{Al^{3+}}/m^3_{H^+}$ that were close to the equilibrium value resulted in values of log K of 7.71 and 7.65, which are in excellent agreement with that of 7.735 adopted in the present study (Peryea and Kittrick, 1988; Palmer and Wesolowski, 1992). Such close agreement is consistent with the fact that Frink and Peech (1962) repeatedly washed their gibbsite sample with 4 *m* HCl, which apparently removed at least part of the cryptocrystalline gibbsite from the grain surfaces. Hemingway (1982) and Hemingway, Robie, and Apps (1991) notwithstanding, it appears that the experimental data generated by Frink and Peech (1962) provide no evidence of a Cl^- surface effect on the solubilities of gibbsite measured in their study. However, it should be noted in this regard that adsorption of Cl^- on aluminum oxides and hydroxides does indeed occur in acid solutions to compensate for the positive charge on the surfaces of the mineral grains, which has been documented by titration measurements carried out by Hingston, Posner, and Quirk (1972), Feldkamp and others (1981), and Schulthness and Sparks (1987). The results of these studies, as well as spectroscopic observations (Serna, White, and Hem, 1977) indicate that Cl^- is primarily involved in outer-sphere electrostatic interactions with charged surfaces, but apparently it does not form strong surface complexes with Al^{3+}. Hingston and others

(1967) and Stumm and Morgan (1981) note that the tendency of ligands to form surface complexes is similar to that of ligands to form metal complexes in solution. This observation applies to Al-OH-Cl interactions because aluminum apparently does not form complexes with Cl^- even in concentrated chloride brines (Palmer and Wesolowski, 1992). Although adsorption of Cl^- on alumina and oxidizing aluminum metal has been invoked to explain electrokinetic phenomena in several electrochemical studies (for example, Morfopoulos and Parreira, 1967; Diggle, Downie, and Goulding, 1970), there is no indication that Cl^- plays a special role in determining the equilibrium solubility of gibbsite. For example, Palmer and Wesolowski (1992) measured the solubility of gibbsite in solutions with concentrations of Cl^- ranging from 10^{-3} to 5 molal and obtained remarkably consistent equilibrium quotients for reaction (1) for the whole range of NaCl concentrations, which leaves little doubt that the presence of Cl^- had no significant effect on the equilibrium constants derived in their study. In fact, Palmer and Wesolowski (1992, p. 1094) observed that "at 30°C samples were analysed after 20, 33, 53, and 132 days with equilibrium (that is, constant aluminum concentration) being attained after 20 days for those samples with salinities above about 1 molal NaCl, whereas 53 days were required for samples with lower NaCl concentrations." Faster dissolution rates for gibbsite in concentrated acid NaCl solutions does not support the hypothesis that the adsorption of Cl^- on mineral surfaces inhibits gibbsite dissolution.

Equilibrium constants for reaction (1) derived from experimental solubilities of acid pretreated samples of gibbsite reported by Bloom and Weaver (1982), Peryea and Kittrick (1988), Nagy and Lasaga (1992), and Palmer and Wesolowski (1992) are plotted in figure 2 as a function of temperature at P_{SAT}, together with a corresponding curve representing log K calculated with the aid of SUPCRT92 using the thermodynamic data for gibbsite and Al^{3+} given in tables 2 and 3. It can be seen in this figure that the curve generated in the present study is consistent with all of the experimental data shown in the figure.

Palmer and Wesolowski (1992) used their experimental values of log K for reaction (1) at 30°, 50°, and 70°C (7.431, 6.310, and 5.322, respectively) to calculate values of $\Delta\overline{H}^\circ_f$ and $\overline{S}^\circ$ for the aluminum ion at 25°C and 1 bar, which resulted in $-129{,}278 \pm 980$ cal mol^{-1} and -82.70 cal K^{-1} mol^{-1}, respectively. The log K values at these temperatures computed in the present study (7.439, 6.344, and 5.379, respectively) are consistent with their data to within the reported experimental uncertainty of $\pm$ 0.06. In fact, the latter values are within $\pm$ 0.02 of those computed by Palmer and Wesolowski (1992) using the Pitzer ion interaction approach without considering higher-order electrostatic mixing terms. These calculations yielded 7.461, 6.346, and 5.361 for log K of reaction (1) at 1 bar and 30°, 50°, and 70°C, respectively. The value of log K at 80°C computed in the present study (4.94) is in better agreement with its experimental counterpart (5.00 ± 0.08) reported by Nagy and Lasaga (1992) than that calculated by Palmer and Wesolowski (1992), who obtained 4.87. Such close agreement among equilibrium constants at elevated temperatures

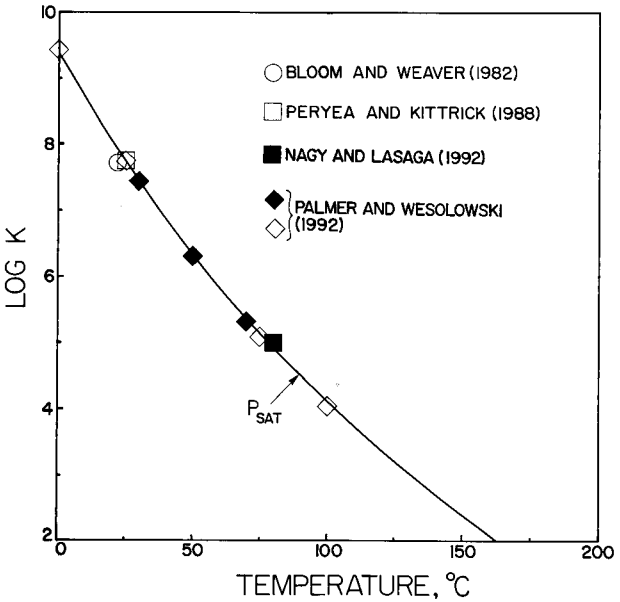

Fig. 2. Logarithm of the equilibrium constant for $Al(OH)_3$(gibbsite) + $3H^+ \rightleftharpoons Al^{3+} + 3H_2O$ as a function of temperature as P_{SAT}. The open diamonds represent values of log K calculated by Palmer and Wesolowski (1992). The curve was generated in the present study (see text).

generated from different experimental solubility studies using well characterized gibbsite and those calculated in the present study using the calorimetric properties of gibbsite at 25°C and 1 bar and the revised HKF equations of state strongly supports the validity of the standard partial molal thermodynamic properties and equations of state parameters for Al^{3+} given in table 3.

$Al(OH)_4^-$ and $NaAl(OH)_4^0$

It is commonly assumed that aluminum is present primarily as the aluminate ion ($Al(OH)_4^-$) in alkaline solutions saturated with crystalline aluminum hydroxides and oxyhydroxides. However, this *a priori* assumption is not a requisite for interpreting experimental solubilities of gibbsite, boehmite, and diaspore in NaOH aqueous solutions, which may contain substantial concentration of other aqueous aluminum species (see below). As noted in table 1, solubility data of this kind are available in the literature for temperatures ranging from 6.4° to 350°C at P_{SAT} (Fricke and Jucaitis, 1930; Tsirlina, 1936; Magarshak, 1938; Fulda and Ginsberg, 1951; Druzhinina, 1955; Russell, Edwards, and Taylor, 1955; Bernshtein and Matsenok, 1961, 1965; Ikkatai and Okada, 1962; Kittrick, 1966; Lyapunov, Khodakova, and Galkina, 1964; Apps, ms; Berecz and Szita, 1970; Chang, Pak, and Li, 1979; Packter, 1979; Kuyunko, Malinin, and

Khodakovsky, 1983; Apps, Neil, and Jun, 1989; Verdes, ms; Castet, ms; Wesolowski, 1992; Castet and others, 1993; and others). The sodium hydroxide solutions used in these studies vary from highly dilute solutions to those saturated with crystalline sodium aluminate hydrate[3] (Fricke and Jucaitis, 1930; Jucaitis, 1934; Apps, Neil, and Jun, 1989). Thermodynamic analysis of these various data requires provision for possible complexing of sodium and aluminate ions as well as formation of $NaOH^0$. Experimental evidence summarized in app. C indicates that $NaOH^0$ and $NaAl(OH)_4^0$ ion pairs may be present in sodium aluminate solutions, even at 25°C. Hence, these species should be taken into account in carrying out thermodynamic analyses of mineral solubilities in the system Al_2O_3–H_2O–NaCl–NaOH. However, it should be noted in this regard that theoretical considerations (Helgeson, Kirkham, and Flowers, 1981; Oelkers and Helgeson, 1991) indicate that the activity coefficients of these neutral on pairs in solutions with high effective ionic strengths may be substantially greater than unity, which tends to lower their degrees of formation.

Experimental evidence (see app. C) indicates that $Al(OH)_4^-$ in concentrated sodium hydroxide solutions tends to disproportionate to form H_2O, $AlO(OH)_2^-$, and AlO_2^-. All these various aluminum species are represented in the regression calculations described below by AlO_2^- with the understanding that this formulation carries no explicit implication with respect to the hydration states of the various aluminate species it represents, all of which contribute implicitly to the thermodynamic properties of AlO_2^- derived below (see footnote 1). The use of AlO_2^- in retrieval calculations is advantageous for both dilute solutions, where any assumption regarding the state of hydration of the aluminate ion bears no consequences on the results of such calculations, and for concentrated solutions in which AlO_2^- may predominate over other aluminate species. The dissolution of gibbsite, boehmite, and diaspore in alkaline solutions can be described in terms of AlO_2^- by writing

$$\underset{\text{(gibbsite)}}{Al(OH)_3} + OH^- \rightleftharpoons AlO_2^- + 2H_2O \tag{3}$$

$$\underset{\text{(boehmite)}}{AlO(OH)} + OH^- \rightleftharpoons AlO_2^- + H_2O \tag{4}$$

$$\underset{\text{(diaspore)}}{AlO(OH)} + OH^- \rightleftharpoons AlO_2^- + H_2O. \tag{5}$$

It follows from these reactions, that the activity of H_2O must be taken into account explicitly in order to compute accurate equilibrium quotients $m_{AlO_2^-}/m_{OH^-}$ for the concentrated NaOH solutions (up to 10 *m*) considered in the present study.

[3] $NaAlO_2 \cdot nH_2O$, where n varies from 1 to ~ 1.3.

The regression calculations summarized below are predicated on the following hypotheses: (1) The activity coefficients of charged aqueous species can be closely approximated with the aid of the Hückel equation using the extended-term parameter (b_γ) for the supporting electrolyte, which is consistent with the approach taken by Helgeson, Kirkham, and Flowers (1981); (2) the activity coefficients of $NaOH^0$ and $NaAlO_2^0$ in sodium aluminate solutions are essentially equivalent to that of $NaOH^0$ in NaOH solutions; and (3) the activity of H_2O in mixed NaOH + $NaAlO_2$ electrolyte solutions is essentially equal to that in NaOH solutions of equal stoichiometric ionic strength.

Activity coefficients for charged species in aqueous electrolyte solutions in which the supporting electrolyte (MX) substantially predominates over any other solute component can be calculated from the Hückel equation (Hückel, 1925; Helgeson, Kirkham, and Flowers, 1981), which can be written for a given aqueous species as

$$\log \bar{\gamma} = -\frac{A_\gamma Z^2 \bar{I}^{1/2}}{1 + \mathring{a} B_\gamma \bar{I}^{1/2}} + \Gamma_\gamma + b_{\gamma,MX}\bar{I}, \tag{6}$$

where $\bar{\gamma}$ refers to the individual ion activity coefficient of the species, $b_{\gamma,MX}$ represents the extended-term parameter for the supporting electrolyte MX, which is a function of pressure and temperature, å stands for the ion size parameter for the electrolyte, Z denotes the formal charge on the species, $\bar{I}$ designates the effective ionic strength of the solution on the molal scale of concentration ($\bar{I} = \frac{1}{2}\Sigma_i Z_i^2 m_i$), Γ_γ refers to the mole fraction to molality conversion factor given by

$$\Gamma_\gamma = -\log (1 + 0.0180153m^*), \tag{7}$$

where m^* symbolizes the sum of the molalities of all of the solute species in solution, and A_γ and B_γ represent the Debye-Hückel solvent parameters defined by

$$A_\gamma \equiv \frac{1.8248 \cdot 10^6 \rho^{1/2}}{(\epsilon T)^{3/2}}, \tag{8}$$

and

$$B_\gamma \equiv \frac{50.291 \cdot 10^8 \rho^{1/2}}{(\epsilon T)^{1/2}}, \tag{9}$$

where ρ and ϵ stand for the density and dielectric constant of the solvent, respectively. The activity coefficients of neutral aqueous species can be computed from the Setchénow equation, which can be written as

$$\log \bar{\gamma}_n = \Gamma_\gamma + b_{\gamma,MX^0}\bar{I}, \tag{10}$$

where b_{γ,MX^0} refers to the Setchénow coefficient for the neutral ion pair MX^0 in MX–H_2O solutions.

The activity of water (a_w) and osmotic coefficient (ϕ) for symmetric electrolytes in which only one ion pair forms to an appreciable degree can be computed from (Helgeson, Kirkham, and Flowers, 1981).

$$\ln a_w = \frac{\phi m^*}{55.51}, \tag{11}$$

and

$$\phi = -2.303\left(\frac{|Z_+Z_-|\, A_\gamma \bar{I}^{1/2}\sigma(\mathring{a}B_\gamma \bar{I}^{1/2})}{3} + \frac{\psi\Gamma_\gamma}{0.0180153\nu\bar{I}} - \frac{b_{\gamma,MX}\bar{I}}{2}\right), \tag{12}$$

where $\psi = 1$ for 1:1 electrolytes, ν refers to the stoichiometric number of moles of ions in one mole of the electrolyte, and

$$\sigma(\mathring{a}B_\gamma \bar{I}^{1/2}) = \frac{3}{\mathring{a}^3 B_\gamma^3 \bar{I}^{3/2}}\left(\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right), \tag{13}$$

where

$$\Lambda = 1 + \mathring{a}B_\gamma I^{1/2}. \tag{14}$$

Values of the extended-term parameter ($b_{\gamma,NaOH}$) for aqueous NaOH together with those of the Setchénow coefficient ($b_{\gamma,NaOH^0}$) were generated in the present study using the equations and approach summarized in app. B.

Regression strategy.—The regression calculations described below were carried out using the standard partial molal thermodynamic properties of gibbsite shown in table 2, which correspond to those adopted by Robie, Hemingway, and Fisher (1978). The Maier-Kelley heat capacity power function (Maier and Kelley, 1932) coefficients given in table 2 for gibbsite, boehmite, and diaspore were calculated from calorimetric data reported by Hemingway and others (1977), Hemingway, Robie, and Apps (1991), and Perkins and others (1979), respectively. The values of $\Delta\bar{G}_f^\circ$ for boehmite and diaspore shown in the table were computed by regressing solubility data. The regression calculations were carried out by first minimizing the Gibbs free energy for sodium aluminate solutions saturated with gibbsite assuming $\bar{\gamma}_{OH^-} \approx \bar{\gamma}_{AlO_2^-}$ and the dissociation constants for $NaAlO_2^0$ and $NaOH^0$ ($K_{NaAlO_2^0}$ and K_{NaOH^0}, respectively) to be equivalent. The calculations were carried out using activity coefficients and values of log K_{NaOH^0} generated independently from equations summarized in app. B and experimental solubilities of gibbsite reported in the literature for temperatures ranging from 6.4° to 130°C. The bulk compositions of the saturated solutions were specified in the calculations, which permitted retrieval of values of log K for reaction (3) at various temperatures by taking account of

$$K = \frac{a_{AlO_2^-}a_w^2}{a_{OH^-}} \approx \frac{m_{AlO_2^-}}{m_{OH^-}}a_w^2 \approx Qa_w^2, \tag{15}$$

and

$$m_{Al} = m_{AlO_2^-} + m_{NaAlO_2^0}, \tag{16}$$

where $a_{AlO_2^-}$, $m_{AlO_2^-}$, a_{OH^-}, m_{OH^-}, and $m_{NaAlO_2^0}$ refer to the activities and molalities of the subscripted species, a_w stands for the activity of H_2O, m_{Al} designates the total molality of aluminum in solution, and Q denotes the equilibrium quotient for reaction (3) ($m_{AlO_2^-}/m_{OH^-}$). The values of log K retrieved from the regression calculations were used to generate initial values of $\Delta\overline{G}_f^\circ$, $\Delta\overline{H}_f^\circ$, and $\overline{S}^\circ$ for AlO_2^-. Values of these properties together with equations of state coefficients for AlO_2^- (table 3) and experimental solubilities of boehmite and diaspore (reactions 4 and 5) were then used to calculate initial values of the standard molal Gibbs free energies of formation of the minerals. These calculations were carried out for dilute solutions in which the presence of $NaAlO_2^0$ is negligible. Finally, mineral solubilities reported in the literature for wide ranges of NaOH concentration and temperature were regressed using the thermodynamic data for gibbsite shown in table 2 and those for boehmite, diaspore, and AlO_2^- obtained in the manner described above to compute initial values of the equilibrium constant at various temperatures for

$$NaAlO_2^0 \rightleftharpoons Na^+ + AlO_2^-. \tag{17}$$

The entire retrieval procedure was then repeated after replacing the initial values of $K_{NaAlO_2^0}$ used in the Gibbs free energy minimization calculations with that computed from the previous iteration. This process was continued until convergence was obtained and accurate representation of the whole solubility data set was achieved. The Gibbs free energy minimization calculations were carried out using computer code GIBBS (Shvarov, ms). The results of the retrieval calculations are discussed in detail below.

Regression results.—Experimental solubilities of gibbsite at temperature ranging from 6.4° to 130°C at P_{SAT} are shown in figure 3 together with regression curves generated in the present study.[4] It can be seen in this figure that the solubility of gibbsite increases to an increasing degree with increasing molality of NaOH at $m_{NaOH} \geq 3$ at temperatures ≤ 100°C. This behavior can be attributed to the decreasing activity of H_2O accompanied by increasing formation of $NaAlO_2^0$ with increasing m_{NaOH}. Although $NaAlO_2^0$ becomes more stable with increasing temperature, the stability of AlO_2^- increases even more. In concentrated solutions, the activity of H_2O increases with increasing temperature. These two factors

[4] In cases where only initial molalities of NaOH are reported in the references cited in figure 3 and subsequent figures, final molalities were computed in the present study by taking account of the formation of H_2O during mineral hydrolysis.

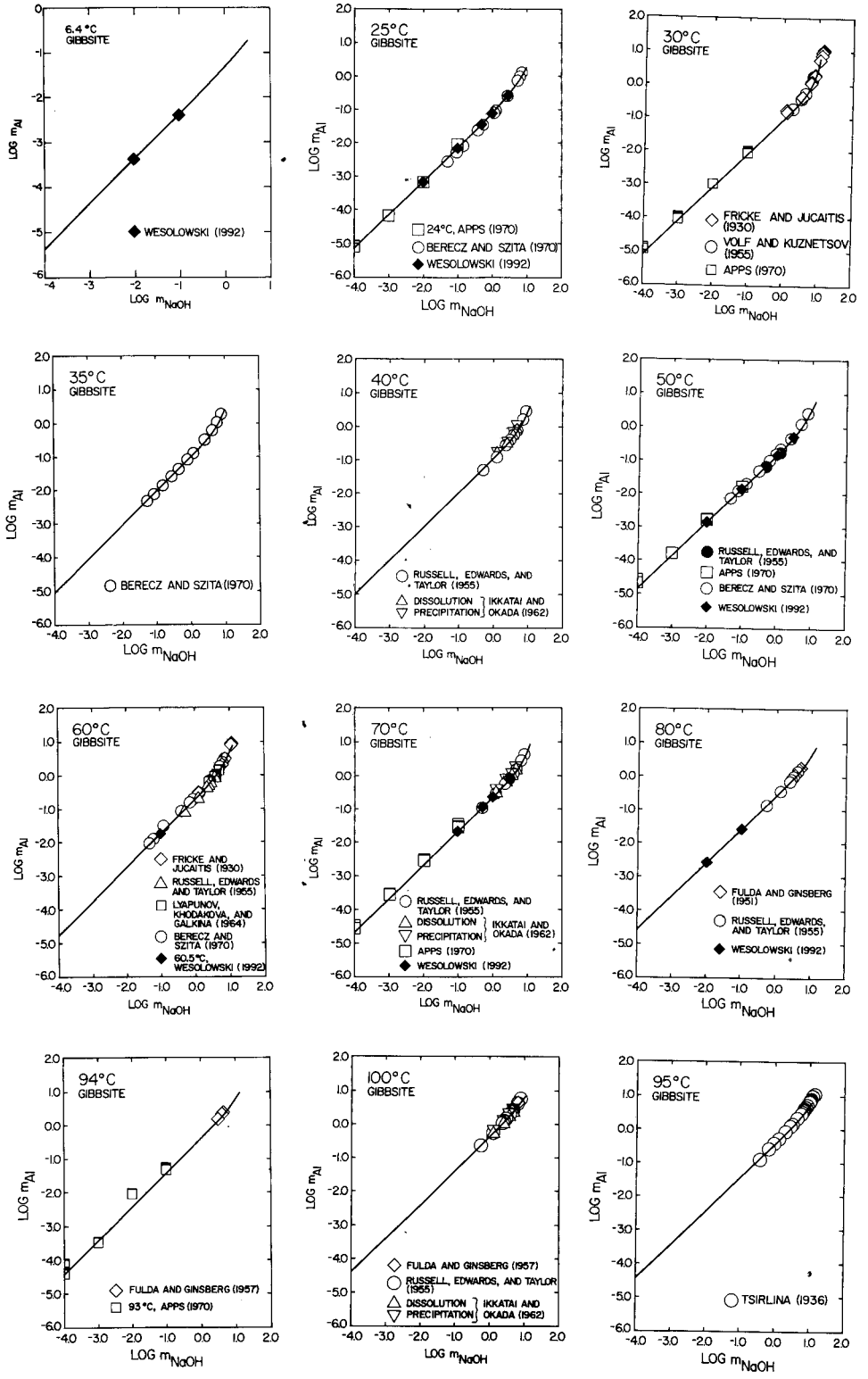
6.4 °C
GIBBSITE
WESOLOWSKI (1992)
25°C
GIBBSITE
24°C, APPS (1970)
BERECZ AND SZITA (1970)
WESOLOWSKI (1992)
30°C
GIBBSITE
FRICKE AND JUCAITIS (1930)
VOLF AND KUZNETSOV (1955)
APPS (1970)
35°C
GIBBSITE
BERECZ AND SZITA (1970)
40°C
GIBBSITE
RUSSELL, EDWARDS, AND TAYLOR (1955)
DISSOLUTION
PRECIPITATION
IKKATAI AND OKADA (1962)
50°C
GIBBSITE
RUSSELL, EDWARDS, AND TAYLOR (1955)
APPS (1970)
BERECZ AND SZITA (1970)
WESOLOWSKI (1992)
60°C
GIBBSITE
FRICKE AND JUCAITIS (1930)
RUSSELL, EDWARDS AND TAYLOR (1955)
LYAPUNOV, KHODAKOVA, AND GALKINA (1964)
BERECZ AND SZITA (1970)
60.5°C, WESOLOWSKI (1992)
70°C
GIBBSITE
RUSSELL, EDWARDS, AND TAYLOR (1955)
DISSOLUTION
PRECIPITATION
IKKATAI AND OKADA (1962)
APPS (1970)
WESOLOWSKI (1992)
80°C
GIBBSITE
FULDA AND GINSBERG (1951)
RUSSELL, EDWARDS, AND TAYLOR (1955)
WESOLOWSKI (1992)
94°C
GIBBSITE
FULDA AND GINSBERG (1957)
93 °C, APPS (1970)
100°C
GIBBSITE
FULDA AND GINSBERG (1957)
RUSSELL, EDWARDS, AND TAYLOR (1955)
DISSOLUTION
PRECIPITATION
IKKATAI AND OKADA (1962)
95°C
GIBBSITE
TSIRLINA (1936)
LOG m_{Al}
LOG m_{NaOH}

Figure 3

are primarily responsible for the fact that the curves in figure 3 approach linearity with increasing temperature.

Experimental solubilities of gibbsite reported by Russell, Edwards, and Taylor (1955) for 40°, 60°, 70°, and 80°C are depicted in figure 4. The dashed curves in the figure represent computed solubilities assuming AlO_2^- to be the only aqueous aluminum species with an appreciable concentration in solution. In contrast, the solid curves were generated by taking into account the formation of both AlO_2^- and $NaAlO_2^0$. It can be deduced from the curves shown in figure 4 that $NaAlO_2^0$ forms to a negligible degree at concentrations of NaOH $\sim \leq 0.5$ *m*, but it contributes appreciably to the solubility of gibbsite at higher NaOH concentrations. Note also that the relative stability of $NaAlO_2^0$ increases with increasing temperatures from 40° to 80°C.

Although it is not readily apparent in figures 3 and 4, comparison of the calculated and experimental solubilities of gibbsite depicted in these figures leads to the observation that the computed solubilities are slightly but systematically lower than their experimental counterparts in solutions with NaOH concentrations exceeding ~5 molal. Thermodynamic calculations indicate that these discrepancies cannot be attributed solely to uncertainties in calculated values of activity coefficients and/or the activity of H_2O. Instead, they are probably a consequence of the formation of polyatomic ions such as $Al_2O(OH)_6^{2-}$, $Al(OH)_6^{3-}$, $NaAl_2O(OH)_6^-$, and $Na_2Al(OH)_6^-$ at high NaOH concentrations, which were not taken into account in the regression calculations. This possibility is consistent with both spectroscopic data (see app. C) and theoretical calculations reported by Oelkers and Helgeson (1990, 1993a and b).

If $\bar{\gamma}_{OH^-} \approx \bar{\gamma}_{AlO_2^-}$, it follows from eqs (6) and (15) that values of Qa_w^2 computed from solubility data should be independent of the effective ionic strength ($\bar{I}$) of the solution. It can be seen in figure 5 that this is indeed the case for the bulk of the experimental data represented by the symbols at effective ionic strengths up to at least 7 at temperatures from 6.4° to 130°C at P_{SAT}.

The values of log *K* for reaction (3) that correspond to the logarithms of the values of Qa_w^2 represented by horizontal lines in figure 5 (see eq 15) are plotted as a function of temperature at P_{SAT} in figure 6 together with those taken directly from Kittrick (1966), Packter (1979), Apps, Neil, and Jun (1989), and Verdes, Gout, and Castet (1992). The curve shown in the figure was generated in the present study by regression of the data with eq (A-6) in app. A and

$$\log K = -\frac{\sum_i \hat{n}_i \Delta \bar{G}_i^o}{2.303RT}, \tag{18}$$

Fig. 3. Logarithm of the solubility of gibbsite in NaOH solutions at various temperatures and P_{SAT}. The curves represent the total concentration of aluminum computed as the sum of the molalities of AlO_2^- and $NaAlO_2^0$ (see text).

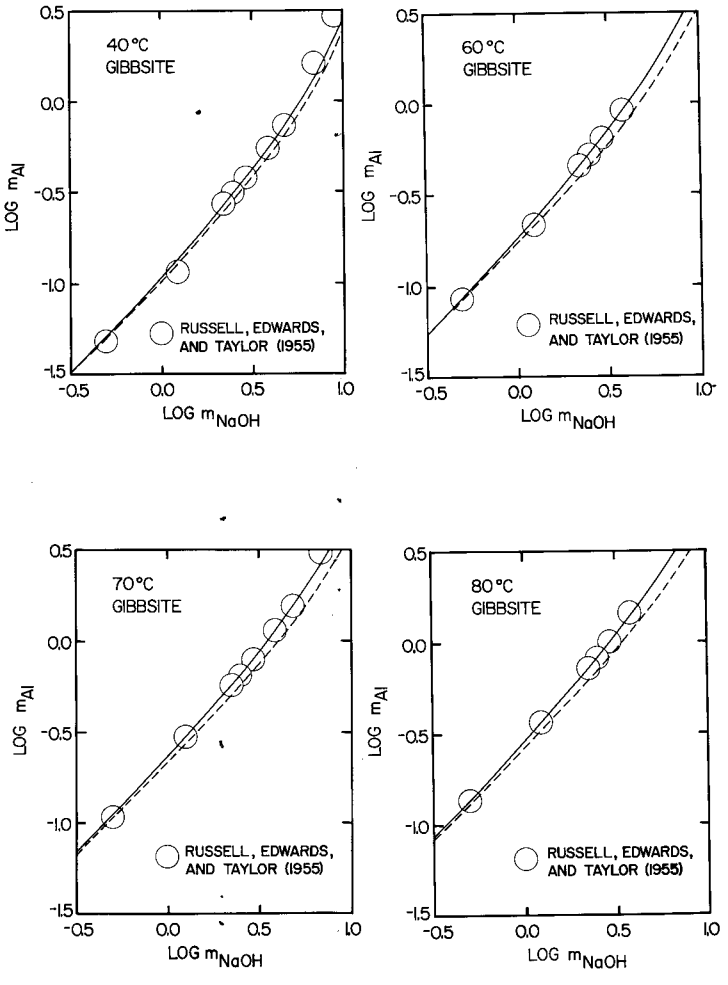

Fig. 4. Logarithm of the solubility of gibbsite in NaOH solutions at 40°, 60°, 70°, and 80°C. The dashed curves were generated assuming AlO_2^- to be the only aluminum species in solution. The solid curves represent the total concentration of aluminum computed as the sum of the molalities of AlO_2^- and $NaAlO_2^0$ (see text).

where $\Delta\overline{G}_i^\circ$ stands for the apparent standard partial molal Gibbs free energy of formation of the ith species in the reaction, $\hat{n}_i$ refers to the reaction coefficient of the subscripted species (which is positive for products and negative for reactants), and K denotes the equilibrium constant for the reaction. It can be seen in figure 6 that the regression curve is in close agreement with the bulk of the experimental data represented by the symbols. The difference in the trend of the highest temperature symbols and the regression curve in figure 6 is probably a

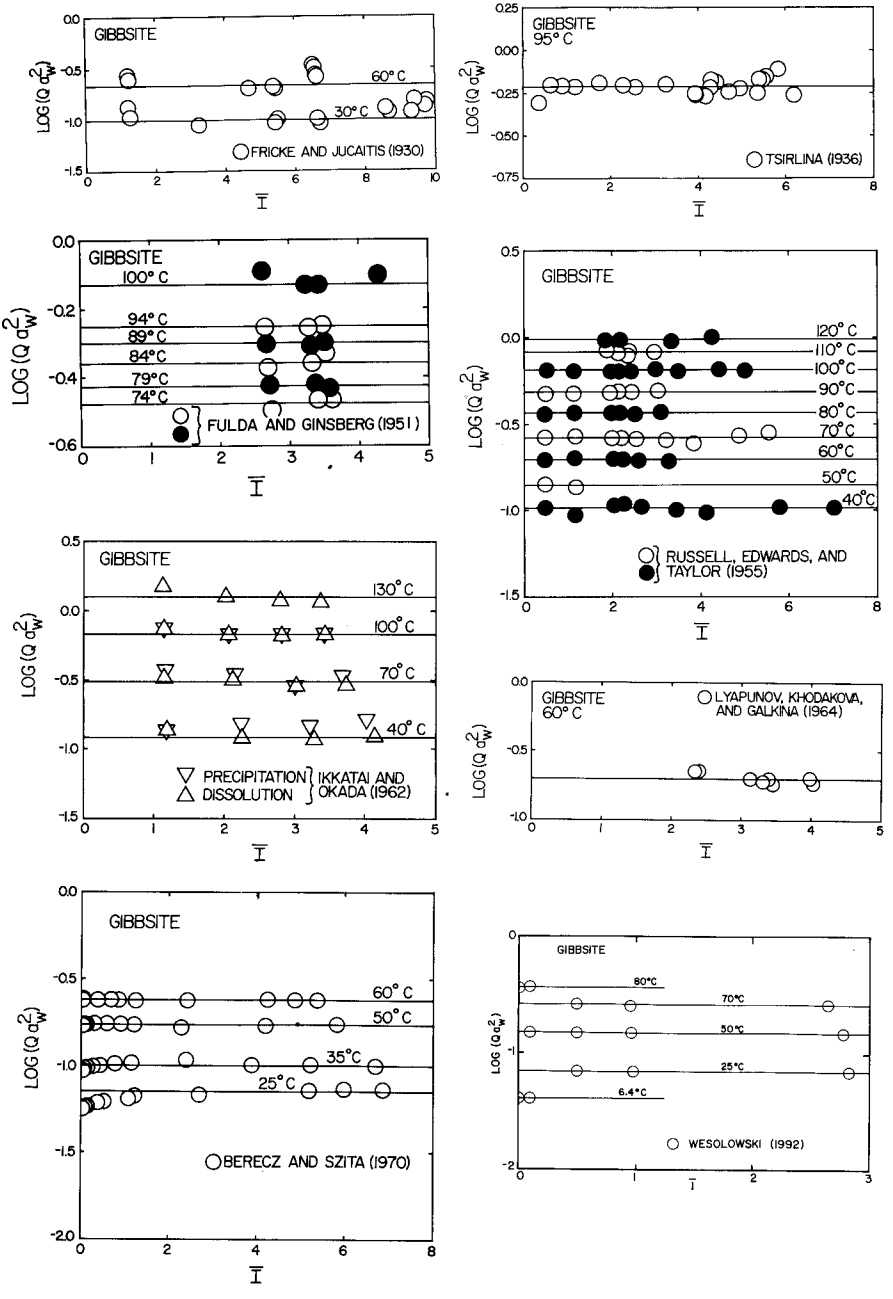

Fig. 5. Logarithm of Qa_w^2 (eq 15) for $Al(OH)_3$(gibbsite) + $OH^- \rightleftharpoons AlO_2^-$ + $2H_2O$ as a function of the effective ionic strength of the solution at various temperatures and P_{SAT}.

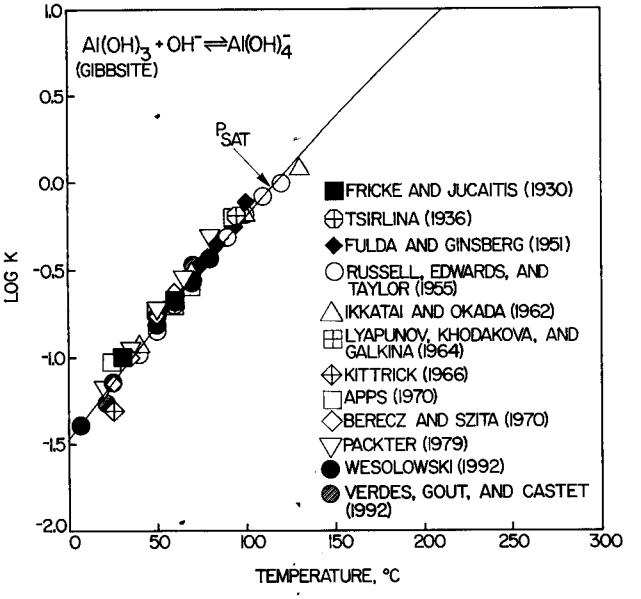

Fig. 6. Logarithm of the equilibrium constant for $Al(OH)_3$(gibbsite) + OH^- ⇌ $Al(OH)_4^-$ as a function of temperature at P_{SAT}. The symbols represent values of log K computed from experimental solubility data (see fig. 5) or taken directly from the literature. The curve was generated by regression of the data (see text).

consequence of the rapid dehydration of gibbsite at high temperatures to form boehmite in the experimental runs (Russell, Edwards, and Taylor, 1955; Khodakovsky, Katorcha, and Kuyunko, 1980). Regression of the experimental data represented by symbols in figure 6 resulted in values of $\Delta\overline{G}_f^\circ$ and $\overline{S}^\circ$ for AlO_2^- at 25°C and 1 bar of −198,700 ± 300 cal mol^{-1} and −7.0 ± 0.3 cal K^{-1} mol^{-1}, respectively. The first of these values is exactly consistent with that for $Al(OH)_4^-$, and the second is consistent to within 0.2 cal K^{-1} mol^{-1} with the value of $\overline{S}^\circ$ for $Al(OH)_4^-$ given by Wesolowski (1992) (see footnote 1). The value of $\Delta\overline{G}_f^\circ$ at 25°C and 1 bar for AlO_2^- calculated in the present study is also closely consistent with previous estimates by Shock and Helgeson (1988), Apps, Neil, and Jun (1989), and Hovey, Hepler, and Tremaine (1988), −198,465, −198,506, and −198,790 cal mol^{-1}, respectively.

Combining the values of $\Delta\overline{G}_f^\circ$ and $\overline{S}^\circ$ for AlO_2^- generated in the present study with $\overline{S}^\circ$ for $Al_{(c)}$, $O_{2(g)}$, and $H_{2(g)}$, and $\Delta\overline{H}_f^\circ$ for H_2O given by Cox, Wagman, and Medvedev (1989) yields a value of the standard partial molal enthalpy of formation from the elements of $Al(OH)_4^-$ at 25°C and 1 bar of −358,709 ± 310 cal mol^{-1} which is in fair agreement with recent calorimetric values generated by Chen, Xu, and Hepler (1991) and Zeng, Chen, and Chen (1994), who report −359,171 ± 360 and −359,575 ± 240 cal mol^{-1}, respectively.

Boehmite solubility data taken from the literature are represented by the symbols in figure 7. The solid curves in this figure represent solubilities computed in the present study by taking into account the formation of both AlO_2^- and $NaAlO_2^0$ in solution. The dashed curves represent the equilibrium concentration of AlO_2^- in the saturated solutions. It can be deduced in figure 7 that $NaAlO_2^0$ contributes substantially to the solubility of boehmite in NaOH solutions at temperatures $\geq$ 80°C and NaOH concentrations in excess of ~0.3 molal. The regression calculations resulted in a value of $-219{,}599 \pm 340$ cal mol^{-1} for $\Delta\overline{G}_f^\circ$ of boehmite at 25°C and 1 bar. This value is in close agreement with that of $-219{,}503 \pm 500$ cal mol^{-1} given by Hemingway, Robie, and Kittrick (1978), which was adopted by Hemingway, Robie, and Apps (1991).

Experimental solubilities of diaspore taken from the literature are depicted as symbols in figure 8. The calculated solubilities corresponding to the curves represent the cumulative contribution of both AlO_2^- and $NaAlO_2^0$ to the solubility of diaspore. Regression of the data led to a value of $\Delta\overline{G}_f^\circ$ for diaspore at 25°C and 1 bar of $-220{,}150 \pm 300$ cal mol^{-1}. It can be shown that this value is closely consistent with phase equilibrium relations among diaspore and corundum determined experimentally by Fyfe and Hollander (1964) and Haas (1972). Note in figure 8 that the solubilities computed from the thermodynamic properties of diaspore and the aqueous species given in tables 2 and 3 accurately reproduce all the experimental data, except those reported by Chang, Pak, and Li (1979). The latter values are systematically lower than those obtained from other experimental sources. At and above 330°C, diaspore tends to dehydrate to form corundum, which was observed experimentally by Wefers (1967) and confirmed by calculations carried out in the present study.[5]

Apps, Neil, and Jun (1989) carried out numerous solubility measurements of diaspore in dilute NaCl and NaCl + NaOH solutions at temperatures ranging from 99° to 350°C at P_{SAT}. Their experimental solubilities in 0.01 *m* NaCl solutions after adding NaOH to adjust the initial pH to 10.7 are depicted as a function of temperature in figure 9, together with solubility curves generated in the present study using thermodynamic data taken from tables 2 and 3. These experiments were carried out by raising the temperature every 12 hrs in 25°C increments from 100° to 350°C and then reducing the temperature by 25°C every 12 hrs until the temperature again reached 100°C. Solution samples were taken at the end of each equilibration period. It can be seen in the figure that the calculated solubilities represented by the solid curve are in close agreement with their experimental counterparts in samples collected with increasing temperature from 175° to 325°C. In contrast, the experimental solubilities in the samples collected with decreasing temperature

[5] At P_{SAT} diaspore dehydrates in pure H_2O at 360° ± 7°C (Fyfe and Hollander, 1964). However, in NaOH solutions the dehydration of diaspore may occur at temperatures as low as 320°C due to the decrease in the activity of H_2O by the presence of NaOH and $NaAlO_2$ in solution.

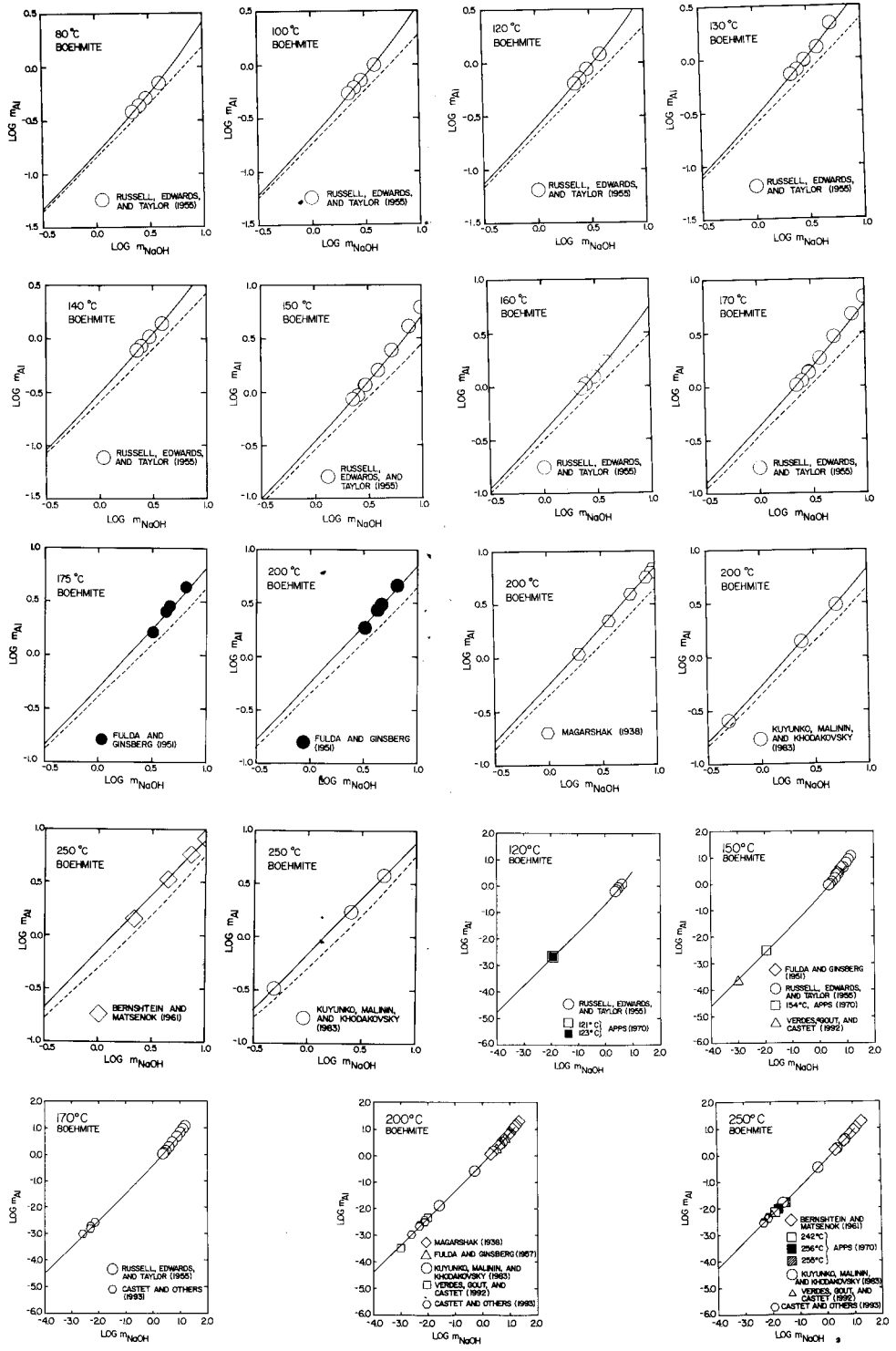

Fig. 7. Logarithm of the solubility of boehmite in NaOH solutions at various temperatures and P_{SAT}. The dashed curves were generated assuming AlO_2^- to be the only Al species in solution. The solid curves represent the total concentration of aluminum computed as the sum of the molalities of AlO_2^- and $NaAlO_2^0$ (see text).

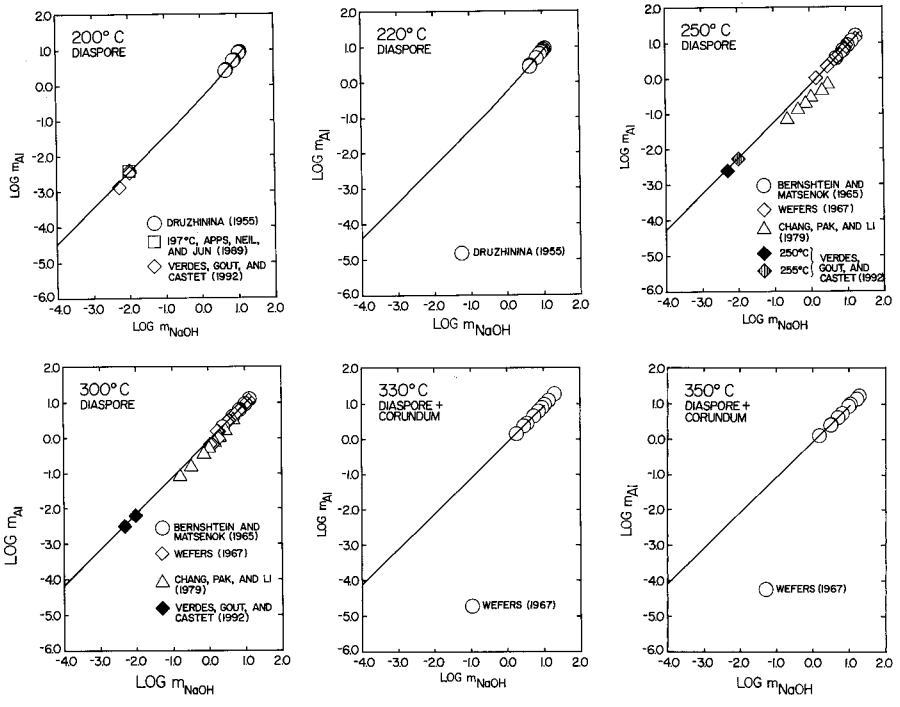

Fig. 8. Logarithm of the solubility of diaspore in NaOH solutions at various temperatures and P_{SAT}. The curves represent the total concentration of aluminum computed as the sum of the molalities of AlO_2^- and $NaAlO_2^0$.

from 350° to 275°C are systematically lower than the solid curve. These discrepancies can be attributed to reaction of the steel vessel used in the study with the aqueous phase which changed the pH and increased the total concentration of Fe, Mo, and other metals in the experimental solutions (Apps, Neil, and Jun, 1989). To assess the consequences of such a pH change, solubilities of diaspore were calculated in the present study using pH values reported by Apps, Neil, and Jun (1989). The results of these calculations are depicted as the dashed curve in figure 9, which is in close agreement with experimental data reported by Apps, Neil, and Jun (1989) for the decreasing temperature runs from 350° to 275°C. The fact that the solid curve in figure 9 is systematically higher than the experimental solubilities measured with increasing temperature at and below 150°C and lower than the experimental measurements made with decreasing temperature below 200°C is probably a consequence of the slow dissolution and precipitation rates at temperatures $\leq$ 175°C noted by Apps, Neil, and Jun (1989). It thus appears that the experimental solubilities

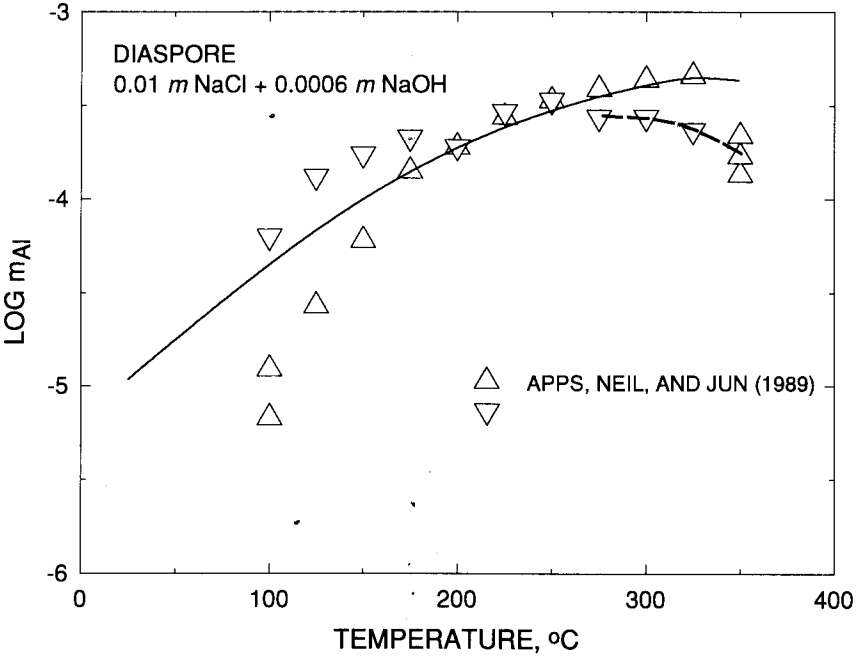

Fig. 9. Logarithm of the solubility of diaspore in NaCl + NaOH solutions as a function of temperature at P_{SAT}. The symbols represent experimental solubility measurements after successively raising the temperature in 25°C increments from 100° to 350°C (△) and then reversing the process (▽). The curves were generated in the present study (see text).

depicted in figure 9 are consistent with the thermodynamic properties of diaspore and AlO_2^- adopted in the present study.[6]

Values of log K for reaction (17) computed from experimental solubilities of gibbsite, boehmite, and diaspore are depicted as symbols in figure 10. Regression of these values with eqs (18) and (A-6) in app. A using thermodynamic data for Na^+ and AlO_2^- taken from table 3 resulted in the curve shown in the figure, together with the values of the standard molal thermodynamic properties and c_1, c_2, and $\omega_{Pr,Tr}$ parameters for $NaAlO_2^0$ shown in this table. It can be seen in figure 10 that the regression curve is in close agreement with all but a few of the log K values represented by the symbols. The computed value of log K for reaction (17) at 300°C and P_{SAT} (−1.72) is within 0.02 log units of the value (−1.70) derived by Castet and others (1992) from their solubility study of boehmite in NaCl + NaOH solutions.

[6] Calculations carried out in the present study at the electrolyte concentrations used by Apps, Neil, and Jun (1989) indicate that $NaAlO_2^0$ did not contribute substantially to the total Al concentrations in these solutions.

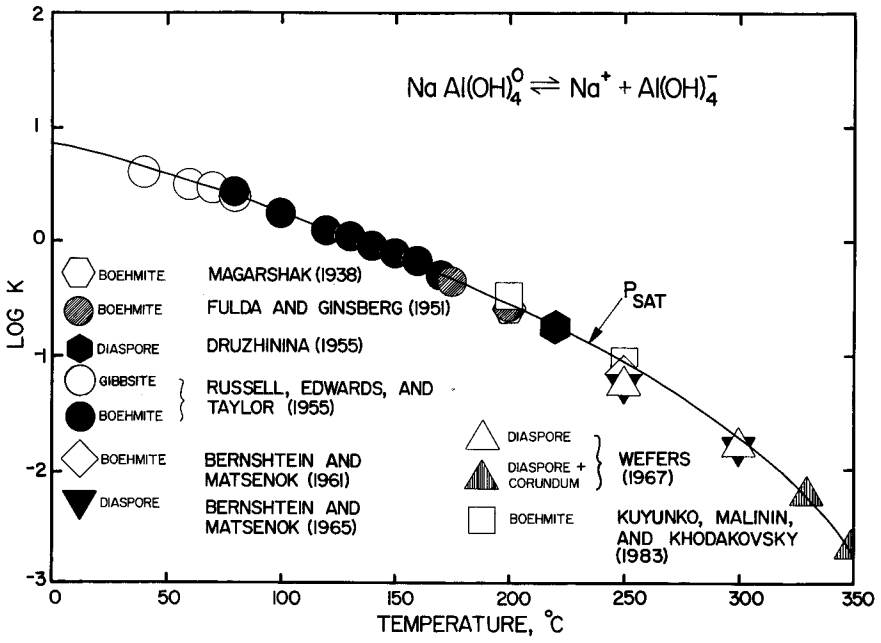

Fig. 10. Logarithm of the dissociation constant of $NaAl(OH)_4^0$ as a function of temperature at P_{SAT}. The symbols represent values of log K retrieved in the present study from solubility data reported in the literature, but the curve was generated using thermodynamic data taken from table 3 (see text).

The solubility data for P_{SAT} shown in figures 7 and 8 cannot be used to retrieve values of the a_1, a_2, a_3, and a_4 equations of state parameters for $NaAlO_2^0$ because the effect of P_{SAT} on log K is negligible. However, these parameters can be estimated in a first approximation by adopting the hypothesis that the pressure dependence of log K for reaction (17) is similar to that of log K for the dissociation of $NaBO_2^0$ reported by Rowe, Tran, and Atkinson (1989) and Rowe and Atkinson (1990). Assuming this to be the case, Rowe, Tran, and Atkinson's (1989) values of the standard partial molal compressibility and volume of dissociation of $NaBO_2^0$ at 25°C and 1 bar (-1.6×10^{-3} cm^3 mol^{-1} bar^{-1} and 8.39 cm mol^{-1}, respectively) were used together with eqs (A-1), (A-2), and (A-19) to (A-22) to estimate the provisional values of a_1, a_2, a_3, and a_4 for $NaAlO_2^0$ listed in table 3. The thermodynamic data and equations of state parameters for Na^+, AlO_2^-, and $NaAlO_2^0$ given in this table were then used to predict log K for reaction (17) over a wide range of pressure and temperature. These values are represented by the curves depicted in figure 11.

The thermodynamic properties at 25°C and 1 bar, together with the equations of state parameters for AlO_2^- and $NaAlO_2^0$ generated in the

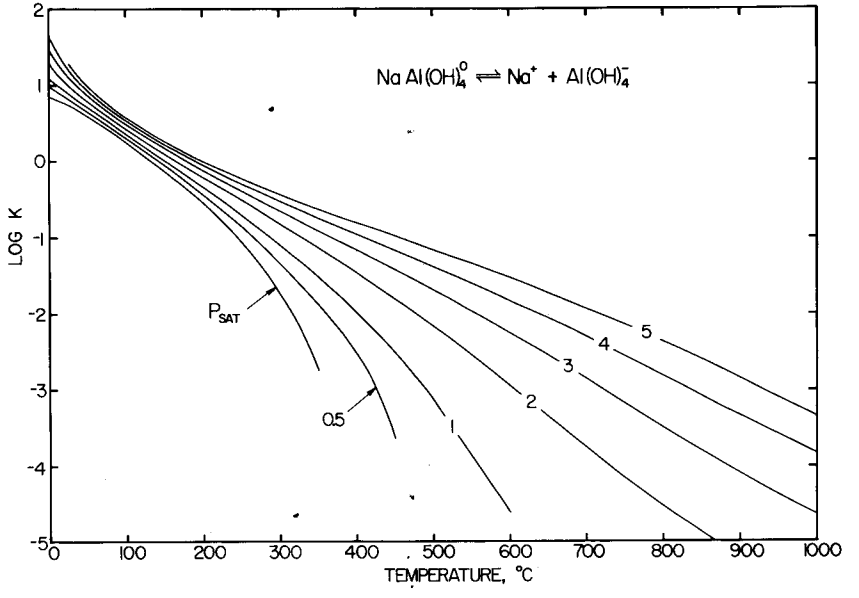

Fig. 11. Logarithm of the dissociation constant of $NaAl(OH)_4^0$ as a function of temperature and pressure (see text).

manner described above (table 3) can be used to predict mineral solubilities in alkaline solutions over wide ranges of pressure and temperature. Comparison of such predictions with experimental solubilities that were not used in regression calculations affords a test of both the validity of the thermodynamic data and parameters retrieved in the present study and the speciation models employed in the solubility calculations. A number of such comparisons are summarized below.

The logarithms of experimental solubilities of gibbsite in NaCl + NaOH solutions reported for 6.4° to 80°C by Lyapunov, Khodakova, and Galkina (1964) and Wesolowski (1992) are depicted as a function of log m_{NaCl} in figure 12, together with solubility curves generated independently in the present study. The predicted curves in this figure are within ±0.05 log units of the experimental solubilities at NaCl concentrations up to 5 molal. The slight increase in the logarithm of the solubility of gibbsite with increasing NaCl concentration in figure 12 is a consequence of the increasing degree of formation of $NaAlO_2^0$ in these solutions.

Experimental solubilities of corundum in NaOH solutions at temperatures from 400° to 700°C and pressures from 0.3 to 7 kb have been reported by Yalman, Shaw, and Corwin (1963), Barns, Laudise, and Shields (1963), Anderson and Burnham (1967), and Pascal and Anderson (1989). A number of these data are represented by the symbols plotted in the diagrams depicted in figure 13. The solid curves in these

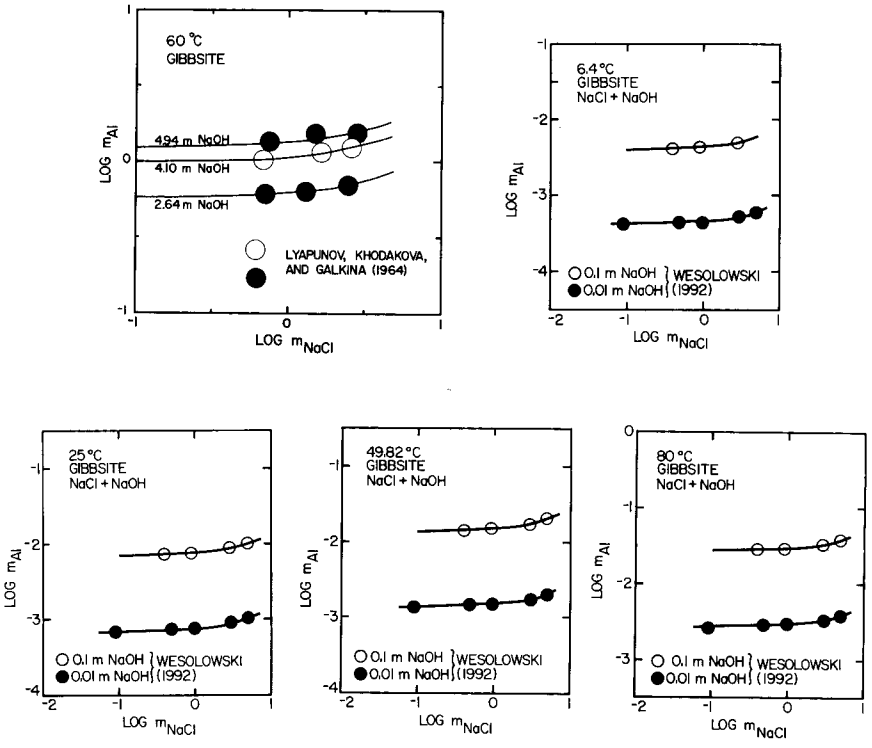

Fig. 12. Logarithm of the solubility of gibbsite in NaCl + NaOH solutions at various temperatures and 1 bar. The curves were generated using thermodynamic data given in table 3 (see text).

diagrams correspond to solubilities calculated independently in the present study. These calculations were carried out using b_γ values for aqueous NaOH taken from table B-3 in app. B by assuming in a first approximation that the Setchénow coefficients for $NaOH^0$ and $NaAlO_2^0$ in supercritical NaOH solutions are equal to those calculated by Oelkers and Helgeson (1991) for $NaCl^0$ in NaCl solutions. The dashed curves represent calculated concentrations of AlO_2^- in the saturated solutions. It can be deduced from figure 13 that $NaAlO_2^0$ is present in these solutions at concentrations that are comparable to or exceed those of AlO_2^- by up to a log unit. The solubility curves generated independently from the experimental data represented by the symbols in figures 12 and 13 are within ± 0.05 log units of their experimental counterparts at temperatures from 6.4° to 700°C and pressures from 1 to 2500 bar. This observation strongly supports the validity and generality of the equations of state predictions based on the thermodynamic analysis of low-temperature solubility data described in the preceeding pages.

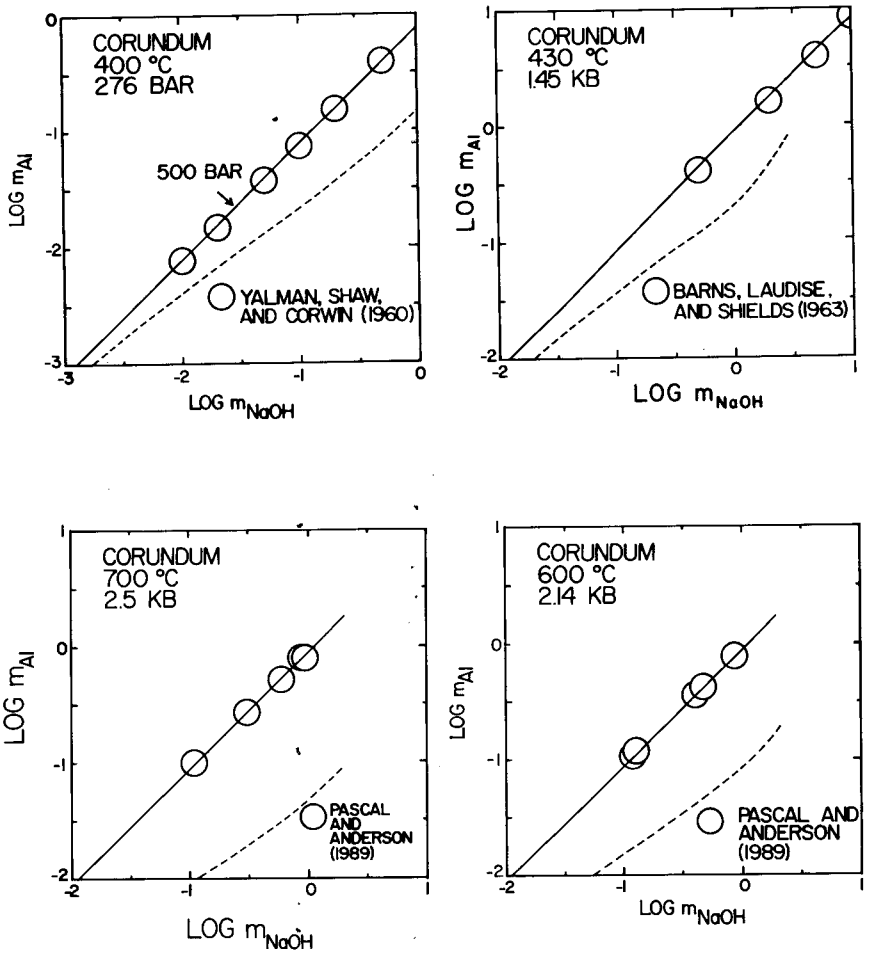

Fig. 13. Logarithm of the solubility of corundum in NaOH solutions at high pressures and temperatures. The solid curves were generated assuming possible contributions by both AlO_2^- and $NaAlO_2^0$ to the solubility, but the dashed curves represent equilibrium concentrations of AlO_2^- in these solutions (see text).

As indicated above, the standard partial molal thermodynamic properties and equations of state parameters for Al^{3+} and $Al(OH)_4^-$ computed in the present study were generated independently of one another. Similarly, $\Delta\overline{G}_f^o$ of boehmite (which was calculated from experimental solubilities in alkaline solutions) was obtained independently from the thermodynamic properties of the aluminum ion. Consequently, these various properties and parameters can be used in conjunction with one another to assess their validity by predicting equilibrium constants at

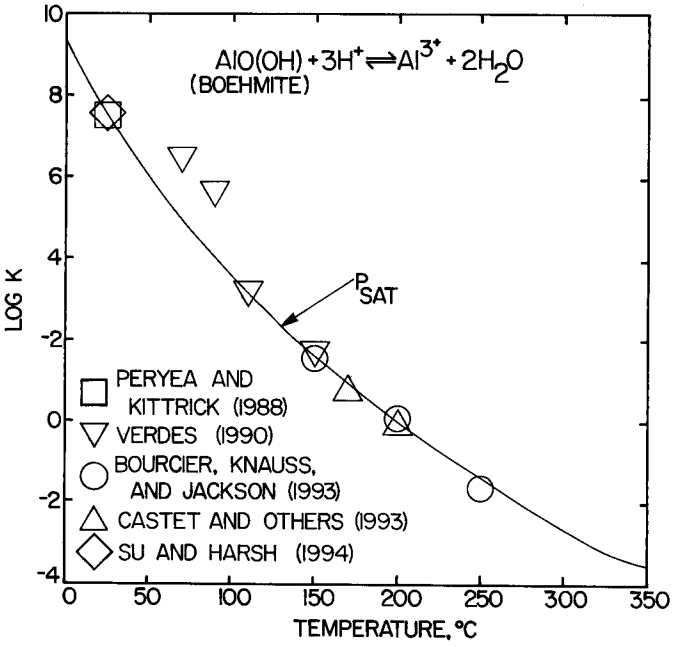

Fig. 14. Logarithm of the equilibrium constant for AlO(OH)(boehmite) + $3H^+ \rightleftharpoons Al^{3+} + 2H_2O$ as a function of temperature at P_{SAT}. The symbols represent experimental data taken from the literature, but the curve was generated independently using data taken from tables 2 and 3 (see text).

elevated temperatures for reactions for which experimental data are available but were not used in the regression calculations. For example, the logarithm of the equilibrium constant for the reaction

$$\underset{\text{(boehmite)}}{AlO(OH)} + 3H^+ = Al^{3+} + 2H_2O \qquad (19)$$

is shown as a function of temperature at P_{SAT} in figure 14. The symbols in this figure represent experimental data reported in the literature, but the curve was generated independently in the present study. It can be seen in figure 14 that the predicted curve is in close agreement with all the experimental data, except for those at 70° and 90°C reported by Verdes (ms).[7] At 25°C and 1 bar, the value of log K computed in the present study (7.551) is in excellent agreement with the experimental values measured by Peryea and Kittrick (1988) and Su and Harsh (1994), who report 7.49 ± 0.09 and 7.54 ± 0.07, respectively. It should perhaps be emphasized that values of log K for reaction (19) retrieved from solubility measurements at elevated temperatures are subject to comparable or

[7] Quoted by Castet (ms).

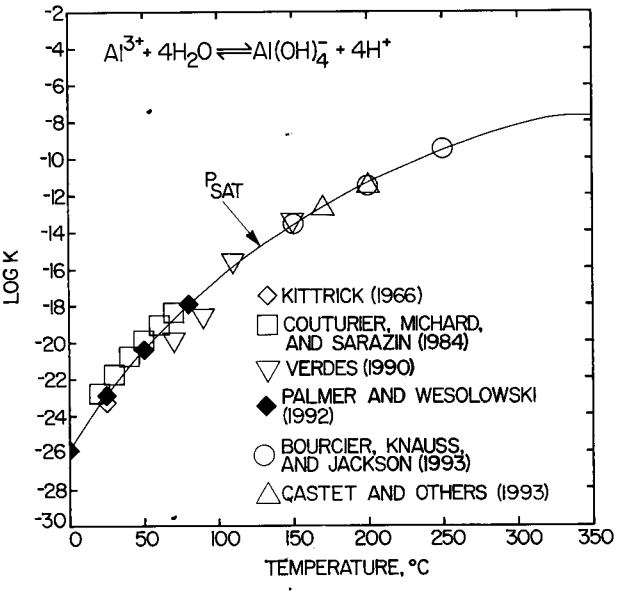

Fig. 15. Logarithm of the equilibrium constant for $Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+$ as a function of temperature at P_{SAT}. The symbols represent experimental data taken from the literature, but the curve was generated independently in the present study (see text).

higher uncertainties than those associated with the predicted curve shown in figure 14. The small concentration of Al^{3+} in the experimental solutions and ambiguities in assessing activity coefficients of Al^{3+} in solutions with high ionic strengths are primarily responsible for these uncertainties.

The logarithm of the equilibrium constant for

$$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+ \qquad (20)$$

can also be predicted independently of those reported in the literature. Computed and experimental values of log K for reaction (20) are shown as a function of temperature at P_{SAT} in figure 15, where it can be seen that the predicted equilibrium constants represented by the curve are closely consistent with those retrieved from gibbsite solubilities in acid and alkaline solutions by Wesolowski (1992) and Palmer and Wesolowski (1992). The curve generated in the present study is also in reasonable agreement with log K values retrieved from experimental boehmite solubilities at temperatures from 90° to 250°C reported by Verdes (ms), Bourcier, Knauss, and Jackson (1993), and Castet and others (1993). However, the predicted curve is ~0.6 log units lower than the log K values for reaction (20) calculated by Couturier, Michard, and Sarazin (1984) from their potentiometric measurements at temperatures ranging from 20° to 80°C.

$Al(OH)^{2+}$ and $Al(OH)_2^+$

The thermodynamic properties at 25°C and 1 bar together with the equations of state parameters for the aluminum ion adopted in the present study (table 3) were used in conjunction with experimental data reported in the literature for the hydrolysis of Al^{3+} to calculate thermodynamic properties and equations of state coefficients for $Al(OH)^{2+}$ and $Al(OH)_2^+$. Values of $\Delta\overline{G}_f^o$, $\overline{S}^o$, c_1, and c_2 for these species were computed from experimental values of log K as a function of temperature at P_{SAT} for reaction (2) and

$$Al(OH)^{2+} + H_2O = Al(OH)_2^+ + H^+, \qquad (21)$$

using values of ω_{P_r,T_r} estimated from correlation algorithms given by Shock and Helgeson (1988). Because the effect of P_{SAT} on log K for reactions (2) and (21) is negligible at temperatures $\sim <300$°C, the a_1, a_2, a_3, and a_4 equations of state parameters for the aqueous species in the reactions were set to zero. The regression calculations were carried out using the experimental value of log K for reaction (2) at 25°C and 1 bar (-4.95 ± 0.03) reported by Palmer and Wesolowski (1993) to compute $\Delta\overline{G}_f^o$ for $Al(OH)^{2+}$, together with a value of $\Delta\overline{H}_f^o$, for $Al(OH)^{2+}$ generated from the value of $\Delta\overline{H}^o$ for reaction (2) at 25°C and 1 bar (11,900 ± 500 cal mol^{-1}) given by Baes and Mesmer (1976). $\overline{S}^o$ for $Al(OH)^{2+}$ was then calculated from $\Delta\overline{S}^o$ for reaction (2). These values of $\Delta\overline{G}_f^o$, $\Delta\overline{H}_f^o$, and $\overline{S}^o$ for $Al(OH)^{2+}$ at 25°C and 1 bar are given in table 3. The computed uncertainties associated with them are ±310 and ±620 cal mol^{-1} and ±2.3 cal mol^{-1} K^{-1}, respectively.

It can be seen in figure 16 that the regression curve is consistent to within ±0.1 log unit with the bulk of the experimental values of log K derived from experimental potentiometric and solubility measurements at temperatures ≤200°C. Palmer and Wesolowski (1993) report $\Delta\overline{H}^o$ for reaction (2) to be 13,241 ± 240 cal mol^{-1}. This value is based on their potentiometric measurements at temperatures ranging from 25° to 125°C, adjusted equilibrium constants taken from Schofield and Taylor (1954) and Volokhov and others (1971) and those given by Castet and others (1993). This value differs from Baes and Mesmer's (1976) value adopted in the present study (see above) by 1341 cal mol^{-1}. Activity coefficient adjustments made by Palmer and Wesolowski (1993) of the log K values for reaction (2) given by Schofield and Taylor (1954) and Volokhov and others (1971) are well within the experimental uncertainties of the potentiometric titrations. Hence, these adjustments cannot account for the large difference in $\Delta\overline{H}^o$ for reaction (2) noted above. Palmer and Wesolowski (1993) regressed a set of selected values of log K for reaction (2) as a function of temperature assuming the standard partial molal heat capacity of the reaction to be zero. However, thermodynamic calculations carried out in the present study indicate that $\Delta\overline{C}_P^o$ for reaction (2) may be as large as 20 cal mol^{-1}·K^{-1}, which would more than account for the

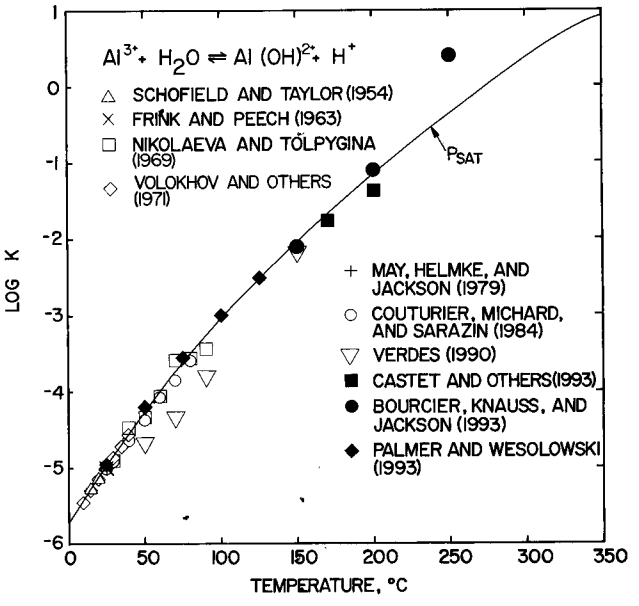

Fig. 16. Logarithm of the equilibrium constant for $Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$ as a function of temperature at P_{SAT}. The symbols represent experimental data taken from the literature, but the curve was generated by regression of the data (see text).

discrepancy in the values of $\Delta\overline{H}^o$ for reaction (2) given by Palmer and Wesolowski (1993) and Baes and Mesmer (1976).

The logarithm of the equilibrium constant for reaction (21) is depicted as a function of temperature at P_{SAT} in figure 17. It can be seen in this figure that the values of log K for this reaction generated from potentiometric data by Frink and Peech (1963), Nazarenko and Nevskaya (1969), Nikolayeva and Tolpygina (1969), Brown and others (1985) and solubililty measurements by May, Helmke, and Jackson (1979), Kuyunko, Malinin, and Khodakovsky (1983), Verdes (ms), Bourcier, Knauss, and Jackson (1993), Castet and others (1993), and Wesolowski and Palmer (1994) differ by as much as 1 log unit at temperatures ranging from 25° to 250°C. These large discrepancies can be attributed to the fact that $Al(OH)_2^+$ predominates only over a narrow range of pH where Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_3^0$ may be present in somewhat smaller but comparable concentrations.

The value of log K for reaction (21) reported by May, Helmke, and Jackson (1979) (-5.15 ± 0.3) was calculated from their experimental gibbsite solubilities in dilute (0.001 M) acetate solutions with pHs ranging from 5 to 6. Calculations carried out in the present study using stability constants for $Al(CH_3COO)^{2+}$, $Al(CH_3COO)_2^+$, $Al(OH)(CH_3COO)^+$, and $Al(OH)_2(CH_3COO)^0$ summarized by Palmer and Bell (1994) indicate that

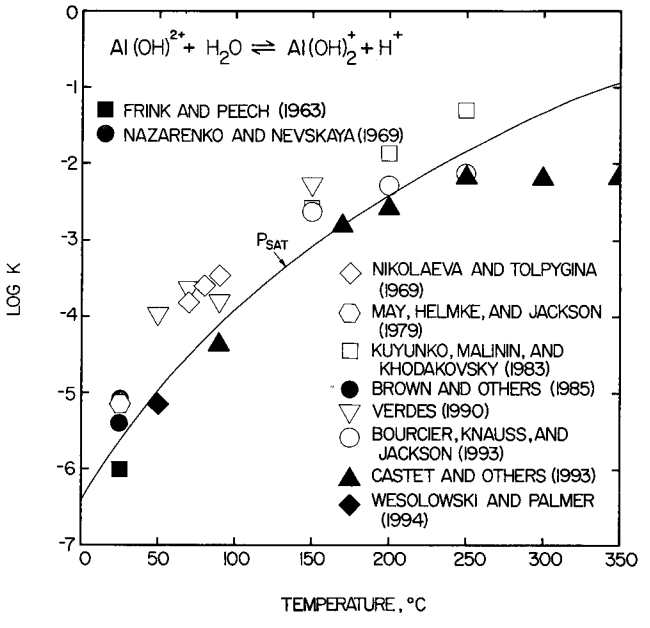

Fig. 17. Logarithm of the equilibrium constant for $Al(OH)^{2+} + H_2O = Al(OH)_2^+ + H^+$ as a function of temperature at P_{SAT}. The symbols represent experimental data taken from the literature, but the curve was generated by regression of the data (see text).

these species did not contribute significantly to the gibbsite solubilities measured by May, Helmke, and Jackson (1979). Recently, Wesolowski and Palmer (1994) carried out an extensive study of the solubility of gibbsite at 50°C using acetate, Bistris, and Tris pH buffers. In doing so, Wesolowski and Palmer (1994) obtained a value of -5.15 ± 0.18 for log K of reaction (21) at 50°C and 1 bar, which they concluded is consistent with -5.39 ± 0.22 at 25°C and 1 bar. The latter value is nearly the same as that (-5.40 ± 0.05) calculated by Wesolowski and Palmer (1994) from potentiometric data reported by Brown and others (1985), and it is consistent within the reported uncertainties with that given by May, Helmke, and Jackson (1979).

It can be seen in figure 17 that the values of log K for reaction (21) derived by Kuyunko, Malinin, and Khodakovsky (1983) from their boehmite solubility data at 200° and 250°C are substantially greater than those reported by Bourcier, Knauss, and Jackson (1993) and Castet and others (1993). The higher solubilities in acid solutions reported by Kuyunko, Malinin, and Khodakovsky (1983) are probably due at least in part to the presence in solution of F^- leached from the teflon used in their reaction vessel, which was demonstrated by Castet (ms) to be a potential problem in using teflon in hydrothermal experiments. The

standard partial molal thermodynamic properties and HKF c_1 and c_2 coefficients for $Al(OH)_2^+$ given in table 3 were generated by regressing the values of log K corresponding to the symbols shown in figure 17 that represent experimental values taken from Brown and others (1985) and Wesolowski and Palmer (1994) at 25° and 50°C, respectively, together with those for temperatures from 170° to 250°C reported by Bourcier, Knauss, and Jackson (1993) and Castet and others (1993). However, the value of log K at 90°C given by Castet and others (1993) was omitted from the regression calculations, because it can be demonstrated (see below) that the solubilities they report for boehmite in acid solutions at 90°C are not thermodynamically consistent with the solubilities they obtained at higher temperatures. The calculations resulted in $\log K = -5.63 \pm 0.3$ for reaction (21) at 25°C and 1 bar and values of $\Delta\overline{G}_f^\circ$, $\Delta\overline{H}_f^\circ$, and $\overline{S}^\circ$ for $Al(OH)_2^+$ at the reference temperature and pressure of $-215{,}465 \pm 510$ cal mol^{-1}, $-241{,}825 \pm 710$ cal mol^{-1}, and -17.00 ± 2.9 cal K^{-1} mol^{-1}, respectively. The latter values are listed in table 3 together with the regression values of c_1 and c_2 for the species.

The thermodynamic properties and equations of state parameters given in tables 2 and 3 for boehmite, $Al(OH)^{2+}$, and $Al(OH)_2^+$ were used to calculate values of the logarithm of the equilibrium constants for

$$\underset{\text{(boehmite)}}{AlO(OH)} + 2H^+ \rightleftharpoons Al(OH)^{2+} + H_2O, \tag{22}$$

and

$$\underset{\text{(boehmite)}}{AlO(OH)} + H^+ \rightleftharpoons Al(OH)_2^+, \tag{23}$$

as a function of temperature at P_{SAT}. These values are represented by the curves depicted in figures 18 and 19. The symbols in the figures correspond to values of log K taken from the literature. It can be seen in figures 18 and 19 that the log K values for reactions (22) and (23) computed in the present study fall within the scatter of the experimentally derived values at temperatures ≥ 150°C. Because the curves in these figures are within the combined experimental and computational uncertainties reported by Bourcier, Knauss, and Jackson (1993), the values of the standard molal thermodynamic properties and equations of state parameters generated in the present study for $Al(OH)^{2+}$ and $Al(OH)_2^+$ (table 3) afford close approximation of the experimental solubilities of boehmite measured by Bourcier, Knauss, and Jackson (1993) at temperatures from 150° to 250°C (see below).

$Al(OH)_3^0$

Values of the thermodynamic properties of this species are difficult to calculate from solubility data at low temperatures because the species is present under these conditions only at low concentrations which are of

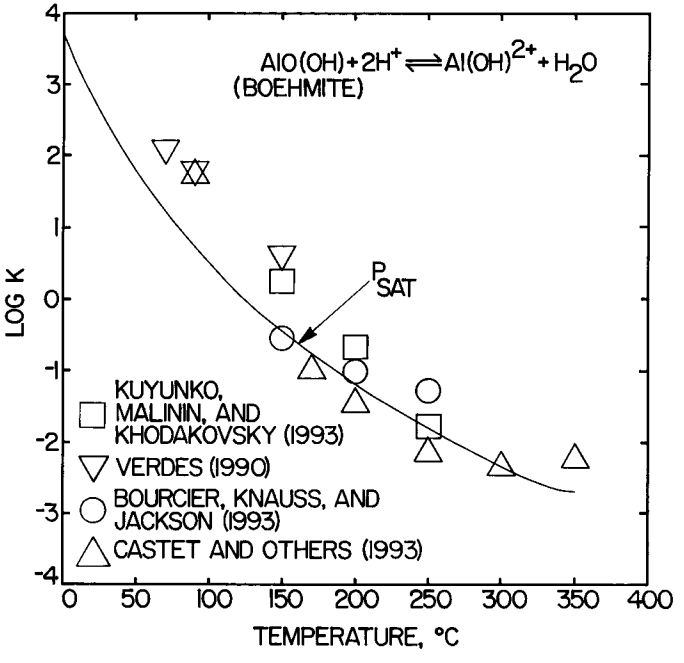

Fig. 18. Logarithm of the equilibrium constant for reaction AlO(OH)(boehmite) + $2H^+ \rightleftharpoons Al(OH)^{2+} + H_2O$ as a function of temperature at P_{SAT}. The symbols represent experimental data taken from the literature, but the curve was generated independently in the present study (see text).

the same order of magnitude as the analytical detection limit for aluminum in near-neutral solutions. For example, May, Helmke, and Jackson (1979) and Khodakovsky, Katorcha, and Kuyunko (1980) estimated the concentration of $Al(OH)_3^0$ in equilibrium with gibbsite at 25°C and 1 bar to be $\leq 10^{-8}$ mol kg^{-1}. On the basis of their gibbsite solubility data, Wesolowski and Palmer (1994) estimated the equilibrium concentration of $Al(OH)_3^0$ at 50°C to be $10^{-8.6}$ mol kg^{-1}. The standard partial molal thermodynamic properties of $Al(OH)_3^0$ were calculated in the present study from experimental solubilities of boehmite consistent with

$$\underset{\text{(boehmite)}}{AlO(OH)} + H_2O \rightleftharpoons Al(OH)_3^0, \tag{24}$$

together with those of corundum in supercritical H_2O (see below).

Experimental values of log K reported in the literature for reaction (24) at temperatures ≤ 350°C at P_{SAT} are represented by the symbols in figure 20. The arrows in the figure denote ranges of estimates of log K at 25° and 50°C computed in the present study by assuming that the equilibrium concentrations of $Al(OH)_3^0$ in solutions saturated with gibb-

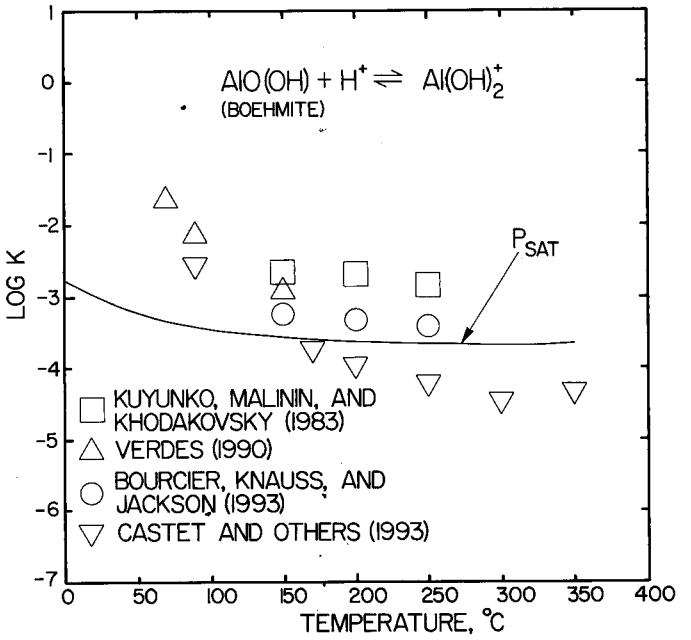

Fig. 19. Logarithm of the equilibrium constant for AlO(OH)(boehmite) + $H^+ \rightleftharpoons Al(OH)_2^+$ as a function of temperature at P_{SAT}. The symbols represent experimental data taken from the literature, but the curve was generated independently in the present study (see text).

site at these temperatures do not exceed 10^{-8} mol kg^{-1} (May, Helmke, and Jackson, 1979; Wesolowski and Palmer, 1994).[8] The solid curve in figure 20 was generated by regression of the experimental values of log K shown in the figure, together with the solubilities of corundum in H_2O at 670°C and pressures from 3 to 5 kb reported by Becker, Cemič, and Langer (1983) (see below). It can be seen in figure 20 that the curve falls within the scatter of the experimental data represented by the symbols. The large discrepancies among the various data represented by the

[8] The value of $\Delta\overline{G}_f^\circ$ for Al^{3+} adopted in the present study and that of log K for reac-tion (1) given by May, Helmke, and Jackson (1979) (8.11) are consistent with −275,513 cal mol^{-1} for $\Delta\overline{G}_f^\circ$ of gibbsite at 25°C and 1 bar. Although this value is 512 cal mol^{-1} less negative than that shown in table 2, it represents the gibbsite sample used in their experiments. Accordingly, this value was used together with that of $\Delta\overline{G}_f^\circ$ for boehmite in table 2 to compute the logarithm of the equilibrium constant at 25°C and 1 bar for

$$\underset{\text{(gibbsite)}}{Al(OH)_3} \rightleftharpoons \underset{\text{(boehmite)}}{AlO(OH)} + H_2O,$$

which resulted in −0.56. Adding this value to the logarithm of the molality of $Al(OH)_3^0$ in equilibrium with gibbsite at 25°C and 1 bar estimated by May, Helmke, and Jackson (1979) (−8.0) yields an upper concentration limit for $Al(OH)_3^0$ in equilibrium with boehmite of $10^{-8.56}$ *m* at the reference pressure and temperature.

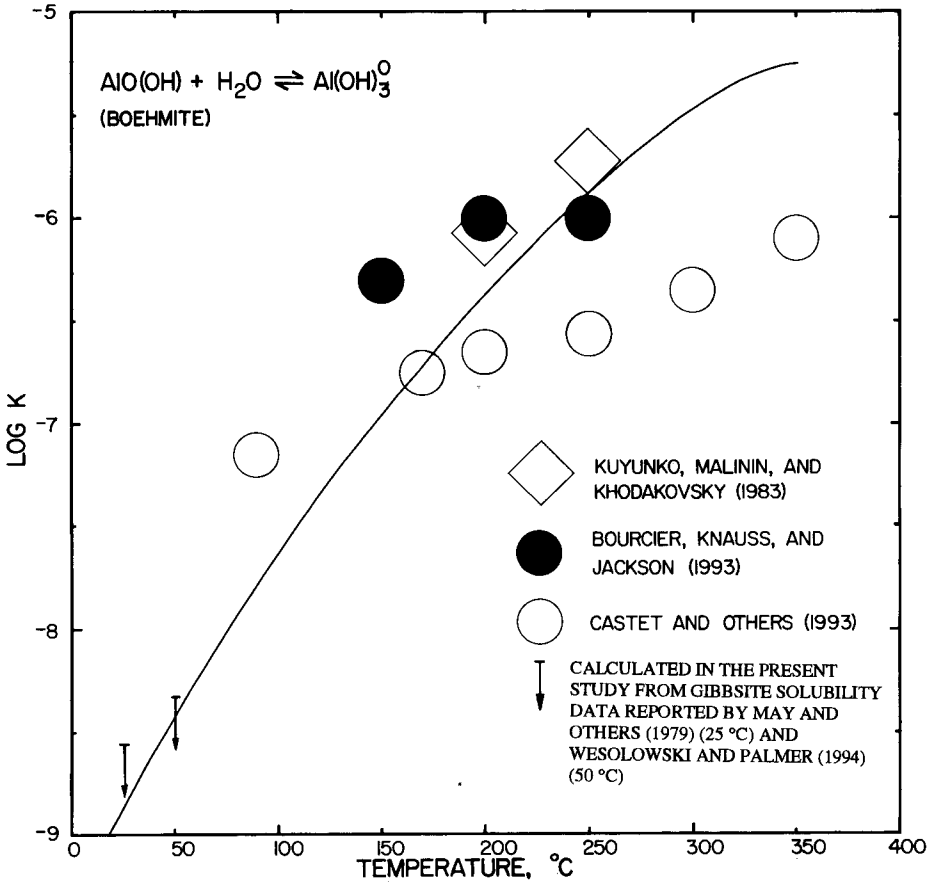

Fig. 20. Logarithm of the equilibrium constant for AlO(OH)(boehmite) + $H_2O \rightleftharpoons Al(OH)_3^0$ as a function temperature at P_{SAT}. The symbols represent experimental data taken from the literature, but the curve was generated by regression of the data (see text).

symbols shown in this figure can only be resolved by further experimentation. In the meantime, the curve in figure 20 provides an interim prediction of log K for reaction (24) which is consistent with the corundum solubilities in H_2O discussed below.

Thermodynamic calculations carried out by Pokrovskii and Helgeson (1989) and Anderson and others (1991) indicate that corundum dissolves in water to yield comparable concentrations of $Al(OH)_3^0$ and $Al(OH)_4^-$ at supercritical temperatures and pressures. Accordingly, both of these species were considered in regressing experimental corundum solubilities reported in the literature. Experimental solubilities of corundum in H_2O have been reported by Morey (1957), Anderson and Burnham (1967) Burnham, Ryzhenko, and Schitel (1973), Ganeyev and

Rumyantsev (1974), Becker, Cemič, and Langer (1983), and Ragnarsdóttir and Walther (1985). However, the general agreement among the various data sets is poor. Thermodynamic analysis of these various experimental corundum solubilities indicates that those reported by Becker, Cemič, and Langer (1983) for pressures ranging from 3 to 20 kb at 670°C are probably the most reliable.

Becker, Cemič, and Langer (1983) used a weight loss method to measure the solubility in H_2O of polished synthetic corundum spheres at 670°C and pressures from 2.5 to 20 kb. Although the pHs of the solutions after the experiments and the extent to which the contaminants present in the corundum sample (Ti, Cr, and Fe) affected the results of their study are not known, it can be shown that the pressure dependence of the experimental solubilities they report is consistent with predominance of $Al(OH)_3^0$ over $Al(OH_4^-$ in their saturated solutions. This is not true of the solubilities reported by Ragnarsdóttir and Walther (1985), which exibit virtually no dependence on pressure. The latter behavior would be expected if $Al(OH)_4^-$ were the predominant aluminum species in solution.[9]

Ragnarsdóttir and Walther (1985) measured corundum solubilities at temperatures ranging from 400° to 700°C at pressures from 0.7 to 3 kb. They used synthetic corundum powder (Fisher Alundum 60 RR) which contained 0.3 wt percent Na_2O in the form of sodium-bearing $\beta - Al_2O_3$. To minimize the effect of the Na_2O on their solubility measurements, Ragnarsdóttir and Walther (1985) used the same crystals in all runs and discarded their initial solubility measurements, which were up to two orders of magnitude higher than the solubilities reported in this paper. Despite this precaution, it remains unclear to what extent the experimental data reported by Ragnarsdóttir and Walther (1985) represent corundum solubilities in pure H_2O because they did not report the pH of their experimental solutions. Differences in the solution pH in the various experiments carried out by Ragnarsdóttir and Walther (1985) could account for the scatter in their experimental results. Accordingly, their data were not included in the regression calculations.

Experimental solubilities of corundum at 670°C measured by Becker, Cemič, and Langer (1983) are depicted as a function of pressure in figure 21. The curve in the figure was generated by regression of the data by taking into account the possible presence of both $Al(OH)_3^0$ and $Al(OH)_4^-$ in solution and the log K values for reaction (24) shown in figure 20. It can be seen in figure 21 that the regression curve closely represents the experimental data at pressures from 3 to 6 kb. Note that the solubility value at 2.5 kb appears to be inconsistent with the rest of the solubilities measured by Becker, Cemič, and Langer (1983). The solubility of corun-

[9] Experimental solubilities of corundum in supercritical alkaline solutions reported by Yalman, Shaw, and Corwin (1960), Barns, Laudise, and Schields (1963), Anderson and Burnham (1967), Pascal and Anderson (1989), and those calculated in the present study (see fig. 13) indicate that the solubility of corundum in these solutions is virtually independent of pressure over a wide range of temperature.

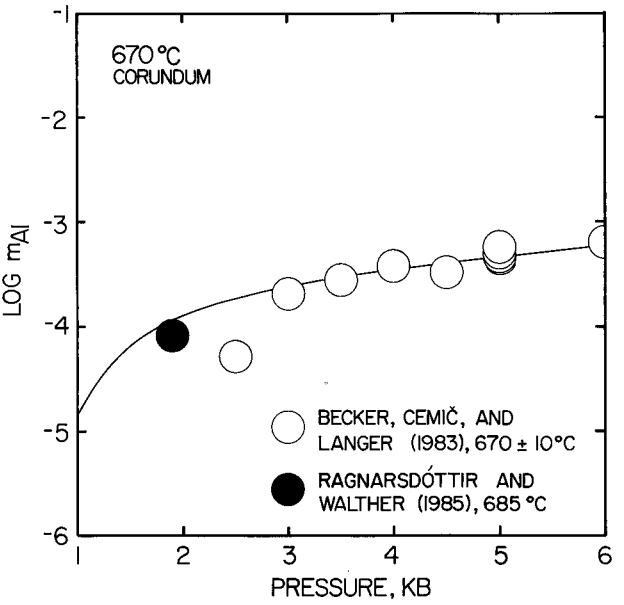

Fig. 21. Logarithm of the solubility of corundum in H_2O as a function of pressure at 670°C. The symbols represent experimental data taken from the literature, but the curve was generated by regression of the data (see text).

dum shown in figure 21 at 685°C and 2 kb reported by Ragnarsdóttir and Walther (1985) was not used in the regression calculations.

The extent to which $Al(OH)_4^-$ contributes to the solubility of corundum in H_2O can be assessed in figure 22, where the logarithm of the total molality of aluminum (m_{Al}) at 1 kb is plotted as a function of temperature, together with computed logarithms of the molalities of $Al(OH)_3^0$ and $Al(OH)_4^-$ in the saturated solutions. It can be seen in this figure that the solubility of corundum is 0.1 to 0.4 log units higher than log $m_{Al(OH)_3^0}$, which is caused by the presence of appreciable concentrations of $Al(OH)_4^-$ in solution. Note in figure 22 that $Al(OH)_4^-$ predominates over $Al(OH)_3^0$ at temperatures $\sim <300$°C, but the opposite is true at higher temperatures. Nevertheless, the computed concentrations of the species are comparable at temperatures $\sim <400$°C.

The calculations discussed above resulted in values of $\Delta\overline{G}_f^\circ$, $\Delta\overline{H}_f^\circ$, and $\overline{S}^\circ$ at 25°C and 1 bar for the species $HAlO_2^0$ (which represents $Al(OH)_3^0$—see footnote 1) of $-207{,}500 \pm 530$ cal mol^{-1}, $-230{,}730 \pm 600$ cal mol^{-1}, and -6.5 ± 2.7 cal K^{-1} mol^{-1}, respectively. These values are listed in table 3, together with the HKF equations of state parameters for $HAlO_2^0$. The properties and parameters shown in this table for $HAlO_2^0$ were used together with those for AlO_2^- and corundum adopted in the present study to generate the curve shown in figure 23, where it can be seen that the independently predicted solubilities of corundum at 500°C

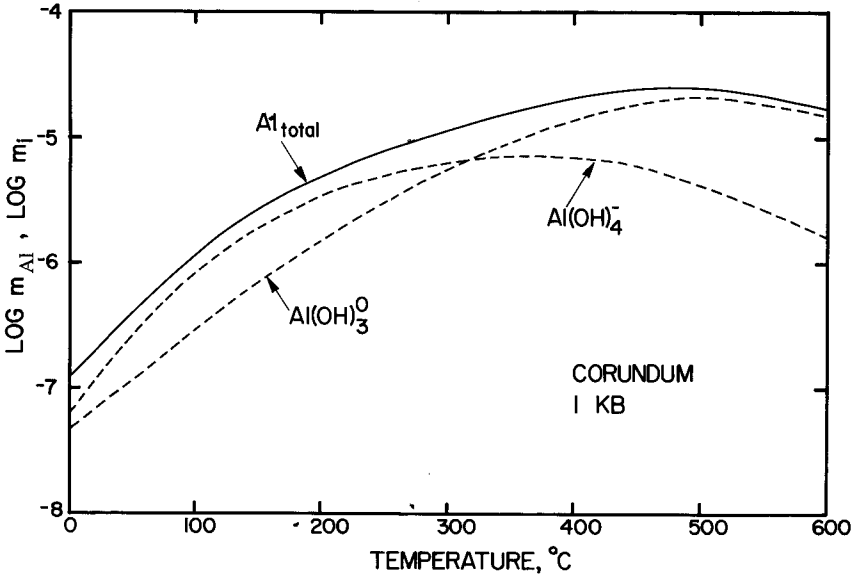

Fig. 22. Logarithm of the solubility of corundum in H_2O as a function of temperature at 1 kb. The solid curve represents computed total molalities of aluminum, but the dashed curves correspond to the molalities of $Al(OH)_3^0$ and $Al(OH)_4^-$ in solutions saturated with corundum.

are within 0.3 log units or less of the experimental solubilities represented by the symbols. The fact the the experimental solubilities shown in figure 23 are higher than those computed in the present study may be an indication that the experimental solutions were slightly alkaline. Morey's (1957) solubility value was obtained in a flow autoclave made of steel. It has been demonstrated that reaction of water with steel at high temperatures may raise the pH of the solution (Apps, Neil, and Jun, 1989). Note in figure 23 that the predicted solubility curve is consistent with the upper solubility limit extrapolated in the present study from experimental solubilities of corundum in HCl solutions reported by Korzhinskii (1987).

The logarithm of the solubility of corundum in H_2O over a wide range of temperatures and pressures is plotted as isobaric curves in figure 24. The curves shown in this figure were generated by minimizing the Gibbs free energy for the system Al_2O_3–H_2O using thermodynamic properties and equations of state parameters taken from tables 2 and 3. It can be shown that the pressure and temperature dependence of the solubility of corundum in H_2O depicted in figure 24 is similar to that of α-quartz computed by Walther and Helgeson (1977) and Fournier and Potter (1982). The configuration of the curves at temperatures $\sim < 50°C$ in this figure is presumably a consequence of the formation of appreciable concentrations of $Al(OH)_2^+$ with increasing pressure at low tem-

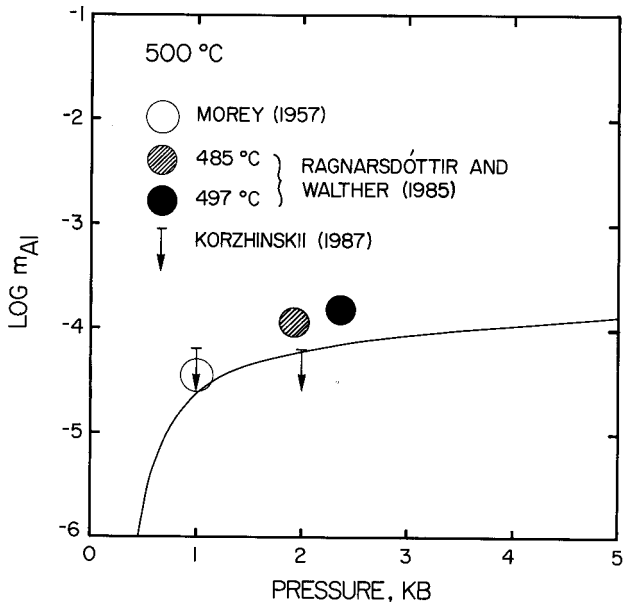

Fig. 23. Logarithm of the solubility of corundum in H_2O as a function of pressure at 500°C. The symbols represent experimental data taken from the literature, but the curve was generated independently using thermodynamic data given in tables 2 and 3.

peratures, where $Al(OH)_2^+$ achieves concentrations comparable to that of $Al(OH)_3^0$.

The standard partial molal properties and HKF equations of state parameters for $Al(OH)_2^+$, $Al(OH)_3^0$, and $Al(OH)_4^-$ generated in the manner described above were used to calculate equilibrium constants at elevated temperatures for

$$Al(OH)_2^+ + H_2O \rightleftharpoons Al(OH)_3^0 + H^+ \tag{25}$$

and

$$Al(OH)_3^0 + H_2O \rightleftharpoons Al(OH)_4^- + H^+, \tag{26}$$

which are represented by the curves shown in figures 25 to 27. Although the experimental values shown in figures 25 and 26 exibit considerable scatter, it can be seen that the independently generated curves are in general agreement with the experimental data. Note in figure 27 that the curves representing computed values of log K for reaction (26) as a function of temperature at various pressures maximize between ~200° and 300°C.

Computed solubilities of boehmite can be compared with their experimental counterparts in figure 28, where log m_{Al} is depicted as a function of pH at various temperatures at P_{SAT}. For comparative pur-

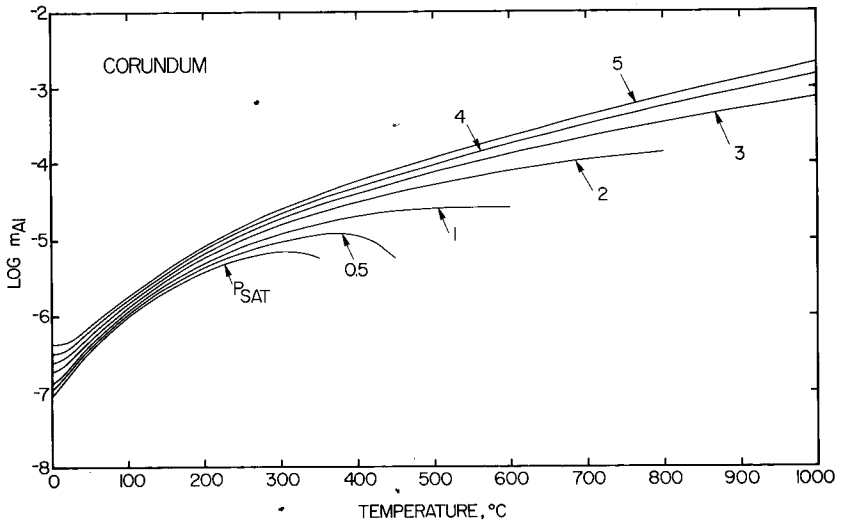

Fig. 24. Logarithm of the solubility of corundum in H_2O as a function of pressure and temperature. The curves were generated using thermodynamic data given in tables 2 and 3 (see text).

poses, the solubilities of boehmite reported by Bourcier, Knauss, and Jackson (1993) in acetate solutions were adjusted before plotting them in figure 28 by substracting the contribution of aluminum acetate complexes computed from stability constants for the species reported by Palmer and Bell (1994). The pH values at which the experimental data reported by Kuyunko, Malinin, and Khodakovsky (1983) are plotted in figure 28 are those recalculated by Bourcier, Knauss, and Jackson (1993).

It can be seen in figure 28 that the solubility curve generated in the present study for boehmite at 90°C is substantially lower and exhibits a different dependence on pH than the trend of the experimental values reported by Castet and others (1993) at pHs > 3. It should perhaps be emphasized that the slope of the solubility curve in the pH range from 3 to 4 is controlled primarily by the equilibrium constant for reaction (2), which is well documented at 90°C (see fig. 16). The cause of the discrepancies between the calculated and experimental solubilities of boehmite at this temperature is unclear. Note in figure 28 that at 170°C there are no such discrepancies. However, many of the experimental data at higher temperatures exhibit considerable scatter, part of which may be attributed to the fact that Bourcier, Knauss, and Jackson (1993) carried out their solubility measurements in solutions with buffered pHs, but Castet and others (1993) did not. Both experimental data (Bourcier, Knauss, and Jackson, 1993) and the thermodynamic calculations described above indicate that at temperatures greater than 200°C the relative stability of aqueous $Al(OH)_3^0$ is substantially higher than that calculated by Castet and others (1993). It should be emphasized in this

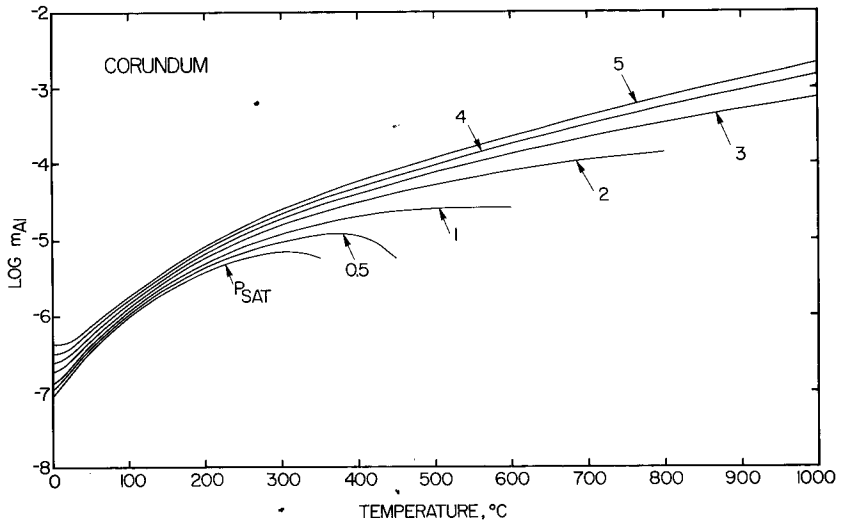

Fig. 24. Logarithm of the solubility of corundum in H_2O as a function of pressure and temperature. The curves were generated using thermodynamic data given in tables 2 and 3 (see text).

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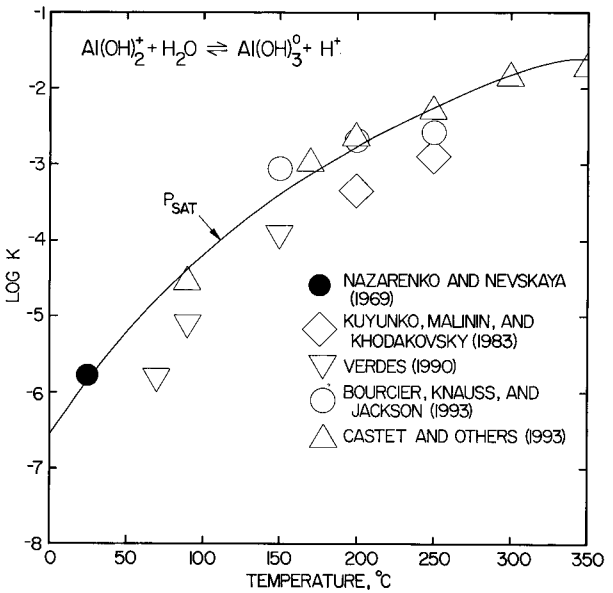

Fig. 25. Logarithm of the equilibrium constant for $Al(OH)_2^+ + H_2O \rightleftharpoons Al(OH)_3^0 + H^+$ as a function temperature at P_{SAT}. The symbols represent experimental data taken from the literature, but the curve was generated independently in the present study (see text).

regard that the thermodynamic properties of $Al(OH)_3^0$ adopted in the present study (table 3) are consistent with the experimental solubilities of diaspore represented by the symbols in figure 29. The curve shown in this figure was generated independently in the present study. Although the experimental points are somewhat scattered, it can be seen that the curve is in close agreement (within ~0.1 log unit) with the bulk of the experimental data. This agreement supports the observation made above that the relative stability of $Al(OH)_3^0$ is considerably higher than that computed by Castet and others (1993).

Stoichiometric correlation of the thermodynamic properties of Al hydroxide species

It has been demonstrated by Hovey (ms) and Tremaine (1990) that the thermodynamic properties of mononuclear aluminum hydroxide complexes correlate with the number of OH^- ligands (n_{OH^-}) in the species. Correlations of this kind are shown in figure 30, where the nonsolvation standard partial molal entropies and volumes at 25°C and 1 bar ($\Delta\overline{S}^{\circ}_{n,P_r,T_r}$ and $\Delta\overline{V}^{\circ}_{n,P_r,T_r}$, respectively) of these species are plotted against n_{OH^-}. In accord with app. A, these properties were computed from (Shock and others, 1992)

$$\Delta\overline{S}^{\circ}_{n,P_r,T_r} = \overline{S}^{\circ}_{P_r,T_r} - \omega_{P_r,T_r} Y_{P_r,T_r} \qquad (27)$$

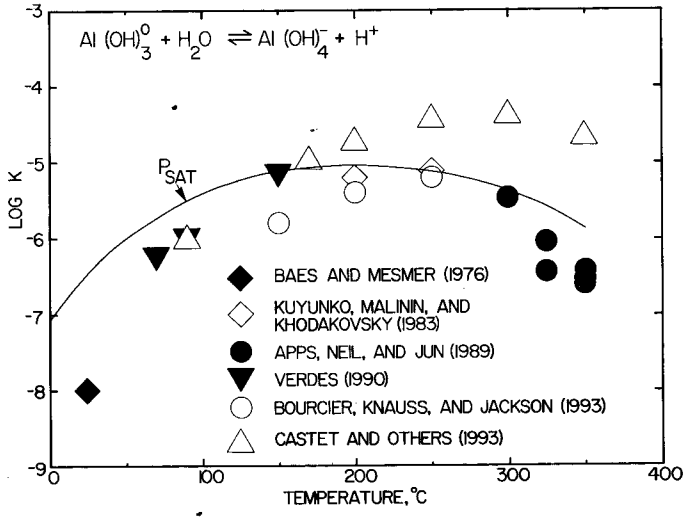

Fig. 26. Logarithm of the equilibrium constant for $Al(OH)_3^0 + H_2O \rightleftharpoons Al(OH)_4^- + H^+$ as a function temperature at P_{SAT}. The symbols represent experimental data taken from the literature, but the curve was generated independently in the present study (see text).

and

$$\Delta\overline{V}^{o}_{n,P_r,T_r} = a_1 + \frac{a_2}{\Psi + P} + \frac{a_3}{T - \Theta} + \frac{a_4}{(\Psi + P)(T - \Theta)} \tag{28}$$

using values of $\overline{S}^{o}_{P_r,T_r}$, a_1, a_2, a_3, a_4, and ω_{P_r,T_r} taken from table 3. The equations of the lines in figure 30 are given by

$$\Delta\overline{S}^{o}_{n,P_r,T_r} = -62.9 + 25.0n_{OH^-} \tag{29}$$

and

$$\Delta\overline{V}^{o}_{n,P_r,T_r} = -36.0 + 22.0n_{OH^-}. \tag{30}$$

Eq (30) was used in the present study to calculate estimates of $\Delta\overline{V}^{o}_{n,P_r,T_r}$ for $Al(OH)^{2+}$ and $Al(OH)_2^+$, which resulted in -14.0 and 8.0 cm^3 mol^{-1}, respectively. Values of a_1, a_2, a_3, and a_4 for $Al(OH)^{2+}$ and $Al(OH)_2^+$ were then computed by combining eq (28) with correlation algorithms developed by Shock and Helgeson (1988) (see app. A).

AQUEOUS ALUMINUM SPECIATION AT HIGH PRESSURES AND TEMPERATURES

The relative stabilities of aqueous aluminum species in dilute NaOH–HCl–H_2O solutions at various temperatures and pressures are shown as a function of pH in figure 31. The curves shown in this figure represent equal activities of the species in the adjoining relative stability fields. The curves were generated with the aid of eq (18) and those summarized in app. A, using thermodynamic properties and equations of state param-

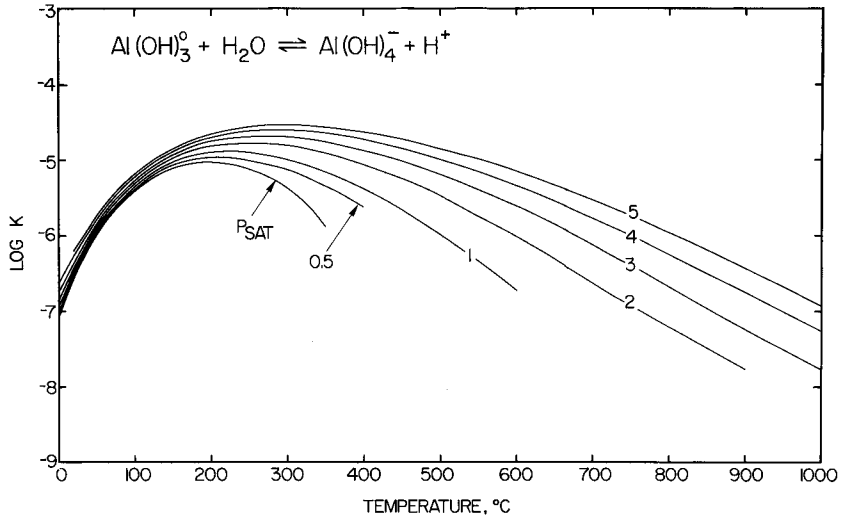

Fig. 27. Logarithm of the equilibrium constant for $Al(OH)_3^0 + H_2O \rightleftharpoons Al(OH)_4^+ + H^+$ as a function temperature and pressure. The curves were generated using thermodynamic data given in tables 2 and 3 (see text).

eters taken from table 3. These equations, properties, and parameters were also used to calculate the degrees of formation (α) of aluminum hydroxide species depicted in figure 32. The values of α shown in this figure were computed from

$$\alpha = \frac{m_{Al(OH)_n^{3-n}}}{m_{Al}}, \tag{31}$$

where $n = 0$, 1, 2, 3, or 4. It can be deduced from figure 31 that the hydrolysis of aqueous aluminum species decreases with increasing pressure. However, increasing temperature has the opposite effect. At temperatures >300°C, $Al(OH)_3^0$ and $Al(OH)_4^-$ predominate in dilute solutions over the entire pH range of geologic interest. However, the aluminum ion together with $Al(OH)^{2+}$ and $Al(OH)_2^+$ may nevertheless contribute substantially to the total concentration of Al in highly acid solutions.

The cumulative effect of increasing chloride concentration on aluminum hydroxide speciation can be assessed in figure 33, where the logarithm of the solubility of diaspore at 300°C and 1 kb is plotted as a function of log m_{Cl} in solutions containing 0.105 m HCl, 0.001 m $AlCl_3$, and various concentrations of NaCl. The symbols shown in this figure represent experimental values reported by Red'kin and Chevychelova (1988), but the curve was generated independently in the present study with the aid of activity coefficients for aqueous species computed from eq (6) using the value of b_γ for NaCl taken from Oelkers and Helgeson

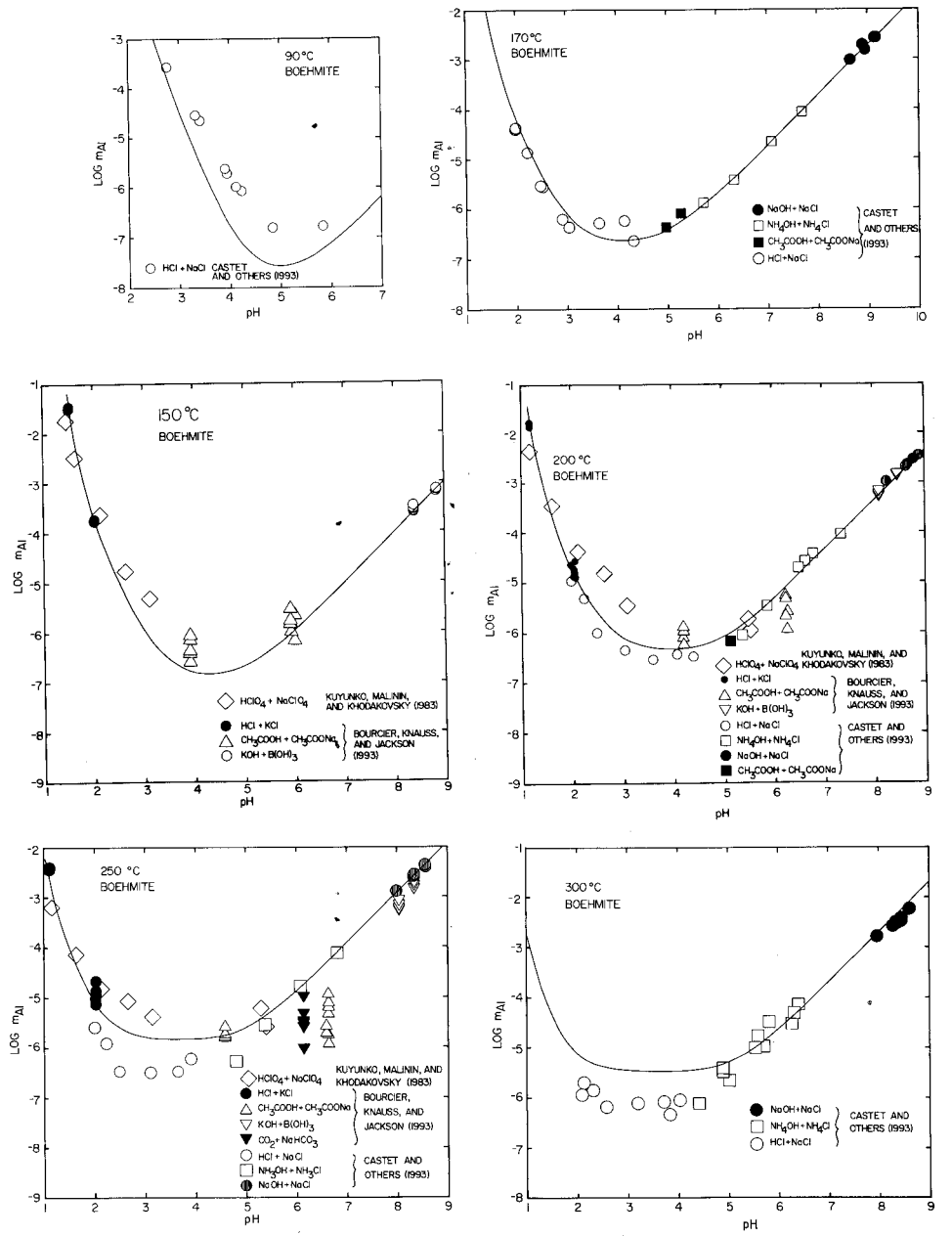

Fig. 28. Logarithm of the solubility of boehmite in aqueous electrolyte solutions at various temperatures and P_{SAT}. The symbols represent experimental data taken from the literature, but the curves were generated using thermodynamic data given in tables 2 and 3 (see text).

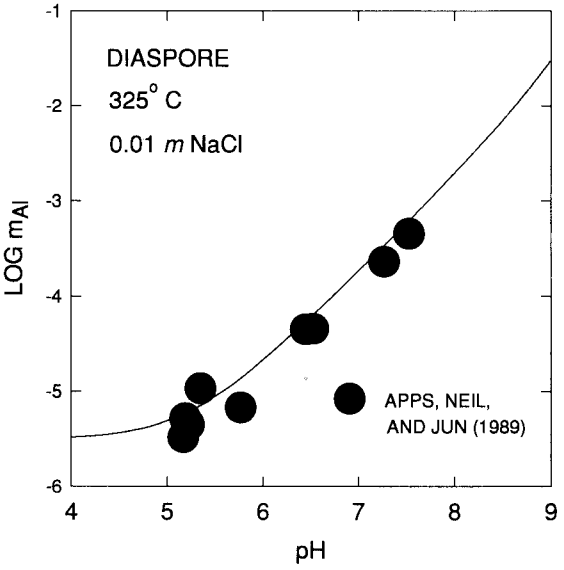

Fig. 29. Logarithm of the solubility of diaspore in dilute NaCl + NaOH solutions at 325°C and P_{SAT} as a function of solution pH. The symbols represent experimental data taken from the literature, but the curve was generated using thermodynamic data given in tables 2 and 3 (see text).

(1990). It can be deduced from figure 33 that the experimental and predicted solubilities of diaspore are within 0.2 log units at total chloride concentration up to 6 molal. The substantial increase in the solubility of diaspore with increasing chloride concentrations shown in figure 33 is due primarily to the progressive decrease in the activity coefficients of Al^{3+} and $Al(OH)^{2+}$. The calculations indicate that these are the predominant aluminum species at chloride concentrations $\sim > 1$ *m*. Despite the relatively high uncertainties associated with computing activity coefficients for aqueous species at high temperatures (Helgeson, Kirkham, and Flowers, 1981), the general correspondence of the curve and symbols in the figure indicates that aluminum chloride complexing does not occur to appreciable degrees in these solutions at 300°C at 1 kb. In contrast, experimental measurements of the solubility of corundum in concentrated HCl, NaCl, and KCl solutions at temperatures $\leq$450°C and pressures ranging from 1 to 2 kb reported by Korzhinskii (1987), Baumgartner and Eugster (1988), and Pascal, Puaya, and Roux (1989) indicate that aluminum chloride complexes may be forming to appreciable degrees in these supercritical solutions.

CONCLUDING REMARKS

The thermodynamic properties and HKF equations of state parameters for the aluminum ion and its hydroxide complexes computed above can be used to calculate equilibrium constants for a wide variety of hydrothermal

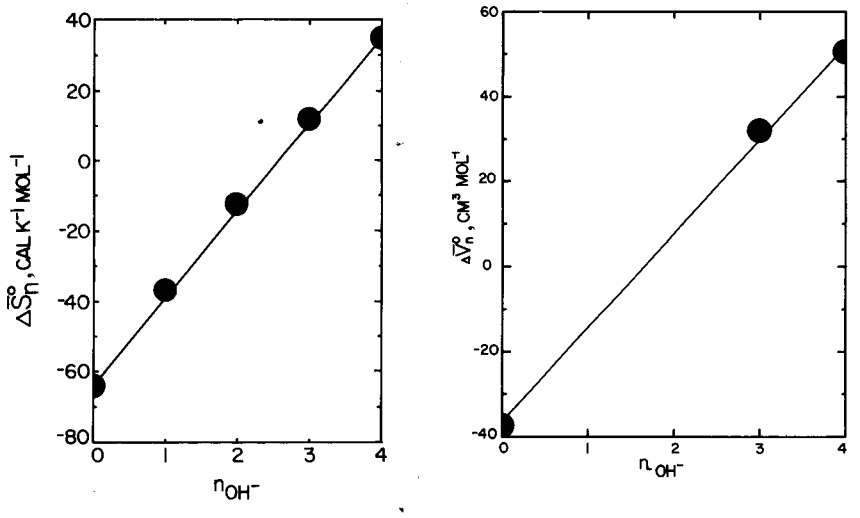

Fig. 30. Correlation of the standard partial molal non-solvation entropies ($\Delta\overline{S}^{o}_{n,P_r,T_r}$) and volumes ($\Delta\overline{V}^{o}_{n,P_r,T_r}$) of aluminum hydroxide complexes with the number of OH^- ions (n_{OH^-}) in the complexes (see text).

reactions involving aqueous aluminum species as well as degrees of formation of aluminum complexes and mineral solubilities in high temperature-pressure electrolyte solutions. The thermodynamic data for minerals and aqueous species generated in the present study have been used to compute values of $\Delta\overline{G}^{o}$ for these minerals and aqueous species included in the Gibbs free energy compilation generated recently by Oelkers and others (1995). In addition, plans call for incorporating them into a revised data file in an expanded and updated SUPCRT software package (Pokrovskii and Helgeson, ms). When available, the code and data file can be obtained at no cost from the Laboratory of Theoretical Geochemistry, University of California, Berkeley, California 94720. Although the thermodynamic properties of aqueous species discussed above are consistent with a vast array of experimental observations, new solubility measurements of boehmite and corundum in H_2O and acid solutions are required to better constrain the relative stabilities of $Al(OH)^{2+}$, $Al(OH)^{+}_{2}$, and $Al(OH)^{0}_{3}$ at temperatures $\geq 200°C$ and pressures $\geq P_{SAT}$.

ACKNOWLEDGMENTS

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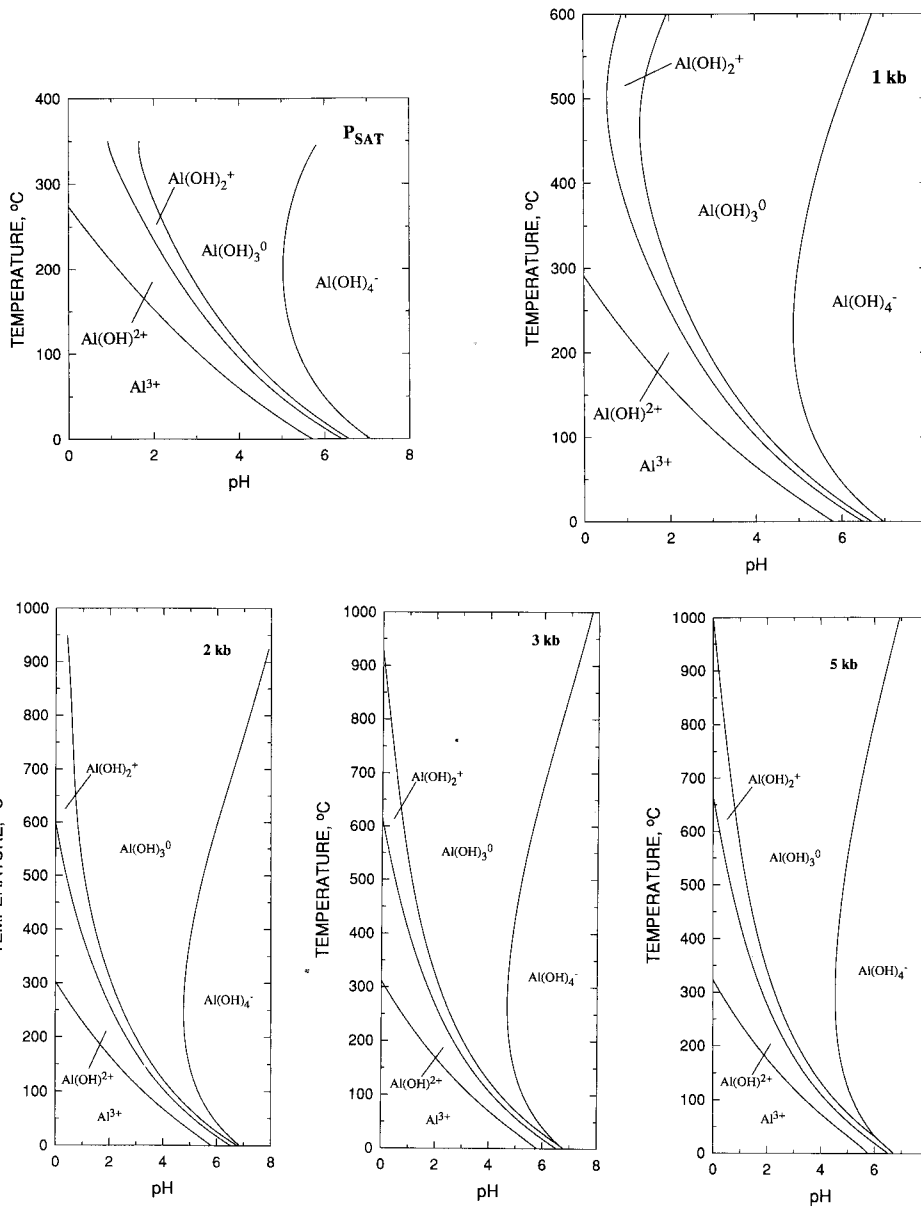

Fig. 31. Equilibrium distribution of aqueous aluminum species in dilute HCl-NaOH solution as a function of pH at various pressures and temperatures (see text).

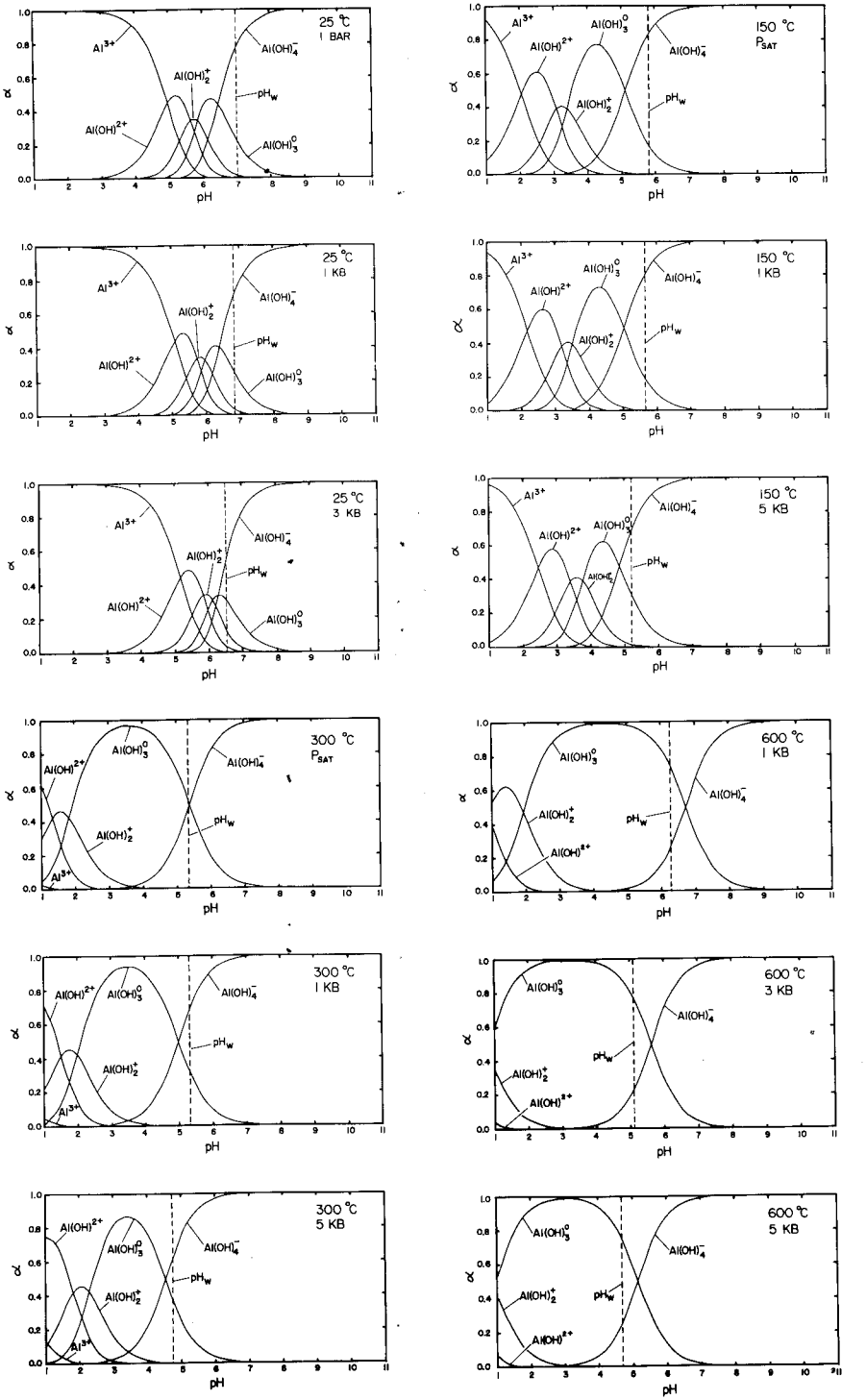

Fig. 32. Degrees of formation (α) of aluminum hydroxide complexes as a function of pH at various temperatures and pressures (see text).

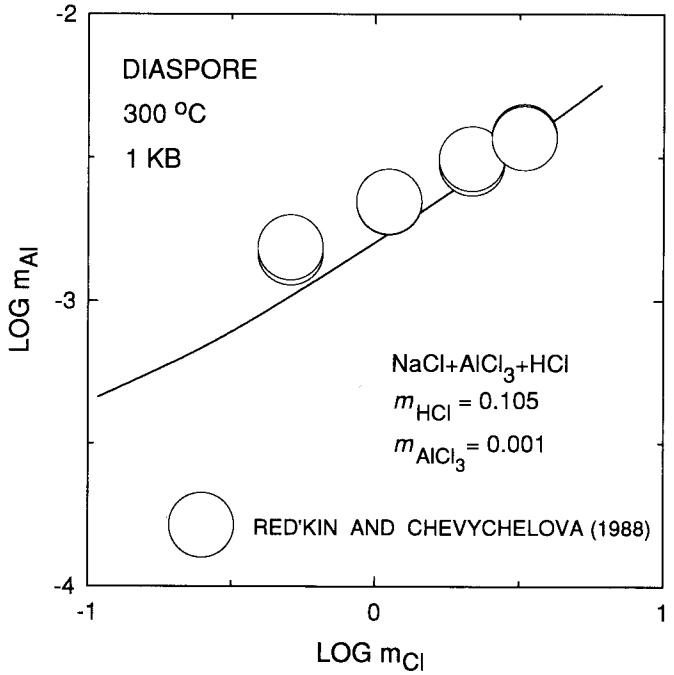

Fig. 33. Logarithm of the solubility of diaspore in NaCl + HCl +$AlCl_3$ solutions at 300°C and 1 kb. The circles represent experimental data reported in the literature, but the curve was generated independently in the present study (see text).

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Appendix A

Summary of the revised Helgeson-Kirkham-Flowers equations of state for aqueous species

The revised HKF (Helgeson, Kirkham, and Flowers, 1981) equations of state (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock, Helgeson, and Sverjensky, 1989)

for the standard partial molal isothermal compressibility ($\overline{\kappa}^o$), volume ($\overline{V}^o$), heat capacity ($\overline{C}_P^o$), entropy ($\overline{S}^o$), and the apparent standard partial molal enthalpy ($\Delta\overline{H}^o$) and Gibbs free energy of formation ($\Delta\overline{G}^o$) of an aqueous species at a given pressure and temperature are given by

$$\overline{\kappa}^o = \left(a_2 + \frac{a_4}{T-\Theta}\right)\left(\frac{1}{P+\Psi}\right)^2 + \omega N + 2Q\left(\frac{\partial\omega}{\partial P}\right)_T - \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial^2\omega}{\partial P^2}\right)_T, \tag{A-1}$$

$$\overline{V}^o = a_1 + a_2\left(\frac{1}{P+\Psi}\right) + \left(a_3 + a_4\left(\frac{1}{P+\Psi}\right)\right)\left(\frac{1}{T-\Theta}\right) - \omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T, \tag{A-2}$$

$$\overline{C}_P^o = c_1 + \frac{c_2}{(T-\Theta)^2} - \frac{2T}{(T-\Theta)^3}\left(a_3(P-P_r) + a_4 \ln\left(\frac{P+\Psi}{P_r+\Psi}\right)\right) + \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_P - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_P, \tag{A-3}$$

$$\overline{S}^o = \overline{S}^o_{T_r,P_r} + c_1 \ln\left(\frac{T}{T_r}\right) - \frac{c_2}{\Theta}\left(\frac{1}{T-\Theta} - \frac{1}{T_r-\Theta} + \frac{1}{\Theta}\ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right) + \left(\frac{1}{T-\Theta}\right)^2\left(a_3(P-P_r) + a_4\ln\left(\frac{P+\Psi}{P_r+\Psi}\right)\right) + \omega Y - \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial T}\right)_P - \omega_{P_r,T_r}Y_{P_r,T_r}, \tag{A-4}$$

$$\Delta\overline{H}^o \equiv \Delta\overline{H}^o_f + (\overline{H}^o_{T_r,P_r} - \overline{H}^o_{T_r,P_r}) = \Delta\overline{H}^o_f + c_1(T-T_r) - c_2\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right) + a_1(P-P_r) + a_2\ln\left(\frac{P+\Psi}{P_r+\Psi}\right) + \left(\frac{2T-\Theta}{(T-\Theta)^2}\right)\left(a_3(P-P_r) + a_4\ln\left(\frac{P+\Psi}{P_r+\Psi}\right)\right) + \omega\left(\frac{1}{\epsilon} - 1\right) + \omega TY - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial T}\right)_P - \omega_{T_r,P_r}\left(\frac{1}{\epsilon_{T_r,P_r}} - 1\right) - \omega_{T_r,P_r}T_rY_{T_r,P_r}, \tag{A-5}$$

and

$$\Delta\overline{G}^o \equiv \Delta\overline{G}^o_f + (\Delta\overline{G}^o_{T,P} - \Delta\overline{G}^o_{T_r,P_r}) = \Delta\overline{G}^o_f - \overline{S}^o_{T_r,P_r}(T-T_r) - c_1\left(T\ln\left(\frac{T}{T_r}\right) - T + T_r\right) + a_1(P-P_r) + a_2\ln\left(\frac{P+\Psi}{P_r+\Psi}\right) - c_2\left(\left(\frac{1}{T-\Theta} - \frac{1}{T_r-\Theta}\right)\left(\frac{\Theta-T}{\Theta}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right) + \frac{1}{T-\Theta}\left(a_3(P-P_r) + a_4\ln\left(\frac{P+\Psi}{P_r+\Psi}\right)\right) + \omega\left(\frac{1}{\epsilon} - 1\right) - \omega_{T_r,P_r}\left(\frac{1}{\epsilon_{T_r,P_r}} - 1\right) + \omega_{T_r,P_r}Y_{T_r,P_r}(T-T_r), \tag{A-6}$$

where a_1, a_2, a_3, a_4, c_1, and c_2 stand for temperature/pressure-independent parameters for the species, T_r and P_r designate the reference temperature of 298.15 K and the reference pressure of 1 bar, respectively, $\Delta\overline{H}^o_f$ and $\Delta\overline{G}^o_f$ denote the standard partial molal enthalpy and Gibbs free energy of formation from the elements in their stable form at T_r and P_r,

$(\overline{H}^{\circ}_{P,T} - \overline{H}^{\circ}_{P_r,T_r})$ and $(\overline{G}^{\circ}_{P,T} - \overline{G}^{\circ}_{P_r,T_r})$ correspond to the differences in the conventional standard partial molal enthalpy and Gibbs free energy of the species at P and T and those at P_r and T_r, ϵ stands for the dielectric constant of H_2O, Ψ and Θ refer to solvent parameters equal to 2600 bar and 228 K, respectively, N, Q, X, and Y represent Born functions given by

$$N = \frac{1}{\epsilon^2}\left(\left(\frac{\partial^2\epsilon}{\partial P^2}\right)_T - \frac{2}{\epsilon}\left(\frac{\partial\epsilon}{\partial P}\right)_T^2\right), \tag{A-7}$$

$$Q = \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial P}\right)_T, \tag{A-8}$$

$$X = \frac{1}{\epsilon}\left(\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_P^2\right), \tag{A-9}$$

$$Y = \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial T}\right)_P, \tag{A-10}$$

and ω stands for the conventional Born coefficient of the species, which can be expressed as

$$\omega = \eta\left(\frac{Z_e^2}{r_{e,P_r,T_r} + |Z|g} - \frac{Z}{3.082 + g}\right), \tag{A-11}$$

where $\eta = 1.66027 \times 10^5$ Å cal mol^{-1}, Z_e and Z refer to the effective and formal charges (which are equal for ionic species), respectively, g stands for a solvent function of density and temperature given by Shock and others (1992), and r_{e,P_r,T_r} denotes the effective electrostatic radius of the species at the reference pressure and temperature, which for monoatomic ions is given by (Helgeson and Kirkham, 1976)

$$r_{e,P_r,T_r} = r_x + |Z|k_Z, \tag{A-12}$$

and for other charged aqueous species by (Shock and Helgeson, 1988)

$$r_{e,P_r,T_r} = \frac{Z^2(\eta Y_{P_r,T_r} - 100)}{\overline{S}^{\circ}_{P_r,T_r} - \alpha_Z}, \tag{A-13}$$

where r_x designates the crystallographic radius of the ion, $k_Z = 0.0$ for anions and 0.94 for cations, Y_{P_r,T_r} refers to the Born function at 25°C (-5.8×10^{-5} K^{-1}), and α_Z is defined by

$$\alpha_Z \equiv 71.5|Z|. \tag{A-14}$$

If the species under consideration has no formal charge, $(\partial\omega/\partial P)_T$, $(\partial\omega/\partial T)_P$, and $(\partial^2\omega/\partial T^2)_P$ in eqs (A-1) to (A-6) are taken to be zero (Shock, Helgeson, and Sverjensky, 1989) and eq (A-11) reduces to

$$\omega = \frac{\eta Z_e^2}{r_{e,P_r,T_r}} \tag{A-15}$$

in which Z_e is taken to be independent of pressure and temperature. Although values of Z_e and r_{e,P_r,T_r} for neutral aqueous species in eq (A15) are not generally available, values of ω for these species can be obtained by regression of experimental data or calculated from (Shock, Helgeson, and Sverjensky, 1989)

$$\omega = -1514.4\overline{S}^{\circ}_{P_r,T_r} + \beta_Z, \tag{A-16}$$

where $\beta_Z = 0.0$ for highly volatile neutral aqueous species such as Ar, Kr, H_2, and O_2, and $\beta_Z = 34{,}000$ for polyatomic and polar neutral aqueous species. In the absence of experimental data at high pressures and temperatures, the pressure/temperature-independent equations of state parameters in eqs (A-1) to (A-6) can be estimated for both charged and neutral aqueous species from Shock and Helgeson (1988); Shock, Helgeson, and Sverjensky (1989); and Helgeson (1992)

$$c_2 = b_1 \overline{C}^{\circ}_{P_r,T_r} - b_2, \tag{A-17}$$

$$c_1 = \overline{C}^{\circ}_{P_r,T_r} - (c_2/4921) + 9.2128 \times 10^{-5}\omega_{P_r,T_r}, \tag{A-18}$$

$$a_1 = 1.3684 \times 10^{-2}\overline{V}^{\circ}_{P_r,T_r} + 3.3796 \times 10^{-7}\omega_{P_r,T_r} + 0.1765, \tag{A-19}$$

$$a_2 = 2601(b_3(0.0239\overline{V}^{\circ}_{P_r,T_r} + 5.903 \times 10^{-7}\omega_{P_r,T_r})b_4 - a_1), \tag{A-20}$$

$$a_4 = -4.134a_2 - 27790, \tag{A-21}$$

and

$$a_3 = 70.15(0.0239\overline{V}^{\circ}_{P_r,T_r} + 5.903 \times 10^{-7}\omega_{P_r,T_r} - a_1 - (a_2/2601)) - (a_4/2601), \tag{A-22}$$

where the constants b_1, b_2, b_3, and b_4 are equal to 0.2037, −3.0346, 1.11, and 1.8, respectively, for ions, neutral inorganic aqueous species, and neutral organic aqueous molecules devoid of functional groups.

Appendix B

Calculation of the extended-term parameter (b_γ) for dissociated NaOH, together with Setchénow coefficients and dissociation constants for $NaOH^0$ at elevated temperatures and pressures

An internally consistent set of values of the extended-term parameter (b_γ) for a 1:1 electrolyte together with the Setchénow coefficient ($b_{\gamma,n}$) and dissociation constant (K) for the neutral ion pair (the stoichiometry of which corresponds to that of the electrolyte) can be computed from experimental values of the stoichiometric mean activity coefficients ($\gamma_\pm$) of the electrolyte using the approach described below (Helgeson, Kirkham, and Flowers, 1981).

Mean ionic activity coefficients of single electrolytes ($\overline{\gamma}_\pm$) can be calculated for both dilute and concentrated solutions from the Hückel equation (Hückel, 1925; Helgeson, Kirkham, and Flowers 1981), which can be written in terms of the molality scale of concentration for the kth electrolyte as

$$\log \overline{\gamma}_{\pm,k} = -\frac{A_\gamma |Z_+Z_-| \overline{I}^{1/2}}{1 + \mathring{a}_k B_\gamma \overline{I}^{1/2}} + \Gamma_\gamma + b_{\gamma,k}\overline{I}, \tag{B-1}$$

where A_γ and B_γ stand for Debye-Hückel solvent parameters, $\mathring{a}_k$ denotes the ion size parameter, Z_+ and Z_- stand for the formal charge of the cation and anion, respectively, $b_{\gamma,k}$ represents the extended-term parameter for the electrolyte, which depends on pressure, temperature, and the identity of the electrolyte, Γ_γ designates the mole fraction to molality conversion factor given by $\Gamma_\gamma = -\log(1 + 0.018053m^*)$, where m^* refers to the sum of the molalities of all the solute species, and $\overline{I}$ denotes the effective ionic strength on the molal scale of concentration ($\overline{I} = \frac{1}{2}\Sigma_i Z_i^2 m_i$, where Z_i and m_i represent the charge and molality of the ith aqueous species). The activity coefficients of neutral aqueous species can be calculated from the Setchénow (1892) equation, which can be expressed for the molality scale of concentration as (Helgeson, Kirkham, and Flowers, 1981)

$$\log \overline{\gamma}_n = \Gamma_\gamma + b_{\gamma,n}\overline{I}, \tag{B-2}$$

where $b_{\gamma,n}$ stands for the Setchénow coefficient of a given neutral aqueous species, which depends on temperature, pressure, and the identity of the electrolyte.

Dissociation of a neutral ion pair designated by MX^0 in a 1:1 single electrolyte solution to form cation M^+ and anion X^- can be described in terms of the reaction

$$MX^0 \rightleftharpoons M^+ + X^-. \tag{B-3}$$

In a solution consisting of only single ions and neutral ion pairs, the law of mass action for reaction (B-3) can be written as

$$K_{MX^0} = \frac{a_{M^+}a_{X^-}}{a_{MX^0}} = \frac{(1 - a_{MX})^2 m\bar{\gamma}^2_{\pm,MX}}{\alpha_{MX}\bar{\gamma}_{MX^0}}, \tag{B-4}$$

where $\bar{\gamma}_{\pm,MX}$ and m stand for the mean ionic activity coefficient and molality of electrolyte, respectively, a_{MX^0}, a_{M^+}, and a_{X^-} refer to the activities of the subscripted species, and α_{MX} represents the degree of association of the electrolyte ($\alpha_{MX} = 1 - (\bar{I}/I)$, where I stands for the stoichiometric ionic strength which is given by $I\ m = \frac{1}{2}(\nu_{M^+}Z^2_{M^+} + \nu_{X^-}Z^2_{X^-})m$, where ν_{M^+} and ν_{X^-} stand for the stoichiometric number of moles of the cation and anion in one mole of the electrolyte, Z_{M^+} and Z_{X^-} represent the formal charges of the subscripted species, and m denotes the molality of the electrolyte).

The relation between the mean ionic activity coefficient ($\bar{\gamma}_\pm$) and the stoichiometric activity coefficient ($\gamma_\pm$) of a single 1:1 electrolyte can be expressed as

$$\gamma_\pm = (1 - \alpha_{MX})\bar{\gamma}_\pm, \tag{B-5}$$

which can be combined with eqs (B-1), (B-2), and (B-4) to give for reaction (B-3)

$$\log K'_{MX^0} = \log\left(\frac{m\gamma^2_{\pm,MX}}{\alpha_{MX}}\right) = \log K_{MX^0} + b_{\gamma,MX^0}\bar{I} + \Gamma_\gamma, \tag{B-6}$$

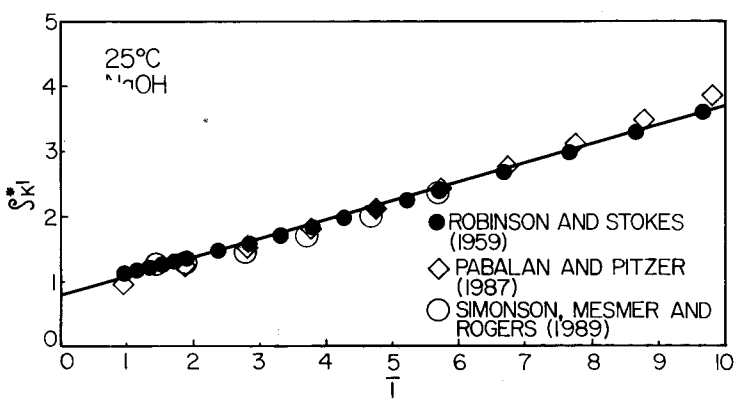

Fig. B-1. ρ^*_K (eq B-7) for $NaOH^0$ as a function of effective ionic strength at 25°C and 1 bar. The symbols represent values of ρ^*_K, computed from stoichiometric mean activity coefficients of $NaOH_{(aq)}$ taken from the literature, but the curve was generated in the present study (see text).

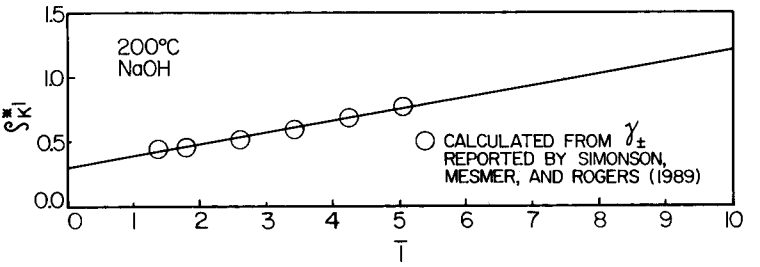

Fig. B-2. $\rho^*_{K'}$ (eq B-7) for $NaOH^0$ as a function of effective ionic strength at 200°C and P_{SAT}. The symbols represent values of $\rho^*_{K'}$ computed from stoichiometric mean activity coefficients of $NaOH_{(aq)}$ taken from the literature, but the curve was generated in the present study (see text).

and

$$\rho^*_{K'} = \log K'_{MX^0} - \Gamma_\gamma = \log K_{MX^0} + b_{\gamma,MX^0}\bar{I}, \tag{B-7}$$

where K'_{MX^0} refers to the effective dissociation constant of the neutral ion pair MX^0, which is defined by (Oelkers and Helgeson, 1991)

$$K'_{MX^0} \equiv K_{MX^0}\bar{\gamma}_{MX^0}. \tag{B-8}$$

It follows from eq (B-7) that a plot of the difference function $\rho^*_{K'}$ against $\bar{I}$ should yield a straight line with a slope corresponding to b_{γ,MX^0} and an intercept equal to $\log K_{MX^0}$. Eq (B-6) can be solved together with eqs (B-1), (B-2), and (B-5) to estimate $\log K$, $b_{\gamma,MX}$, and b_{γ,MX^0} if experimental data for $\gamma_\pm$ are available.

Stoichiometric mean activity coefficients of aqueous NaOH have been tabulated over a wide range of concentrations and temperatures by Åkerlöf and Kegeles (1940), Harned and Owen (1958), Robinson and Stokes (1959), Hamer and Wu (1972), Zarembo, Egorov, and Lvov (1980), Pabalan and Pitzer (1987), Simonson, Mesmer, and Rogers (1989), and others. Values of $\rho^*_{K'}$ for $NaOH^0$ at 25°C and 1 bar computed in the present study from $\gamma_\pm$ given by Robinson and Stokes (1959), Pabalan and Pitzer (1987), and Simonson, Mesmer, and Rogers (1989) using 3.31 Å for the ion size parameter ($å_k$) taken from Helgeson, Kirkham, and Flowers (1981)[B-1] are depicted as symbols in figure B-1. It can be seen in this figure that these values of $\rho^*_{K'}$ exhibit a linear distribution with $\bar{I}$, which is consistent with $\log K = 0.80$, $b_\gamma = 0.10$, and $b_{\gamma,n} = 0.26$, respectively.

The computational approach described above has been used together with values of $å_k$ for $NaOH_{(aq)}$ computed as a function of temperature using equations and parameters given by Shock and others (1992) and values of $\gamma_\pm$ reported by Simonson, Mesmer, and Rogers (1989) to calculate the values of $\log K$, b_γ, and $b_{\gamma,n}$ at temperatures to 250°C at P_{SAT}. To illustrate the results of these calculations, computed values of $\rho^*_{K'}$ at 200°C and P_{SAT} are plotted against $\bar{I}$ in figure B-2. The straight line in this figure is consistent with $\log K = 0.20$, $b_\gamma = 0.048$, and $b_{\gamma,n} = 0.10$, respectively. It can be deduced from figure B-3 that the latter parameters afford close approximation of $\gamma_\pm$ reported by Simonson, Mesmer, and Rogers (1989) at stoichiometric ionic strengths ≤ 6.

The Setchénow coefficients for $NaOH^0$ computed in the present study are depicted in figure B-4 and smoothed values are listed in table B-1. It can be seen in figure B-4 that $b_{\gamma,NaOH^0}$ decreases with increasing temperature from 0° to ~150°C, minimizes between 150°

[B-1] This value is close to that of 3.24 given by Harned and Owen (1958).

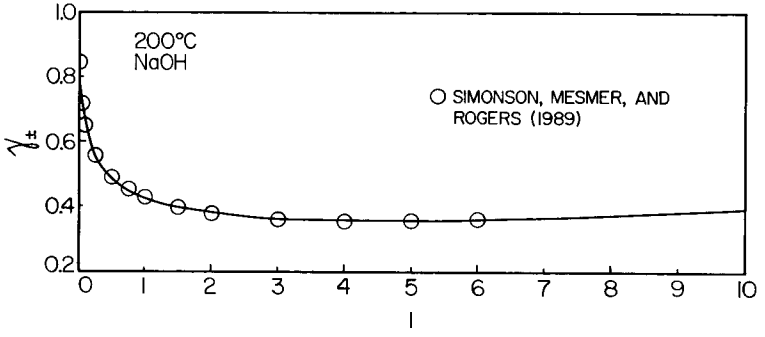

Fig. B-3. Stoichiometric mean activity coefficients ($\gamma_{\pm}$) of aqueous NaOH as a function of stoichiometric ionic strength (I) at 200°C and P_{SAT}. The symbols represent values of $\gamma_{\pm}$ taken from the literature, but the curve was generated in the present study (see text).

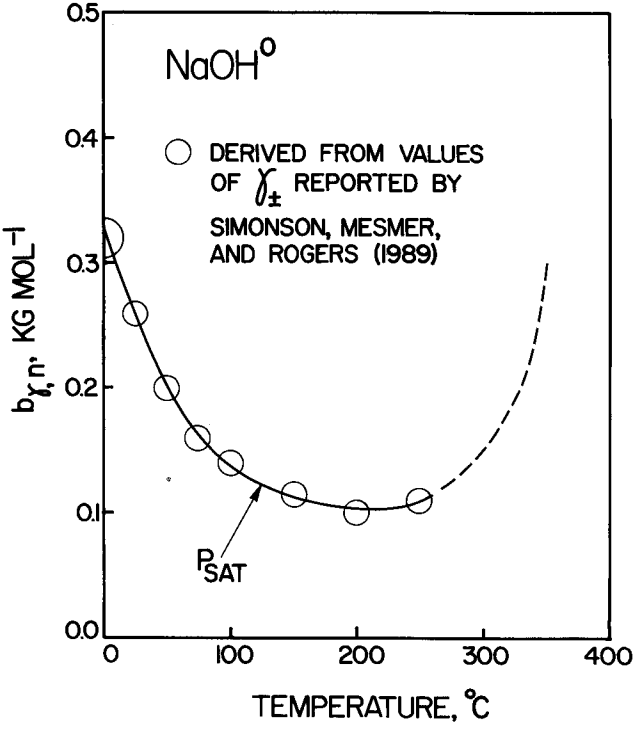

Fig. B-4. Setchénow coefficients ($b_{\gamma,n}$) for $NaOH^0$ as a function of temperature at P_{SAT}. The symbols represent values of $b_{\gamma,n}$ computed in the present study from stoichiometric mean activity coefficients of aqueous NaOH taken from the literature, but the curve was generated by graphic interpolation and extrapolation of the data (see text).

TABLE B-1

Computed Setchénow coefficients ($b_{\gamma,n}$) for $NaOH^0$ (see text)

T°C	$b_{\gamma,n}$ [a]	T°C	$b_{\gamma,n}$ [a]
0	0.35	175	0.11
25	0.26	200	0.105
50	0.20	225	0.105
75	0.16	250	0.11
100	0.13	275	0.125[b]
125	0.12	300	0.150[b]
150	0.115	325	0.20[b]
175	0.11	350	0.30[b]

[a] kg mol^{-1}. [b] Extrapolated value.

and 175°C and then increases with further increase of temperature as the dielectric constant and density of the solvent decrease. The temperature dependence of the extrapolated values of the Setchénow coefficient for $NaOH^0$ consistent with the dashed part of the curve in figure B-4 corresponds to that for $NaCl^0$ and KCl^0 in aqueous NaCl and KCl solutions, respectively (Helgeson, Kirkham, and Flowers, 1981; Pokrovskii and Helgeson, ms).

Values of the extended-term parameter b_γ for aqueous NaOH computed from the stoichiometric mean activity coefficients reported by Simonson, Mesmer, and Rogers (1989) are represented by the symbols in figure B-5, together with the curve generated independently in the present study by taking into account the observation by Helgeson, Kirkham, and Flowers (1981) that the extended-term parameters for the relative partial molal volumes (b_V) and heat capacities (b_J) of electrolytes have the same temperature dependence as the corresponding standard partial molal properties ($\overline{V}^o$ and $\overline{C}^o_P$). Hence, the two sets of properties can be described by analogous functions of temperature and pressure. Values of b_V and b_J can thus be computed from (Oelkers and Helgeson, 1990)

$$\nu b_V/2 = \frac{\nu}{2}\left(\frac{\partial b_G}{\partial P}\right)_T = \hat{a}_1 + \frac{\hat{a}_2}{\Psi + P} + \frac{\hat{a}_3}{T - \Theta} + \frac{\hat{a}_4}{(\Psi + P)(T - \Theta)} + \hat{a}_5\left(-\omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial \omega}{\partial P}\right)_T\right) \tag{B-9}$$

and

$$-\nu b_J/2 = -\frac{\nu}{2}\left(\frac{\partial b_H}{\partial T}\right)_P = -T\frac{\nu}{2}\left(\frac{\partial b_S}{\partial T}\right)_P$$

$$= \hat{c}_1 + \frac{\hat{c}_2}{(T - \Theta)^2} - \left(\frac{2T}{(T - \Theta)^3}\right)\left(\hat{a}_3(P - P_r) + \hat{a}_4 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right) + \hat{a}_5\left(\omega X T + 2TY\left(\frac{\partial \omega}{\partial T}\right)_P - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial^2 \omega}{\partial T^2}\right)_P\right), \tag{B-10}$$

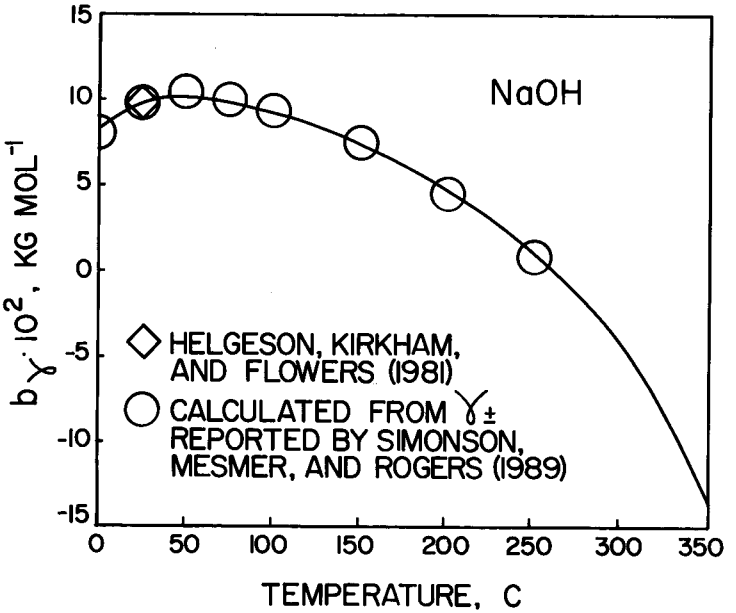

Fig. B-5. Extended term parameter (b_γ) for $NaOH_{(aq)}$ as a function of temperature at P_{SAT}. The symbols represent values of b_γ retrieved from stoichiometric mean activity coefficients of aqueous NaOH taken from the literature, but the curve was generated independently in the present study (see text).

where ν refers to the stoichiometric number of moles of ions in one mole of the electrolyte, $\hat{a}_1$, $\hat{a}_2$, $\hat{a}_3$, $\hat{a}_4$, $\hat{a}_5$, $\hat{c}_1$, and $\hat{c}_2$ correspond to extended-term coefficients for the electrolyte, and b_G, b_H, and b_S refer to the extended-term parameters for calculating the relative partial molal Gibbs free energy, enthalpy, and entropy of the electrolyte. Eqs (B-9) and (B-10) can be used together with the relation

$$b_G = b_H - Tb_s \tag{B-11}$$

to obtain expressions for b_G and b_γ, which are given by

$$-\frac{\nu b_{G,P,T}}{2} = -\frac{\nu b_{G,P_r,T_r}}{2} + \frac{\nu b_{S,P_r,T_r}(T - T_r)}{2}$$

$$-\hat{c}_1\left(T\ln\left(\frac{T}{T_r}\right) - T + T_r\right) + \hat{a}_1(P - P_r) + \hat{a}_2\ln\left(\frac{\Psi + P}{\Psi + P_r}\right)$$

$$-\hat{c}_2\left(\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r - \Theta}\right)\right)\left(\frac{\Theta - T}{T}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right)$$

$$+\left(\frac{1}{T-\Theta}\right)\left(\hat{a}_3(P - P_r) + \hat{a}_4\ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right)$$

$$+\hat{a}_5\left(\omega\left(\frac{1}{\epsilon} - 1\right) - \omega_{P_r,T_r}\left(\frac{1}{\epsilon_{P_r,T_r}} - 1\right) + \omega_{P_r,T_r}Y_{P_r,T_r}(T - T_r)\right) \tag{B-12}$$

TABLE B-2

Equations of state parameters for calculating excess functions for aqueous NaOH[a]

$\hat{a}_1$	0.0301	cal kg bar^{-1} mol^{-2}
$\hat{a}_2$	−202.55	cal kg mol^{-2}
$\hat{a}_3$	−2.9092	cal kg K bar^{-1} mol^{-2}
$\hat{a}_4$	20302.	cal kg K mol^{-2}
$\hat{a}_5$	−0.206 [b]	kg mol^{-1}
$\hat{c}_1$	−1.50	cal kg K^{-1} mol^{-2}
$\hat{c}_2$	53300.0	cal kg K mol^{-2}
ω_{P_r,T_r}	205520. [b]	cal mol^{-1}
b_{G,P_r,T_r}	−267.4 [c]	cal kg mol^{-2}
b_{S,P_r,T_r}	−1.836 [c]	cal kg K^{-1} mol^{-2}

[a] The values shown for $\hat{a}_1$, $\hat{a}_2$, $\hat{a}_3$, $\hat{a}_4$, $\hat{c}_1$ and $\hat{c}_2$ for NaOH were taken to be equal to those for NaCl computed by Oelkers and Helgeson (1990). [b] Helgeson, Kirkham, and Flowers (1981). [c] Computed from equations and parameters given by Helgeson, Kirkham, and Flowers (1981).

and

$$b_{\gamma,P,T} = -\frac{b_{G,P,T}}{2 \times 2.303RT} \tag{B-13}$$

where R represents the gas constant (1.9872 cal mol^{-1} K^{-1}).

The equations of state coefficients required to compute values of the extended-term parameters for aqueous NaOH can be retrieved from experimental partial molal heat capacities, volumes, and compressibilities reported in the literature. As an alternative, the equations of state coefficients $\hat{a}_1$, $\hat{a}_2$, $\hat{a}_3$, $\hat{a}_4$, $\hat{c}_1$, and $\hat{c}_2$ for aqueous NaOH can be approximated by those of aqueous NaCl reported by Oelkers and Helgeson (1990). In addition, $\hat{a}_5$ can be set to −0.206 kg mol^{-1}, which is the value adopted by Helgeson, Kirkham, and Flowers (1981) for dissociated NaCl, NaHS, and $NaHCO_3$. These values are given in table B-2, together with values of b_G, b_S, and ω_{P_r,T_r} for aqueous NaOH computed from equations and parameters given by Helgeson, Kirkham, and Flowers (1981). The parameters shown in this table were used together with eqs (B-11) to (B-13) and the electrostatic properties of H_2O (Shock and others, 1992) to calculate values of b_γ for aqueous NaOH at temperatures to 1000°C and pressures to 5 kb.[B-2] These values are listed in table B-3. The close agreement between the b_γ values retrieved from the stoichiometric mean activity coefficients reported

[B-2] The calculations were carried out using computer code ACTICO written by E.H. Oelkers, which permits calculation of extended-term parameters and activity coefficients of single electrolytes over a wide range of pressures, temperatures, and concentrations.

TABLE B-3

Extended term parameters for calculating activity coefficients of aqueous NaOH to 1000°C and 5 kb (see text)

T°C	$(b_{\gamma,NaOH}$, kg mol$^{-1})$ × 10^2						
	Pressure, kb						
	P_{SAT}	0.5	1.0	2.0	3.0	4.0	5.0
25	9.8	10.8	11.7	13.0	13.9	14.6	15.1
50	10.2	10.9	11.5	12.5	13.3	14.0	14.5
75	9.9	10.5	11.1	12.0	12.7	13.4	13.9
100	9.3	9.9	10.5	11.4	12.1	12.8	13.4
125	8.5	9.1	9.7	10.7	11.5	12.2	12.8
150	7.4	8.2	8.9	9.9	10.8	11.6	12.2
175	6.2	7.2	7.9	9.2	10.1	10.9	11.7
200	4.7	6.0	6.9	8.3	9.4	10.3	11.1
225	3.1	4.6	5.8	7.4	8.7	9.7	10.5
250	1.1	3.1	4.6	6.5	7.9	9.0	9.9
275	−1.3	1.4	3.3	5.6	7.1	8.4	9.4
300	−4.3	−0.5	1.9	4.6	6.3	7.7	8.8
325	−8.0	−2.7	0.4	3.5	5.5	7.0	8.2
350	−13.3	−5.5	−1.2	2.4	4.7	6.3	7.6
375		−6.7	−2.8	1.3	3.8	5.6	7.1
400		−9.6	−4.6	0.1	2.9	4.9	6.5
425		−13.3	−6.6	−1.1	2.0	4.2	5.9
450		−19.1	−8.7	−2.4	1.1	3.5	5.3
475			−11.1	−3.7	0.2	2.8	4.7
500			−13.7	−5.1	−0.8	2.0	4.1
550			−19.5	−8.0	−2.8	0.5	2.9
600			−25.8	−11.2	−5.0	−1.2	1.6
650				−14.7	−7.4	−2.9	0.3
700				−18.3	−9.9	−4.7	−1.1
750				−22.1	−12.6	−6.6	−2.6
800				−25.9	−15.4	−8.6	−4.1
850				−29.8	−18.4	−10.7	−5.6
900				−33.6	−21.3	−12.8	−7.2
950				−37.4	−24.3	−14.9	−8.8
1000				−41.2	−27.1	−16.9	−10.4

by Simonson, Mesmer, and Rogers (1989) represented by the symbols in figure B-5 and the curve generated independently using data and parameters taken from table B-2 strongly supports the assumption that the thermodynamic properties of $NaOH_{(aq)}$ and $NaCl_{(aq)}$ are similar functions of pressure and temperature.

Plyasunov (1988) and Plyasunov and others (1988) employed an approach similar to that described above to calculate log K, b_γ, and $b_{\gamma,n}$ for $NaOH_{(aq)}$ and $NaOH^0$ using values of

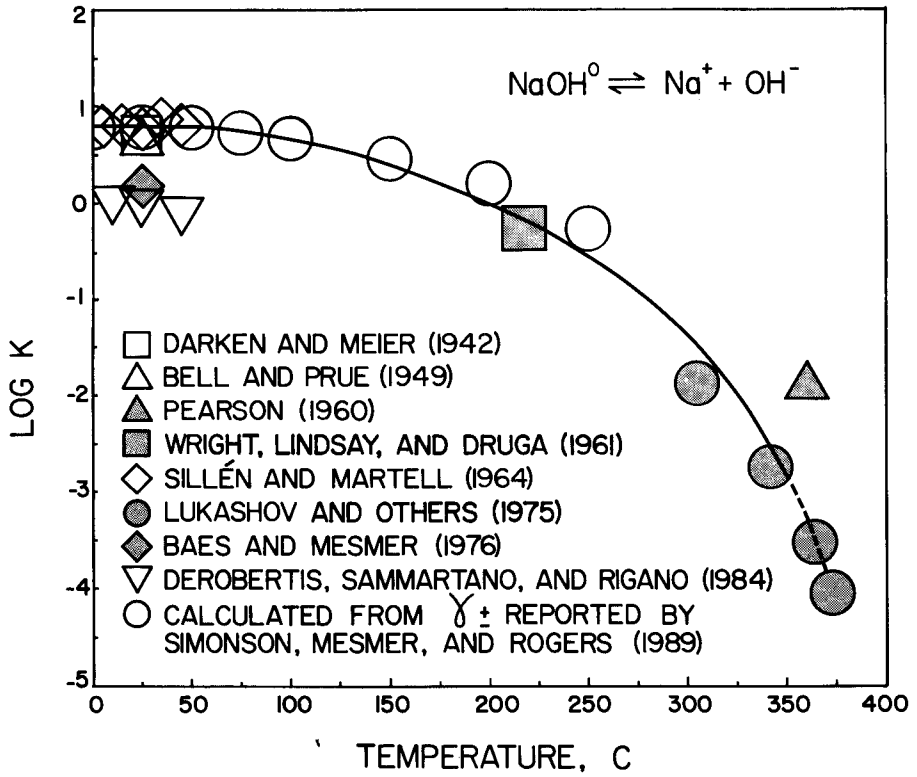

Fig. B-6. Logarithm of the dissociation constant of $NaOH^0$ as a function of temperature at P_{SAT}. The symbols represent values of log K either computed in the present study or taken from the literature, but the curve was generated by selective regression of the data represented by the symbols (see text).

$\gamma_\pm$ reported by Zarembo, Egorov, and Lvov (1980). Later Plyasunov (1990, personal communication) calculated a new set of these parameters using values of $\gamma_\pm$ given by Pabalan and Pitzer (1987). He obtained for 25°C and 1 bar, 0.15, 0.13, and 0.34 for log K, b_γ and $b_{\gamma,n}$, respectively. His value of log K is in excellent agreement with the values given by Baes and Mesmer (1976) and Smith and Martell (1976), who report 0.17 and 0.20, respectively. Plyasunov also reports log K values for 100°, 150°, and 200°C (0.45, 0.25, and 0.20, respectively) which are close to those computed in the present study (0.66, 0.46, and 0.21, respectively). However, the values of b_γ for $NaOH_{(aq)}$ calculated by Plyasunov are not consistent with that for $NaOH_{(aq)}$ at 25°C and 1 bar given by Helgeson, Kirkham, and Flowers (1981) and the high temperature equations of state predictions shown in figure B-5, which are independent of values of b_γ retrieved from $\gamma_\pm$. Nevertheless, the degrees of association of $NaOH_{(aq)}$ from 25° to 200°C computed from parameters reported by Plyasunov are close to those obtained in this study, owing to the fact that his Setchénow coefficients are systematically higher than those given in table B-1.

Values of the logarithm of the dissociation constant of $NaOH^0$ computed in the present study are plotted as a function of temperature in figure B-6 (open circles), together with experimental data reported in the literature. It can be seen in this figure that the log K

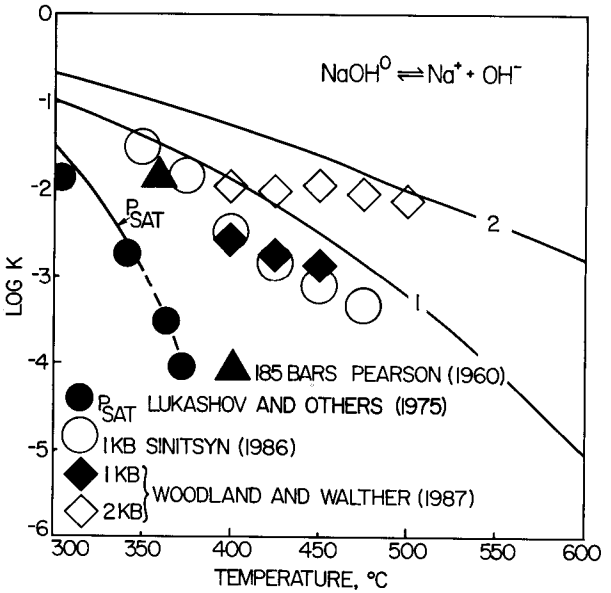

Fig. B-7. Logarithm of the dissociation constant of $NaOH^0$ as a function of temperature at P_{SAT}, 1 and 2 kb. The symbols represent values of log K taken from the literature, but the curves were generated in the present study using thermodynamic properties and equations of state parameters taken from table 3 (see text).

values retrieved from activity coefficients are in close agreement with the those given by Darken and Meier (1942), Bell and Prue (1949), Sillén and Martell (1964), Wright, Lindsay, and Druga (1961), and Lukashov and others (1974). These values were used together with equations summarized in app. A and the thermodynamic properties and the equations of state parameters for Na^+ and OH^- reported by Shock and Helgeson (1988) to calculate the values $\overline{S}^o_{T_r,P_r}$, c_1, c_2, and ω_{P_r,T_r} for $NaOH^0$ given in table 3, which were then used to generate the solid curve in figure B-6. The dashed curve in this figure represents an extrapolation of the solid curve.

Dissociation constants for $NaOH^0$ at temperatures from 350° to 450°C and 1 kb have been computed by Sinitsyn (ms) from his experimental measurements of quartz solubility in NaOH solutions. In addition, Woodland and Walther (1987) report values of log K for $NaOH^0$ retrieved from the compositions of solutions considered to be in equilibrium with the assemblage albite + paragonite + quartz at temperatures ranging from 400° to 500°C at 1 and 2 kb. These various values of log K are plotted as symbols in figure B-7, together with those reported by Pearson (1960)[B-3] and Lukashov and others (1974) at P_{SAT}. It can be shown that the experimental data represented by the symbols are not consistent with one another. Accordingly, in a first approximation, values of a_1, a_2, a_3, and a_4 were estimated independently of the data represented by the symbols in figure B-7 by assuming that the non-solvation contribution to the standard partial molal volume of dissociation of $NaOH^0$ at 25°C and 1 bar is essentially the same as that for $NaCl^0$. This assumption, together with the value of ω_{P_r,T_r} for $NaOH^0$ in table 3 and that for $\overline{V}^o_{P_r,T_r}$ for $NaCl^0$ given by Shock and others (1992) were used with eqs (A-19) to (A-22) in app. A to compute the values of a_1, a_2, a_3, and

[B-3] Quoted by Barnes, Helgeson, and Ellis (1966).

a_4 for $NaOH^0$ shown in table 3. These values were used to generate the curves for 1 and 2 kb in figure B-7. It can be seen in this figure that the experimental data represented by the symbols are for the most part lower by up to ~0.5 log units then the curves for these pressures.

Although the log K values for $NaOH^0$ predicted in the present study are based on the assumption that $\overline{V}^o_{n,P_r,T_r,NaOH^0} = \overline{V}_{n,P_r,T_r,NaCl^0}$ (see above), they are consistent with the dissociational behavior of KOH^0 at supercritical pressures and temperatures (Franck, 1956; Pokrovskii and Helgeson, ms) and experimentally determined solubilities of corundum at high pressures at temperatures (see text). It should be noted in this regard that Woodland and Walther (1987) assumed that the aqueous aluminum in their saturated solutions was present as $Al(OH)^0_3$ and $NaAl(OH)^0_4$. However, consideration of their data using the thermodynamic properties of aqueous aluminum species generated in the present study indicates that $Al(OH)^-_4$, rather than $Al(OH)^0_3$ or $NaAl(OH)^0_4$ was probably the predominant aluminum species in their solutions.

Appendix C

Speciation in concentrated sodium hydroxide and sodium aluminate solutions: a brief survey of the literature

Lippencott, Psellos, and Tobin (1952) concluded on the basis of Raman spectra that aluminum in sodium aluminate solutions is present primarily as the tetrahedrally coordinated $Al(OH)^-_4$ ion. Mal'tsev, Malinin, and Mashovets (1965) measured NMR spectra of undersaturated and saturated sodium aluminate solutions, from which they concluded that increasing aluminum concentration results in dehydration of $Al(OH)^-_4$ to form AlO^-_2. Carreira and others (1966), Mironov and others (1969), and Pavlov and others (1969) reported Raman spectra of highly supersaturated aluminate solutions with starting pHs ranging from 8 to 14. They described the speciation in these solutions in terms of a slow aging process accompanied by a conjugate increase in pH for solutions with pHs < 10. They attributed this process to the formation of polynuclear species of the form $(OH)_2[Al(OH)_4]^{n-2}_n$ in accord with Plumb and Swaine's (1964) conclusions. In highly alkaline solutions (pH ≥ 13), AlO^-_2 was found to be the predominant species in solution, which confirmed the earlier findings by Mal'tsev, Malinin, and Mashovets (1965) adduced above. Moolenaar, Evans, and McKeever (1970), who examined infrared, Raman, and NMR spectra of supersaturated sodium aluminate solutions concluded that $Al(OH)^-_4$ is the predominant species at aluminum concentrations up to 1.5 M. However, at higher concentrations up to 6 M, they observed partial dehydration of the species to form the dimer $Al_2O(OH)^{2-}_6$. Similarly, Chen and others (1993), who generated Raman, ultraviolet, infrared, and NMR spectra of supersaturated sodium aluminate solutions and crystalline aluminate salts, concluded that $Al(OH)^-_4$ predominates by far over $Al_2O(OH)^{2-}_6$ in these solutions. They also invoked the species $Al(OH)^{3-}_6$ to explain their spectra of ultra alkaline solutions. As emphasized by Chen and others (1993), the concentration of aluminate anions may vary in solutions with the same composition, depending on the preparatory history of the solution. It follows that interpretation of spectroscopic data for supersaturated sodium aluminate solutions may not be applicable to prediction of speciation in saturated and undersaturated solutions.

Disproportionation of $Al(OH)^-_4$ to yield H_2O, AlO^-_2, and a species of intermediate hydration state such as $AlO(OH)^-_2$ is supported indirectly by vapor pressure (Dibrov, Mal'tsev, and Mashovets, 1964; Puchkov and Chakhal'yan, 1974, 1976b) and heat of dilution (Puchkov and Chakhal'yan, 1971) data. Further experimental evidence on the formation of $Al(OH)^-_4$, $AlO(OH)^-_2$, and AlO^-_2 in aqueous solutions in the system Al_2O_3–H_2O–NaOH has been summarized by Glastonbury (1969), Eremin, Volokhov, and Mironov (1974), and Khodakovsky, Katorcha, and Kuyunko (1980).

Bjerrum (1926) was among the first to note the formation of $NaOH^0$ in aqueous NaOH solutions. Since then, formation of $NaOH^0$ in such solutions at ambient temperatures has been confirmed by numerous spectroscopic studies (Gutowsky and Saika, 1953; Shoolery and Alder, 1955; Jardetzky and Wertz, 1960; Choppin and Buijs, 1963; Mal'tsev and others, 1965; Griffiths and Socrates, 1968; Sharma and Kashyap, 1972; and others). The dissociation constant for this ion pair has been measured by a multitude of methods at both ambient and elevated temperatures at P_{SAT} (see app. B). It seems likely by analogy that $NaAl(OH)_4^0$ (or $NaAlO_2^0$) may also form to a significant degree in sodium aluminate solutions. It is of interest to note in this regard that OH^- and AlO_2^- have the same effective electrostatic radius 1.40 Å (Shock and Helgeson, 1988).

Formation of sodium aluminate ion pairs has been unequivocally documented by spectroscopic studies (Mal'tsev, Malinin, and Mashovets, 1965; Pavlov and others, 1969; Moolenaar, Evans, and McKeever, 1970) and supported by calorimetric and activity coefficient data (Mal'tsev and Mashovets, 1965; Puchkov and Chakhal'yan, 1974, 1976b). Eremin, Novikov, and Mironov (1974) reviewed experimental evidence supporting the presence of sodium aluminate complexes in concentrated sodium aluminate solutions. They found that Na^+ forms stronger complexes with aluminate ions than with OH^-. Lyapunov, Khodakova, and Galkina (1964), who measured the solubility of gibbsite in NaOH and NaOH + NaCl solutions at 60°C and 1 bar demonstrated that addition of NaCl increases the equilibrium concentration of aluminum, which is consistent with formation of $NaAl(OH)_4^0$. In other solubility studies, Anderson and Burnham (1967, 1983) and Pascal and Anderson (1989) invoked $NaAl(OH)_4^0$ to account for the aqueous solubilities of corundum and aluminosilicates in supercritical alkaline solutions. Supporting evidence is provided by experimental data obtained by Ganeyev, Menkovskii, and Rumyantsev (1970), who measured the solubility of corundum in $NaHCO_3$ and Na_2CO_3 solutions at 460° and 500°C at 1620 bars. Consideration of their data leaves little doubt that sodium aluminate species may be present in substantial concentrations in these solutions. Ganeyev, Menkovskii, and Rumyantsev (1970) noted that the aqueous solubility of Na_2CO_3 increases in the presence of corundum, presumably in response to formation of sodium aluminate complexes.

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