The Gibbs Free Energy of the Formation of the $Al(OH)_4^-$ Ion at Elevated Temperatures

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Synopsis. The Gibbs free energy of the formation of the $Al(OH)_4^-$ ion, $\Delta G_f^\circ[Al(OH)_4^-]$, has been determined from the solubility data of alumina hydrates at temperatures up to 300 °C. According to the results of thermodynamical calculations, $\Delta G_f^\circ[Al(OH)_4^-]$ is -1305.3 kJ/mol at 25 °C, and it decreases almost linearly with an increase in the temperature. Its temperature dependence between 25 and 300 °C can be expressed as follows: $\Delta G_f^\circ[Al(OH)_4^-] = -1152.7 - 3.318T - 5.64\times 10^{-4}T^2 + 1.202T\log T$.

The Gibbs free energy of the formation of the $Al(OH)_4^-$ ion, $\Delta G_f^\circ[Al(OH)_4^-]$, is very important in understanding thermodynamically the alumina production by the Bayer process, the aqueous geochemistry of aluminous minerals, and the corrosion of aluminum in alkaline solutions. Previously, various values for ΔG_f°-$[Al(OH)_4^-]$ at 25 °C have been reported by many investigators.[1–6] Unfortunately, these values are very discrepant, ranging from -1297.2 to -1314.2 kJ/mol. Furthermore, $\Delta G_f^\circ[Al(OH)_4^-]$ at elevated temperatures has not yet been presented. The alumina extraction from bauxite and the formation of alumina minerals proceed usually at a high temperature. It is, therefore, important to know $\Delta G_f^\circ[Al(OH)_4^-]$ at high temperatures.

The present author previously determined the ionic solubility products, K_S, of gibbsite[7] and boehmite[8] in the alkaline pH range by applying an extending Debye-Hückel equation to their solubility data in NaOH solutions. The purpose of this paper is to determine $\Delta G_f^\circ[Al(OH)_4^-]$ at temperatures from 25 to 300 °C, based on K_s°.

The dissolution processes of alumina hydrates are given by the following equations:

a) For gibbsite,

$$Al(OH)_3(s) + H_2O(l) = Al(OH)_4^-(l) + H^+(l), \tag{1}$$

$$K_{s.1}^\circ = a_{Al}a_H/a_w, \tag{2}$$

$$\Delta G_1^\circ = -RT\ln K_{s.1}^\circ. \tag{3}$$

b) For boehmite,

$$AlOOH(s) + 2H_2O(l) = Al(OH)_4^-(l) + H^+(l), \tag{4}$$

$$K_{s.2}^\circ = a_{Al}a_H/a_w^2, \tag{5}$$

$$\Delta G_2^\circ = -RT\ln K_{s.2}^\circ, \tag{6}$$

where a_{Al}, a_H, and a_W are the activities of $Al(OH)_4^-$, H^+ ions, and water, and where ΔG_1° and ΔG_2° are the Gibbs free energy changes in Reaction 1 and 4 respectively.

The temperature dependences of $\log K_s^\circ$ can be expressed throughout the temperature range as follows:

a) For gibbsite,

$$\log K_{s.1}^\circ = -22.11 - 3.368\times 10^{-3}\,T - 5835.9/T + 6.390\ln T. \tag{7}$$

$$(313.2 \leq T \leq 443.2\ \mathrm{K})$$

b) For boehmite,

$$\log K_{s.2}^\circ = -29.64 - 8.149\times 10^{-3}\,T - 2263.0/T + 4.3721\,n\,T. \tag{8}$$

$$(353.2 \leq T \leq 573.2\,K)$$

The above equations are the results of the least-square treatment of the data for K_s° obtained in Refs. 7 and 8.[9]

According to Eq. 1 or 4,

$$\Delta G_f^\circ[Al(OH)_4^-]_1 = \Delta G_1^\circ + \Delta G_f^\circ[Al(OH)_3] + \Delta G_f^\circ(H_2O) - \Delta G_f^\circ(H^+), \tag{9}$$

$$\Delta G_f^\circ[Al(OH)_4^-]_2 = \Delta G_2^\circ + \Delta G_f^\circ(AlOOH) + 2\Delta G_f^\circ(H_2O) - \Delta G_f^\circ(H^+). \tag{10}$$

The Gibbs free energy of the formation of a substance for which heat capacity data are available can be calculated by the usual thermodynamical method. For gibbsite, boehmite, and water, highly accurate heat capacity data have been presented in the literature.[10,11] It is most important and most difficult to evaluate $\Delta G_f^\circ(H^+)$ exactly at high temperatures. In this paper, the $\Delta G_f^\circ(H^+)$ values were calculated approximately by using the "correspondence principle" presented by Criss and Cobble.[12] They demonstrated that reliable estimates of "absolute" (*i.e.* "third law") ionic entropies and heat capacities can be made using their correspondence principle.

The thermodynamic data necessary to evaluate ΔG_f° are listed in Table 1. It should be noted that an ionic entropy of the hydrogen ion at 25 °C, which is usually defined as zero based on the conventional scale, was assigned to 20.92 J/K mol according to the correspondence principle.

TABLE 1. SELECTED STANDARD THERMODYNAMIC DATA FOR GIBBSITE, BOEHMITE, WATER, AND HYDROGEN IONS

Substance	$\Delta G_{f,298}^\circ$ / kJ mol^{-1}	S_{298}° / J K^{-1} mol^{-1}	c_p° / J K^{-1} mol^{-1}
$Al(OH)_3$	-1154.9[a)]	68.44[a)]	$81.57+0.101T-1.75\times 10^6T^{-2}$ [c)]
AlOOH	-915.0[b)]	48.45[a)]	$53.99+8.66\times 10^{-2}T-1.26\times 10^6T^{-2}$ [c)]
$H_2O(l)$	-237.2	69.91	
$H^+(l)$	0	-20.92	

a) From Ref. 5. b) From Ref. 4. c) From Ref. 10.

TABLE 2. THE GIBBS FREE ENERGIES OF FORMATION FOR GIBBSITE, BOEHMITE, WATER, H^+, AND $Al(OH)_4^-$ IONS AT ELEVATED TEMPERATURES

	$\Delta G^\circ_{f,T}$/kJ mol^{-1}						
T/K	298.15	333.15	373.15	423.15	473.15	523.15	573.15
$Al(OH)_3$	−1154.9	−1157.6	−1160.9	−1165.8	—	—	—
AlOOH	−915.0	−916.8	−919.2	−922.7	−926.7	−931.1	−936.0
$H_2O(1)$	−237.2	−239.8	−243.1	−247.7	−252.7	−258.1	−263.9
$H^+(1)$	0	0.5	0.6	−0.3	−2.6	−6.0	−10.1
$Al(OH)_4^{-}$ a)	−1304.7	−1310.3	−1315.5	−1320.0	—	—	—
$Al(OH)_4^{-}$ b)	−1305.2	−1309.2	−1314.2	−1320.7	−1326.8	−1332.6	−1338.7

a) $\Delta G^\circ_f[Al(OH)_4^-]_1$ obtained from Eq. 9. b) $G^\circ_f[Al(OH)^\circ_4]_2$ obtained from Eq. 10.

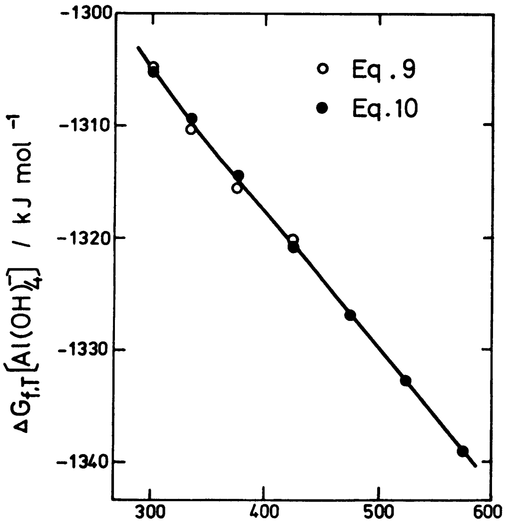

Fig. 1. Temperature dependence of the Gibbs free energy of formation for $Al(OH)_4^-$ ion at temperatures between 25 and 300 °C.

Table 2 gives the results of calculation of the free energies of formation at elevated temperatures for the species in Table 2. The $\Delta G^\circ_f(H_2O)$ values at high temperatures were obtained using the heat capacities of pure water[11] under its saturated vapor pressure at each temperature above 100 °C.

In the temperature range from 25 to 150 °C, $\Delta G^\circ_f[Al(OH)_4^-]_1$ and $\Delta G^\circ_f[Al(OH)_4^-]_2$ are consistent with each other within 1.3 kJ/mol. As is shown in Fig. 1, $\Delta G^\circ_f[Al(OH)_4^-]$ decreases almost linearly with the increase in the temperature; its temperature dependence between 25 and 300 °C can be expressed, after the least-square treatment, as follows:

$$\Delta G^\circ_f[Al(OH)_4^-] = -1152.7 - 3.318\,T - 5.64\times10^{-4}T^2 + 1.202\,T\log T. \tag{11}$$

The value of $\Delta G^\circ_f[Al(OH)_4^-]$ at 25 °C is −1305.3 kJ/mol, which agrees very well with the value of −1305 kJ/mol recently reported by Hemingway.[5]

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