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# Gallium speciation in aqueous solution. Experimental study and modelling: Part 2. Solubility of $\alpha$-GaOOH in acidic solutions from 150 to 250°C and hydrolysis constants of gallium (III) to 300°C

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**Abstract**—The solubility of $\alpha$-GaOOH was measured in low ionic strength (0.025 M) HCl-NaCl solutions over the pH range 1.6–4.1 at 150, 200, and 250°C. A least squares linear regression of these data was used to determine the dissociation constants ($K_{s0}^*$ to $K_{s3}^*$) of the mineral from which hydrolysis constants of aqueous gallium species were derived. The dissociation constants generated in this study were used together with the thermodynamic properties of $\alpha$-GaOOH (Pokrovski et al., 1997) to calculate the standard partial molal thermodynamic properties at 25°C, 1 bar and the equations of state parameters for $Ga^{3+}$, $Ga(OH)^{2+}$, $Ga(OH)_2^+$, and $Ga(OH)_3^0$ within the framework of the revised HKF model (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1992). These thermodynamic properties enabled calculation of gallium speciation as a function of pH and temperature. Our results indicate that the hydrolysis of Ga occurs at low pH and its speciation is strongly dominated by the negatively-charged species $Ga(OH)_4^-$ in the pH range of natural solutions at 25°C. At increasing temperature, the amount of $Ga(OH)_2^+$ and $Ga(OH)_3^0$ becomes significant. These data are used to compare the geochemical behavior of Ga and Al in natural fluids. *Copyright © 1997 Elsevier Science Ltd*

## 1. INTRODUCTION

This paper is the third of a series aimed at providing a coherent set of thermodynamic parameters for Ga aqueous species. The first two papers dealt with the thermodynamic properties of solid Ga oxyhydroxide (Pokrovski et al., 1997) and those of aqueous $Ga(OH)_4^-$ (Diakonov et al., 1997). The present work derives the thermodynamic properties of $Ga^{3+}$ and the other Ga hydrolyzed species at 25°C, 1 bar, from $\alpha$-GaOOH solubility measurements in acidic to near neutral solutions at 150, 200, and 250°C using the revised HKF model (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1992). These data allow calculation of Ga aqueous species distribution as a function of pH and temperature which permits, for the first time, a comparison of Ga and Al geochemical behavior in natural fluids.

## 2. MATERIALS AND METHODS

### 2.1. Solid Phase

Pure, well crystallized $\alpha$-GaOOH (diaspore structural type) was used to perform solubility experiments as this phase is known to be stable between 100 and 300°C (Laubengayer and Engle, 1939; Pokrovski et al., 1997) and probably at lower temperatures. The method of $\alpha$-GaOOH synthesis has already been published in a previous paper of this series (Diakonov et al., 1997). X-ray diffraction analysis of the solid phase showed it to be well-crystallized pure $\alpha$-GaOOH. The surface area of the powder is 0.35 ± 0.05 m²/g as measured by Kr adsorption (BET method). Thermogravimetric

analysis yields a loss of water equal to 8.8 ± 0.1 wt%, depending on the synthetic batch, in good agreement with the theoretical value (8.77%). Differential thermal analysis reveals two endothermic peaks at 430 and 448°C. This split is characteristic of the large grain size (Stoch, 1984; Devidal, 1994), a result consistent with Kr BET results.

### 2.2. Experimental Procedures

Solubilities of $\alpha$-GaOOH were measured at 150, 200, and 250°C at saturated vapor pressure in HCl-NaCl solutions prepared with ultrapure chemical reagents (Prolabo, Normaton). The ionic strength was maintained at a low and nearly constant value (0.025 M) in all experiments to minimize uncertainties in the calculation of the activity coefficients of aqueous species. The experiments were conducted in 350 cm³ pure Ti (UT40) vessels which allow injection of the solid phase at the run temperature. During experiments the suspension was agitated by rocking and maintained at a constant temperature (±2°C). Fifteen cm³ of solution were periodically extracted through an in situ 2 μm porosity Ti filter, then refiltered through a 0.01 μm Sartorius cellulose membrane filter after rapid cooling by means of a water-cooled sampling tube. Each fluid sample was divided into three parts: two aliquots were immediately diluted and acidified to pH = 1 with 0.1 M HNO₃ solution (Normapur, Prolabo) for Ga analysis, and the third was used to measure the pH at 25°C. Measurements of pH were realized with a combined glass electrode (Schott H62) standardized on the activity scale using DIN 19266/NIST standards (pH = 6.865 and 4.008 at 25°C) and a 0.01 M HCl solution (pH = 2.01 at 25°C). The solid/solution weight ratio was 0.001 in all experiments. Analysis by X-ray diffraction performed on the solid phase recovered at the end of each run confirmed that it did not alter during the experiment.

Steady-state was only approached from undersaturation. Equilibrium was assumed to be reached when the Ga concentration remained constant over a sufficient period of time. Typically, over the range of temperature investigated, the concentration plateau was reached after one month. The constancy of the Ga concentration was monitored for one month after the concentration plateau was reached.

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**Table 1.** Values of $H_2O$, NaCl and HCl dissociation constants as a function of temperature.

| $t\,/\,^{\circ}C$ | $\log K_w^{(1)}$ | $\log K_{NaCl}^{(2)}$ | $\log K_{HCl}^{(3)}$ |
|---|---|---|---|
| 25 | -13.995 | 0.780 | 0.670 |
| 150 | -11.631 | 0.210 | 0.410 |
| 200 | -11.284 | -0.090 | 0.090 |
| 250 | -11.167 | -0.470 | -0.490 |

(1) Johnson et al. (1992)
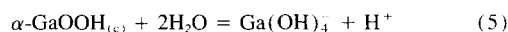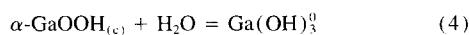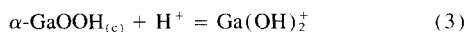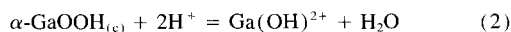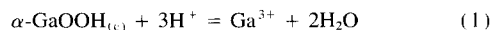(2) Shock et al. (1992)
(3) Ruaya and Seward (1987)

## 2.3. Analytical Methods

The aqueous Ga content was determined by flame or flameless atomic absorption in a graphite furnace (Perkin Elmer Zeeman 5000) over the concentration range 5–40 ppm and 5–30 ppb, respectively. Analysis by atomic absorption used nickel matrix modification in order to increase the sensitivity for Ga (Shan et al., 1985; Diakonov et al., 1997). The reproducibility of the analysis was better than 10% and the detection limit was 3 ppb. For Ga contents lower than 5 ppb, analyses were performed by ICP/MS (Perkin Elmer Elan 5000) (the detection limit for Ga is 5 ppt; the reproducibility and precision are 3%). Gallium calibration solutions were prepared from a 1000 ppm Spectráscan (Technolab ALS) Ga standard solution. All Ga calibrations were realized by using solution matrices that matched those of the samples. The analyses were duplicated on two aliquots of the solution sample. The difference between the measurements never exceeded 3–5% for the lowest concentrations.

## 2.4. Calculation of pH at the Run Temperature, $\alpha$-GaOOH Dissociation Constants and Gallium Hydrolysis Constants

Only mononuclear Ga aqueous species were considered in the calculation of the Ga hydroxide dissociation constants. By analogy with Al (Castet et al., 1993), it is unlikely that polymeric Ga species form to a significant degree in our experiments for which the most concentrated solutions contained less than $10^{-4}$ mol $dm^{-3}$ total Ga. Gallium polymers were only found in solutions containing more than 0.01 M of total Ga (i.e., Haladjian and Carpéni, 1967; Gamsjäger et al., 1969; Baes and Mesmer, 1976). Under oxidizing conditions, only trivalent Ga is stable. The hydrolysis of $Ga^{3+}$ becomes detectable between pH 2 and 3 at 25°C, depending on the concentration of Ga and on the ionic strength (Baes and Mesmer, 1976). As for Al, a classic scheme of $Ga^{3+}$ hydrolysis, with the formation of four hydrolyzed monomers: $Ga(OH)^{2+}$, $Ga(OH)_2^+$, $Ga(OH)_3^0$, and $Ga(OH)_4^-$ has been proposed (i.e., Baes and Mesmer, 1976). In addition, the formation of more hydrolyzed monomeric species has been advocated ($Ga(OH)_5^{2-}$, Kopeykin, 1984; or $Ga(OH)_6^{3-}$, Wagman et al., 1982). No evidence was found for the formation of such species by Diakonov et al. (1997) in the pH range studied by these authors.

Within this framework, $\alpha$-GaOOH solubility can be described from acidic to basic medium by the following reactions:

$$\alpha\text{-GaOOH}_{(c)} + 3H^+ = Ga^{3+} + 2H_2O \qquad (1)$$

$$\alpha\text{-GaOOH}_{(c)} + 2H^+ = Ga(OH)^{2+} + H_2O \qquad (2)$$

$$\alpha\text{-GaOOH}_{(c)} + H^+ = Ga(OH)_2^+ \qquad (3)$$

$$\alpha\text{-GaOOH}_{(c)} + H_2O = Ga(OH)_3^0 \qquad (4)$$

$$\alpha\text{-GaOOH}_{(c)} + 2H_2O = Ga(OH)_4^- + H^+ \qquad (5)$$

We adopted in this study the following classical standard states: at each temperature and pressure considered, unit activity is assumed for the pure solid phase and $H_2O$ and for aqueous species in a hypothetical one molal solution whose behavior is ideal. In dilute

solutions the dissociation constants for reactions 1–5 can be expressed as

$$K_{s0}^* = a_{Ga^{3+}}/a^3_{H^+} \qquad (6)$$

$$K_{s1}^* = a_{Ga(OH)^{2+}}/a^2_{H^+} \qquad (7)$$

$$K_{s2}^* = a_{Ga(OH)_2^+}/a_{H^+} \qquad (8)$$

$$K_{s3}^* = a_{Ga(OH)_3^0} \qquad (9)$$

$$K_{s4}^* = a_{Ga(OH)_4^-} \cdot a_{H^+} \qquad (10)$$

where $a_i$ stands for the activity of the $i$th aqueous species. At a given temperature and pH, the measured total Ga concentration at equilibrium is

$$[Ga]_T = A \cdot a^3_{H^+} + B \cdot a^2_{H^+} + C \cdot a_{H^+} + D + E/a_{H^+} \qquad (11)$$

with

$$A = K_{s0}^*/\gamma_{Ga^{3+}} \qquad (12)$$

$$B = K_{s1}^*/\gamma_{Ga(OH)^{2+}} \qquad (13)$$

$$C = K_{s2}^*/\gamma_{Ga(OH)_2^+} \qquad (14)$$

$$D = K_{s3}^* \qquad (15)$$

$$E = K_{s4}^*/\gamma_{Ga(OH)_4^-} \qquad (16)$$

In these equations, $\gamma_i$ refers to the activity coefficient of the $i$th species. The activity coefficients were calculated using the extended Debye-Hückel equation with the electrostatic parameters taken from Helgeson and Kirkham (1974) and an å parameter of $4 \cdot 10^{-8}$ cm for all the aqueous charged species in solution, regardless of charge and size. Molal activity coefficients of neutral species were assumed to be unity. It should be noted that the value of the $E$ parameter

**Table 2:** $\alpha$-GaOOH solubility measurements at 150, 200 and 250°C in HCl/NaCl aqueous solutions. Experimental results.

| Ref. | $t\,/\,^{\circ}C$ of the run | [Acid]$^{*(1)}$ HCl | [Salt]$^{*(1)}$ NaCl | $pH^{25\,(2)}$ | $pH^T$ calculated | $p[Ga]_T \pm \Delta p[Ga]_T$ |
|---|---|---|---|---|---|---|
| A150 | 150 | $3.16.10^{-2}$ | $3.38.10^{-3}$ | 1.56 | 1.58 | $4.66 \pm 0.01$ |
| B150 | " | $1.99.10^{-2}$ | $5.05.10^{-3}$ | 1.65 | 1.77 | $5.07 \pm 0.02$ |
| C150 | " | $1.00.10^{-2}$ | $2.50.10^{-2}$ | 2.06 | 2.08 | $6.04 \pm 0.03$ |
| D150 | " | $3.16.10^{-3}$ | $2.18.10^{-2}$ | 2.58 | 2.58 | $6.67 \pm 0.03$ |
| E150 | " | $1.00.10^{-3}$ | $2.40.10^{-2}$ | 3.10 | 3.08 | $7.35 \pm 0.03$ |
| F150 | " | $7.94.10^{-4}$ | $2.42.10^{-2}$ | 3.18 | 3.18 | $6.88 \pm 0.03$ |
| G150 | " | $3.16.10^{-4}$ | $2.47.10^{-2}$ | 3.55 | 3.57 | $6.83 \pm 0.04$ |
| H150 | " | $1.10.10^{-4}$ | $2.49.10^{-2}$ | 4.20 | 4.08 | $7.12 \pm 0.02$ |
| A200 | 200 | $2.51.10^{-2}$ | $8.81.10^{-4}$ | 1.65 | 1.69 | $5.24 \pm 0.04$ |
| B200 | " | $1.58.10^{-2}$ | $9.15.10^{-3}$ | 1.95 | 1.89 | $5.63 \pm 0.02$ |
| C200 | " | $1.00.10^{-2}$ | $1.50.10^{-2}$ | 2.04 | 2.09 | $5.53 \pm 0.03$ |
| D200 | " | $1.00.10^{-2}$ | $1.50.10^{-2}$ | 2.04 | 2.09 | $5.78 \pm 0.02$ |
| E200 | " | $3.16.10^{-3}$ | $2.18.10^{-2}$ | 2.53 | 2.59 | $6.23 \pm 0.02$ |
| F200 | " | $1.00.10^{-4}$ | $2.40.10^{-2}$ | 3.14 | 3.09 | $6.28 \pm 0.04$ |
| G200 | " | $6.31.10^{-4}$ | $2.44.10^{-2}$ | 3.32 | 3.29 | $6.32 \pm 0.03$ |
| H200 | " | $3.16.10^{-4}$ | $2.47.10^{-2}$ | 3.90 | 3.59 | $6.27 \pm 0.03$ |
| I200 | " | $1.00.10^{-4}$ | $2.49.10^{-2}$ | 4.34 | 4.09 | $6.14 \pm 0.01$ |
| A250 | 250 | $1.00.10^{-2}$ | $1.50.10^{-2}$ | 2.06 | 2.12 | $4.71 \pm 0.03$ |
| B250 | " | $1.00.10^{-2}$ | $1.50.10^{-2}$ | 2.02 | 2.12 | $5.10 \pm 0.01$ |
| C250 | " | $3.16.10^{-3}$ | $2.18.10^{-2}$ | 2.50 | 2.62 | $5.23 \pm 0.02$ |
| D250 | " | $1.99.10^{-3}$ | $2.30.10^{-2}$ | 2.82 | 2.82 | $5.75 \pm 0.02$ |
| E250 | " | $1.00.10^{-3}$ | $2.40.10^{-2}$ | 3.10 | 3.12 | $5.44 \pm 0.02$ |
| F250 | " | $1.00.10^{-3}$ | $2.40.10^{-2}$ | 3.05 | 3.12 | $5.80 \pm 0.02$ |
| G250 | " | $3.98.10^{-4}$ | $2.46.10^{-2}$ | 3.50 | 3.52 | $5.83 \pm 0.02$ |
| H250 | " | $3.16.10^{-4}$ | $2.47.10^{-2}$ | 3.85 | 3.82 | $5.79 \pm 0.02$ |
| I250 | " | $1.99.10^{-4}$ | $2.48.10^{-2}$ | 4.00 | 3.82 | $5.94 \pm 0.03$ |
| J250 | " | $1.00.10^{-4}$ | $2.49.10^{-2}$ | 4.34 | 4.12 | $5.71 \pm 0.03$ |

(1) Input molalities
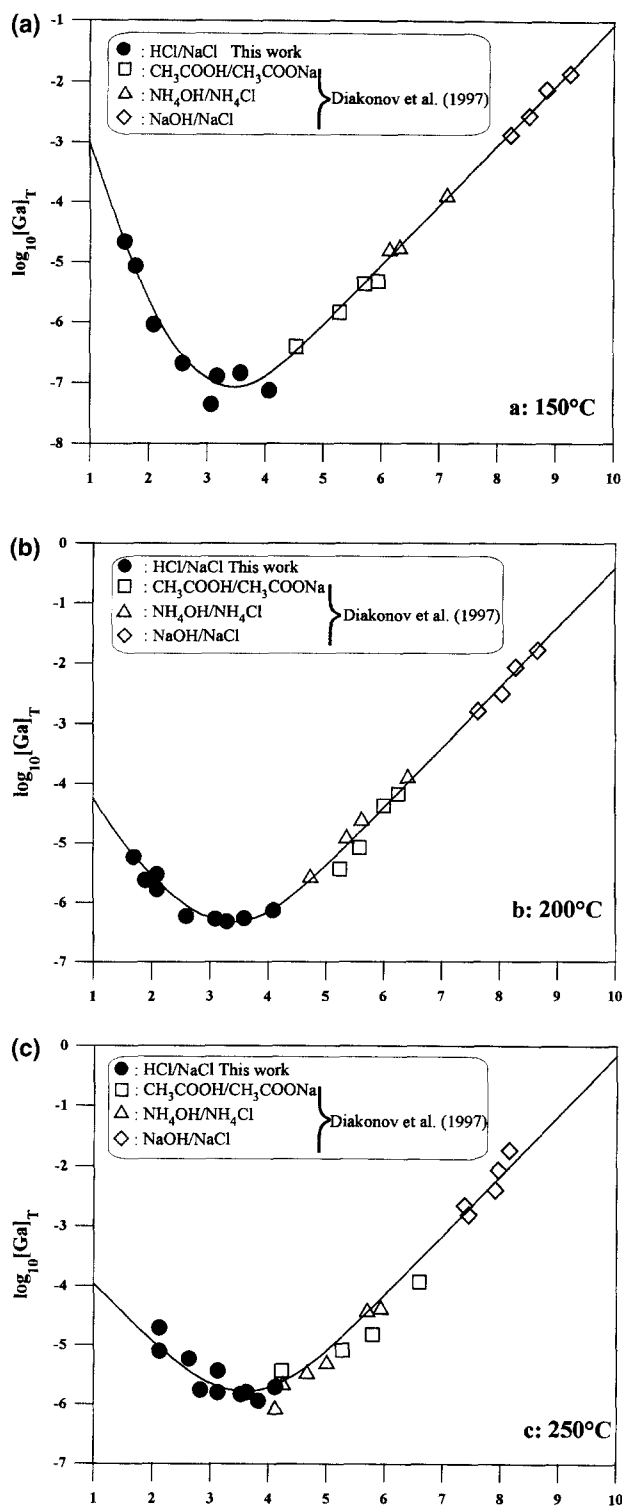(2) Measured at the end of the run ($\Delta pH = \pm 0.02$)

Fig. 1. Measured $\alpha$-GaOOH solubility as a function of pH ($I$ = 0.025 mol kg$^{-1}$). (a) 150°C; (b) 200°C; (c) 250°C. The curves were calculated using $K_{s0}^*$ to $K_{s3}^*$ dissociation constants generated in this study and $K_{s4}^*$ from Diakonov et al. (1997) (see text).

(Eqn. 11) was deduced from the $K_{s4}^*$ constant values determined by Diakonov et al. (1997) between 25 and 250°C.

The solution pH values at the run temperature were calculated by solving a system of nonlinear equations including equilibrium dissociation constants of the components ($H_2O$, $HCl^0$, $NaCl^0$, $\alpha$-GaOOH), mass balance, and charge balance equations. An iterative method was used to calculate activity coefficients. The prerequisite dissociation constants were as follows: $HCl^0$ dissociation constant was taken from Ruaya and Seward (1987); dissociation constants of $NaCl^0$ and $H_2O$ are from Shock et al. (1992) and Johnson et al. (1992), respectively. These data are listed in Table 1 as a function of temperature. As a first approximation, it was assumed that the concentration of Ga aqueous species was sufficiently low to be neglected in the charge balance equation. Calculated pH values then allow the determination of the parameters $A-D$ (Eqn. 11) by using a linear least-square regression program which provided the best fit for the variation of experimental [Ga]$_T$ data vs. H$^+$ activity at each temperature. These parameters allow us to deduce the $\alpha$-GaOOH dissociation constants, $pK_{s0}^*$ to $pK_{s3}^*$, through Eqns. 12–15. The pH was then recalculated taking in account the Ga aqueous species distribution deduced from the $pK_{s0}^*$ to $pK_{s3}^*$ constants and the iteration repeated until the difference between two consecutive values of the dissociation constants was less than 0.05.

Values of the hydrolysis constants $K_{1n}^*$ (with $n$ = 1 to 3) for the three reactions expressed as

$$Ga^{3+} + nH_2O = Ga(OH)_n^{3-n} + nH^+ \qquad (17)$$
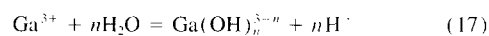
were calculated from $\alpha$-GaOOH dissociation constants using

$$pK_{1n}^* = pK_{sn}^* - pK_{s0}^* \qquad (18)$$

## 3. RESULTS AND DISCUSSION

### 3.1. Solubility Measurements

The results of the solubility experiments carried out at 150, 200, and 250°C are listed in Table 2. In this Table are gathered the temperature of the run, the acid and salt concentrations of the reacting solutions, the pH measured at 25°C at the end of each run, and the negative logarithm of the Ga concentration ($p$[Ga]$_T$) and its uncertainty ($\Delta p$[Ga]$_T$). This parameter corresponds to one standard deviation of the Ga concentration measured after equilibrium was reached. Also included in this Table are the calculated pH at the run temperature with an uncertainty less than ±0.03. This uncertainty only takes account of the measured pH variations at 25°C during a single run. The errors introduced by the calculations are related to the accuracy of the dissociation constants used and are estimated to be ±0.05 pH units. The results of the solubility measurements are illustrated in Fig. 1a–c at 150, 200, and 250°C, respectively. This figure also includes the results obtained by Diakonov et al. (1997) in basic solutions.

The dissociation constants deduced from the $A$, $B$, $C$, and $D$ parameters (Eqn. 11) are reported in Table 3 with their estimated uncertainties. At 250°C, only the parameters $C$ and $D$ and the corresponding dissociation constants $pK_{s2}^*$ and $pK_{s3}^*$ were determined owing to the small amount of $Ga^{3+}$ and $Ga(OH)^{2+}$ species present in solution in the pH range

Table 3: $\alpha$-GaOOH dissociation constants as a function of temperature.

| t / °C | $pK_{s0}^*$ | $pK_{s1}^*$ | $pK_{s2}^*$ | $pK_{s3}^*$ | $pK_{s4}^{*(1)}$ |
|---|---|---|---|---|---|
| 150 | 0.70 ± 0.1 | 2.53 ± 0.1 | 4.25 ± 0.3 | 7.45 ± 0.3 | 11.15 ± 0.1 |
| 200 | — | 2.88 ± 0.1 | 3.75 ± 0.2 | 6.55 ± 0.1 | 10.52 ± 0.1 |
| 250 | — | — | 3.10 ± 0.2 | 5.95 ± 0.1 | 10.28 ± 0.1 |

(1) Diakonov et al. (1997)

**Table 4:** Hydrolysis constants deduced from the dissociation constants (Table 3) as a function of temperature.

| t / °C | pK$_{11}$ | pK$^*_2$ | pK$^*_3$ | pK$^*_4$ | pK$_{14}$ |
|---|---|---|---|---|---|
| 150 | 1.83 | 1.72 | 3.2 | 3.7 | 10.45 |
| 200 | — | 0.87 | 2.8 | 3.97 | — |
| 250 | — | — | 2.85 | 4.33 | — |

**Table 6:** Solubility products deduced from pH and precipitation during hydrolysis of gallium salts. Literature data.

| t / °C | Solubility Products | References |
|---|---|---|
| 25 | $5.0.10^{-37}$ | Fricke and Blencke (1925) |
| 25 | $4.3.10^{-37}$ | Oka (1938) |
| 25 | $3.2.10^{-37}$ | Lacroix (1948) |
| 10 | $1.0.10^{-36}$ | Moeller and King (1950) |
| 25 | $7.0.10^{-36}$ | " |
| 40 | $9.4.10^{-35}$ | " |
| 25 | $1.0.10^{-37}$ | Feitknecht and Schindler (1963) |

investigated. At 200°C, the parameter $A$ and the dissociation constant p$K^*_{30}$ were omitted owing to the small amount of Ga$^{3+}$ present in solution even at pH 1.7. Only at 150°C was the solubility expressed using the four parameter equation and all the dissociation constants p$K^*_{30}$ to p$K^*_{33}$ determined. The equations fitting the measured solubility as a function of H$^+$ activity at 150, 200, and 250°C are:

$$[Ga]_T^{150} = 0.91 \; a^3_{H^+} + 6.71 \times 10^{-3} \; a^2_{H^+} + 6.90$$
$$\times 10^{-5} \; a_{H^+} + 3.55 \times 10^{-8} + 8.69 \times 10^{-12}/a_{H^+} \quad (19)$$

$$[Ga]_T^{200} = 3.43 \times 10^{-3} \; a^2_{H^+} + 2.26 \times 10^{-4} \; a_{H^+}$$
$$+ 2.82 \times 10^{-7} + 4.31 \times 10^{-11}/a_{H^+} \quad (20)$$

$$[Ga]_T^{250} = 1.06 \times 10^{-3} \; a_{H^+} + 1.12$$
$$\times 10^{-6} + 7.00 \times 10^{-11}/a_{H^-} \quad (21)$$

The representative curves of Eqns. 19–21 are plotted in Fig. 1a, b, and c, respectively. Values of Ga hydrolysis constants deduced from $\alpha$-GaOOH dissociation constants (Eqn. 18) are given in Table 4.

## 3.2. Analysis and Discussion of Previous Literature Data

Several studies have reported the thermodynamic properties of monomeric Ga hydrolyzed species at 25°C. They are based on potentiometric, colorimetric, and solubility measurements at various ionic strengths. A review of these works shows inconsistencies in the values of the hydrolysis constants at 25°C and a lack of data at higher temperature.

### 3.2.1. $K^*_{s0}$ and $K^*_{s3}$ dissociation constants

Only a few studies investigated the solubility of $\alpha$-GaOOH. Fetter (1957) measured the solubility of synthetic $\alpha$-GaOOH in acidic and basic conditions at 25°C and calcu-

Table 5. Dissociation constants of $\alpha$-GaOOH, literature data.

| Medium | t / °C | logQ$^*_{s0}$ | logQ$^*_{s4}$ | Ref. |
|---|---|---|---|---|
| I=0 | 25 | 2.9 | -13.665 | 1 |
| 3 mol kg$^{-1}$ NaClO$_4$ | 60 | 3.66±0.06 | | 2 |
| 1 mol kg$^{-1}$ NaClO$_4$ | 50 | 4.29±0.03 | | 3 |

(1) Fetter (1957)
(2) Gamsjäger and Schindler (1967)
(3) Gimblett (1971)

lated values of the dissociation constants $K^*_{s0}$ and $K^*_{s4}$ listed in Table 5. Note that the solid phase used by Fetter probably contained Ga(OH)$_3$ in addition to $\alpha$-GaOOH (Diakonov et al., 1997). Gamsjäger and Schindler (1967) performed $\alpha$-GaOOH solubility measurements at 60°C in acidic 3 M NaClO$_4$ solutions. Equilibrium was assumed to be reached after 6–8 days. Their proposed value for the first hydrolysis quotient (Eqn. 1) is log $Q^*_{s0}$ = 3.66 ± 0.06, from which an extrapolation to zero ionic strength results in log $K^*_{s0}$ = 1.7 ± 0.5 (Gamsjäger et al., 1969). Gimblett (1971) determined the solubility of $\alpha$-GaOOH from precipitation experiments at 50°C in 1 M NaClO$_4$. The solid phase was precipitated by hydrolysis of Ga(III) perchlorate solution for a [OH$^-$]/ [Ga$^{3+}$] ratio ranging between 1.5 and 2.5. The precipitation was monitored by turbidity and pH measurements. From measured Ga content and pH at steady state, Gimblett (1971) deduced log $Q^*_{s0}$ = 4.29 ± 0.03.

Several values of the Ga hydroxide solubility product reported in the literature (Fricke and Blencke, 1925; Fricke and Meyring, 1928; Oka, 1938; Lacroix, 1948; Moeller and King, 1950) were deduced from the Ga concentration and pH measured after precipitation of Ga hydroxide upon the hydrolysis of soluble Ga(III) salts. For example, Fricke and Meyring (1928) titrated GaCl$_3$ solutions with NaOH and KOH and observed the precipitation of a hydrous oxide at pH ranging between 2.8 and 3.1. Lacroix (1948) obtained precipitation from GaCl$_3$ solutions (0.007 M) at pH 3.2 and its dissolution at pH > 6. These authors considered that the trihydrate, Ga(OH)$_3$, precipitated in their experiments. However, the crystallinity of the solid phase was not specified. The solubility products calculated by these different authors are reported in Table 6. Feitknecht and Schindler (1963) calculated a solubility product of approximately $10^{-37}$ for amorphous Ga(OH)$_3$ at 25°C. This value is in the same range of magnitude as the values reported in the literature (Table 6), and suggests that amorphous Ga(OH)$_3$ precipitation may have been a problem in previous investigations.

### 3.2.2. $K_{11}$ to $K_{13}$ hydrolysis constants

Fricke and Meyring (1928) investigated the hydrolysis of Ga at 18°C via potentiometric titration of dilute GaCl$_3$ solutions (3 $\times$ 10$^{-4}$ to 10$^{-2}$ M). Their calculated values of log $Q_{11}$ and log $Q_{12}$ at zero ionic strength are reported in Table

**Table 7:** Values of $Q_{11}$ to $Q_{13}$ $Ga^{3+}$ hydrolysis constants. Literature data.

| Medium (mol dm⁻³) | t / °C | logQ₁₁ | logQ₁₂ | logQ₁₃ | Ref |
|---|---|---|---|---|---|
| 0 | 18 | -2.85 | -6.31 | | 1 |
| 0.001 GaX₃ | 25 | -2.22 | | | 2 |
| 0.002 " | " | -2.71 | | | " |
| 0.004 " | " | -2.91 | | | " |
| 0.006 " | " | -2.99 | | | " |
| 0.008 " | " | -3.01 | | | " |
| 0.01 " | " | -3.03 | | | " |
| 0.02 " | " | -3.09 | | | " |
| 0.05 " | " | -3.15 | | | " |
| 0.1 HCl | 25 | -2.91 | -6.61 | -11.02 | 3 |
| 0.1 NaClO₄ | 25 | -2.87 | -6.55 | -11.07 | 4 |
| 0.3 " | " | -2.48 | -5.67 | -9.69 | " |
| 0.5 " | " | -2.30 | -5.20 | -8.65 | " |
| 1 " | " | -1.78 | -3.88 | -6.16 | " |
| 0 | " | -2.92 | -6.69 | -11.44 | " |
| 0 | 25 | -2.60 | -5.90 | -10.30 | 5 |
| 0.5 NaClO₄ | 10 | -4.17 | -8.21 | | 6 |
| 0.1 " | 25 | -3.50 | -7.67 | | " |
| 0.5 " | " | -3.69 | -7.43 | | " |
| 1.5 " | " | -4.15 | -6.97 | | " |
| 0 | " | -3.46 | -7.70 | | " |
| 0 | 25 | -2.92 | | | 7 |
| 0 | 25 | -2.60 | | | 8 |
| 0.1 KNO₃ | 25 | -3.16 | -7.07 | | 9 |
| 0.5 " | " | -3.73 | -7.15 | | " |
| 1 " | " | -3.92 | -7.79 | | " |
| 1.5 " | " | -4.02 | -7.73 | | " |
| 0 | " | -2.56 | -6.07 | | " |
| 0 | 25 | -2.56 | -6.37 | -11.30 | 10 |

(1) Fricke and Meyring (1928)
(2) Calculated from the data of Moeller and King (1950) with $x$ = Br, Cl or $NO_3$ (see text)
(3) Nazarenko et al. (1968)
(4) Biryuk and Nazarenko (1973)
(5) Calculated by Baes and Mesmer (1976) from the data of Moeller and King (1950) ($K_{11}$) and Nazarenko et al. (1968) ($K_{12}$ and $K_{13}$)
(6) Campisi and Tregloan (1985)
(7) Kudryashov (1986)
(8) Akitt and Kettle (1989)
(9) Brown (1989)
(10) Brown (unpublished values, referenced in Brown, 1989)

7. Moeller and King (1950) determined the values of $Q_{11}$ at 25°C from the degree of hydrolysis $\alpha = 10^{-pH}/c$ (where $c$ stands for the total Ga aqueous concentration) of $GaBr_3$, $GaCl_3$, and $Ga(NO_3)_3$ solutions of various ionic strengths. For Ga concentrations ranging between $4 \times 10^{-3}$ and 0.25 M, they calculated average values of log $Q_{11}$ as reported in Table 7. Note, however, that the degree of hydrolysis should be expressed by the ratio $c_{H^-}/c$ where $c_{H^+}$ stands for the concentration of $H^+$ ($c_{H^+} = 10^{-pH}/\gamma_{H^+}$). In order to compare the results of Moeller and King (1950) with the other literature values, we have recalculated the $Q_{11}$ values using $H^+$ concentration instead of activity. The value of $c_{H^+}$ was deduced from the measured pH reported by Moller and King (1950) and the activity coefficient computed using the Debye-Hückel limiting law: log $\gamma_{H^-} = -A_\gamma Z_i^2 I^{1/2}/(1 + I^{1/2})$ (the value of $A_\gamma$ was taken from Helgeson and Kirkham, 1974). The average values of $Q_{11}$ recalculated for $GaBr_3$, $GaCl_3$, and $Ga(NO_3)_3$ hydrolysis are reported in Table 7 as a function of the ionic strength.

Nazarenko et al. (1968) deduced $Q_{11}$, $Q_{12}$, and $Q_{13}$ values from a spectrophotometric method involving the competition between ligands formed by the hydroxide species with colored organic reagent (Pyrocatechol violet, 9-propyl-2,3,7-trihydroxy-6-fluorone, and 9-o-hydroxyphenyl-2,3,7-trihydroxy-6-fluorone). The hydrolysis quotients were deter-

mined in 0.1 M HCl solutions and for a total Ga concentration of $2 \times 10^{-5}$ M. The results of Moeller and King (1950) and Nazarenko et al. (1968) were extrapolated by Baes and Mesmer (1976) to zero ionic strength. From the data of Moeller and King (1950) obtained at concentrations lower than 0.05 M, Baes and Mesmer (1976) estimated the value of $K_{11}$ at 25°C: log $K_{11} = -2.60$. From the results of Nazarenko et al. (1968), they calculated at 25°C log $K_{12} = -5.90$ and log $K_{13} = -10.30$ (Table 7). The spectrophotometric method was extended by Biryuk and Nazarenko (1973) to $Ga(ClO_4)_3$ solutions ($2 \times 10^{-5}$ M) of various ionic strengths (0.1–1 M $NaClO_4$) with Alizarin-3-sulphonic acid as competing ligand. The authors obtained the values of $Q_{11}$, $Q_{12}$, and $Q_{13}$ as a function of ionic strength and extrapolated their values to zero ionic strength using: log $Q = \log K + bI$ (Table 7).

Ivanov-Emin et al. (1962) estimated from pH measurements in basic Ga solutions the small extent (see Baes and Mesmer, 1976), of the reaction:

$$Ga(OH)_4^- = Ga(OH)_3^0 + OH^-$$

They obtained log $K = -7.15$. This value, combined with the value of log $K_{14} = -16.6$ deduced by Diakonov et al. (1997) from the results of Fetter (1957), leads to log $K_{13} = -9.72$ in fair agreement with the value log $K_{13} = -10.3$ deduced by Baes and Mesmer (1976) from the data of Nazarenko et al. (1968).

Campisi and Tregloan (1985) studied gallium hydrolysis by potentiometric measurements in $NaClO_4$ solutions at 25°C (and one measurement at 10°C) as a function of the ionic strength, and for Ga concentrations ranging between $4 \times 10^{-4}$ and $10^{-2}$ M. From a linear extrapolation of log $Q$ vs. the ionic strength, they deduced the values of $K_{11}$ and $K_{12}$ (Table 7). Kudryashov et al. (1986) calculated the first Ga hydrolysis constant (log $K_{11} = -2.92$) from spectrophotometric and ionic exchange measurements in $10^{-5}$ M $Ga(ClO_4)_3$ solutions. Akitt and Kettle (1989) determined by NMR spectroscopy: log $K_{11} = -2.6$. Brown (1989) carried out potentiometric measurements in $KNO_3$ solutions (0.1–1.5 M) and determined $Q_{11}$ and $Q_{12}$ constants at various ionic strengths; these values were extrapolated to zero ionic strength using an equation derived from the extended Debye-Hückel equation: $\log Q_{pq} = \log K_{pq} + A_\gamma \Delta Z^2 I^{1/2}/(1 + bI^{1/2}) + cI$ where $b$ and $c$ are parameters fitted to the experimental data and $\Delta Z$ stands for the sum of the charge of each species over the reaction. The values obtained are reported in Table 7. In the same paper, Brown (1989) proposed values of $K_{11}$, $K_{12}$, and $K_{13}$ obtained by extrapolation to zero ionic strength using another method (P. L. Brown, unpubl. data). These two extrapolations lead to the same value of $K_{11}$ (log $K_{11} = -2.56$), but the values of $K_{12}$ differ by 0.3 log units (Table 7).

The $Q_{11}$ to $Q_{13}$ hydrolysis quotients measured at 25°C by previous authors are plotted as a function of $I^{1/2}/(1 + I^{1/2})$ in Fig. 2a–c for $Q_{11}$, $Q_{12}$, and $Q_{13}$, respectively. At low ionic strength, the relationship between log $Q_{pq}$ and $I^{1/2}/(1 + I^{1/2})$ should be linear and allows verification of the extrapolation proposed by the authors at infinite dilution.
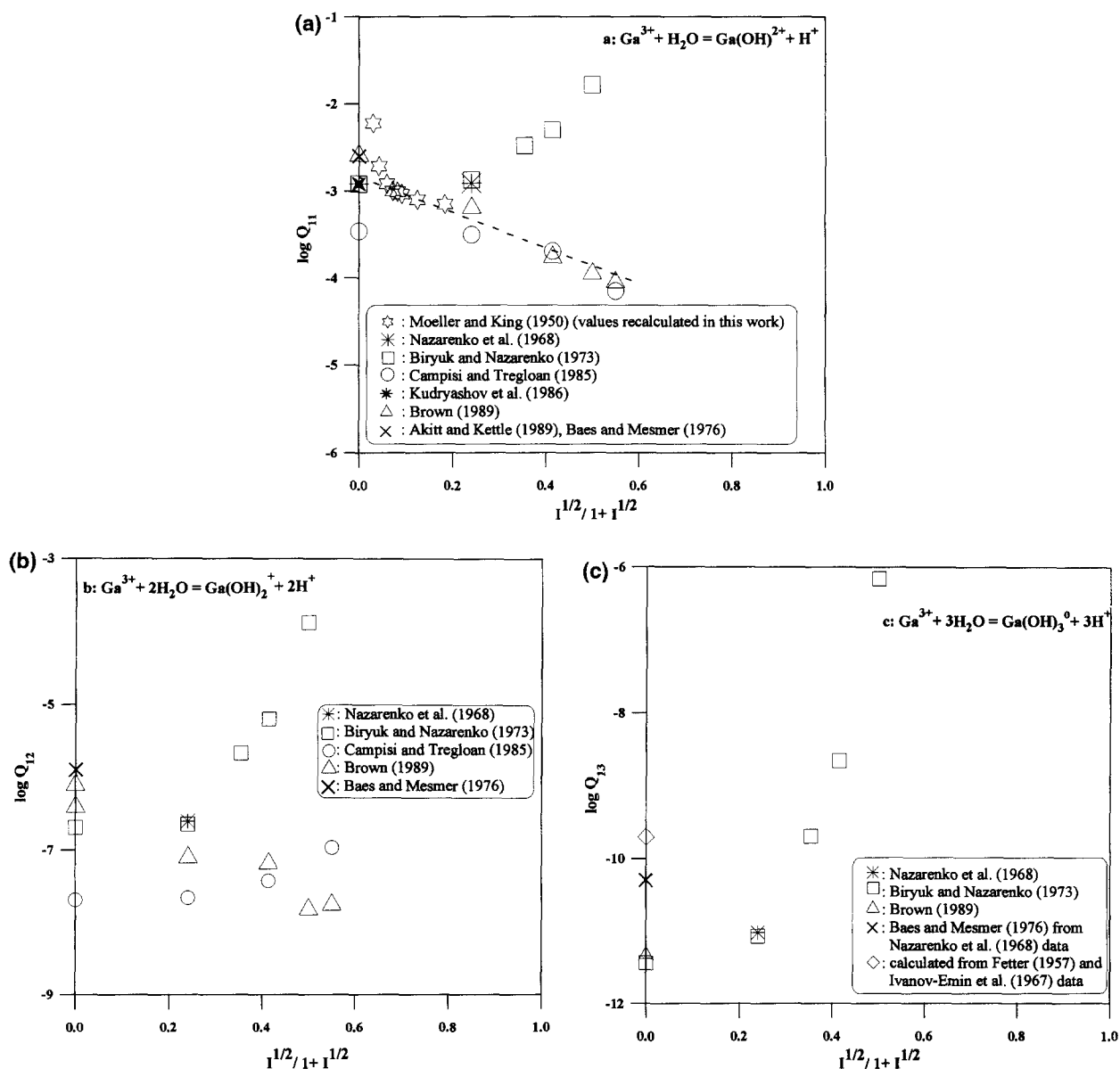
Fig. 2. Logarithm of literature hydrolysis quotient values as a function of $I^{1/2}/(1 + I^{1/2})$ at 25°C. (a) $Q_{11}$; (b) $Q_{12}$; (c) $Q_{13}$. The data at zero ionic strength are extrapolated values. The dashed line is drawn using a linear regression method on selected values with a slope imposed by the Debye-Hückel law (see text).

### 3.2.3. $Q_{11}$ hydrolysis quotient

The values reported in Fig. 2a are in rough agreement with the exception of Biryuk and Nazarenko (1973) values

for which the variation of the hydrolysis quotient as a function of the ionic strength is the opposite compared to the other authors and the slope of the Debye-Hückel law. Moreover, for the same ionic strength, the value obtained by

Table 8. Thermodynamic data at 25°C and 1 bar and heat capacity power function coefficients for $\alpha$-GaOOH (Pokrovski et al., 1997). (heat capacity equation: $Cp° = a + bT - cT^{-2}$).

| | $\Delta G°_{f,298.15}$ kcal/mol | $\Delta H°_{f,298.15}$ kcal/mol | $S°_{298.15}$ cal/mol K | $Cp°_{298.15}$ cal/mol K | $V°_{298.15}$ cm$^3$/mol | $a$ cal/mol K | $b.10^3$ cal/mol K$^2$ | $c.10^{-5}$ cal K/mol |
|---|---|---|---|---|---|---|---|---|
| $\alpha$-GaOOH | -150.07 | -168.57 | 12.335 | 14.53 | 19.70 | 13.00 | 15.34 | 2.70 |

**Table 9:** Standard partial molal thermodynamic properties at 25°C and 1 bar and HKF equation of state parameters for $Ga^{3+}$, $Ga(OH)^{2+}$, $Ga(OH)_2^+$ and $Ga(OH)_3^0$.

| | $\Delta_f G°_{298.15}$ kcal mol⁻¹ | $S°_{298.15}$ cal mol⁻¹ K⁻¹ | $Cp°_{298.15}$ cal mol⁻¹ K⁻¹ | $V°_{298.15}$ cm³ mol⁻¹ | $c_1$ cal mol⁻¹ K⁻¹ | $c_2 \times 10^{-4}$ cal K mol⁻¹ | $a_1 \times 10$ cal mol⁻¹ bar⁻¹ | $a_2 \times 10^{-2}$ cal mol⁻¹ | $a_3$ cal K mol⁻¹ bar⁻¹ | $a_4 \times 10^{-4}$ cal K mol⁻¹ | $\omega_i \times 10^{-5}$ cal mol⁻¹ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Ga^{3+}$ | -38.74[1] | -48.05 | -24.14[2] | -41.00[2] | 16.904 | -7.952 | -2.815 | -14.654 | 11.510 | -2.173 | 2.728 |
| $Ga(OH)^{2+}$ | -91.55[3] | -30.28 | 1.67 | -14.35 | 14.931 | -2.694 | 0.124 | -7.479 | 8.689 | -2.469 | 0.853 |
| $Ga(OH)_2^+$ | -142.18 | 12.02 | 18.68 | 9.64 | 16.602 | 0.770 | 3.063 | -0.302 | 5.869 | -2.766 | -0.056 |
| $Ga(OH)_3^0$ | -192.51 | 31.70 | 26.88 | 30.96 | 21.919 | 2.441 | 6.002 | 6.874 | 3.048 | -3.063 | 0 |

(1) Calculated from Saltman and Nachtrieb (1953) data

(2) Van Gaans (1990)

(3) Calculated from $\Delta G°_{f,298.15}$ ($Ga^{3+}$) and $pK_{11}$ (2.84) from the literature

Nazarenko et al. (1968) is somewhat higher than those of Campisi and Tregloan (1985) and Brown (1989). However, it is difficult to assess the reliability of a hydrolysis quotient obtained for only one ionic strength and one gallium concentration. The constants reported by Nazarenko et al. (1968) and Biryuk and Nazarenko (1973) seem unreliable owing to the use of an indirect method which required a good knowledge of the equilibrium constants of the Ga complexes formed with the organic ligands. The Moeller and King (1950) values deviate from the linear extrapolation for the lower ionic strengths ($<0.002$ M). This could be explained by the uncertainties of potentiometric measurements carried out at low ionic strength. Omitting these unreliable data, we estimated a $K_{11}$ value by a linear regression of the selected data with a slope $\Delta Z^2 A_\gamma = -2.0364$. We obtained log $K_{11}$



Fig. 3. Correlation of the standard partial molal non-solvation entropies ($S° - \Delta S_{Born}$) of Al and Ga hydroxides complexes with the number of $OH^-$ ions ($n_{OH^-}$) in the complexes. The filled circles correspond to the calculated values using data in Table 9 and the solid line is obtained by a linear regression. The open circles and the dashed line correspond to the values for aluminum aqueous species deduced from the data of Castet et al. (1993).

$= -2.84 \pm 0.1$. The uncertainty of this value includes uncertainties in the activity coefficients. This value allows calculation of the Gibbs free energy of formation of $Ga(OH)^{2+}$ using the Gibbs free energy of formation of $Ga^{3+}$ ($-38.74$ kcal/mol), calculated from the data of Saltman and Nachtrieb (1953): $\Delta_f G°_{298.15}$ ($Ga(OH)^{2+}$) $= -91.55$ kcal/mol.

### 3.2.4. $Q_{12}$ and $Q_{13}$ hydrolysis quotients

Measured values of $Q_{12}$ and $Q_{13}$ at 25°C are scarce and inconsistent (Fig. 2b and 2c). Thus, we did not attempt to extrapolate these values to zero ionic strength.

### 4. STANDARD PARTIAL MOLAL THERMODYNAMIC PROPERTIES AT 25°C AND REVISED HKF EQUATIONS OF STATE PARAMETERS OF GALLIUM AQUEOUS SPECIES

The solubility constants determined in this study were used together with the thermodynamic properties of $\alpha$-GaOOH (Pokrovski et al., 1997; Table 8) to generate, within the framework of the revised HKF model (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1992), the standard partial molal thermodynamic properties at 25°C, 1 bar and revised HKF equations of state parameters for $Ga^{3+}$, $Ga(OH)^{2+}$, $Ga(OH)_2^+$, and $Ga(OH)_3^0$. The parameters of this model are the thermodynamic properties for each species at the reference temperature ($\Delta_f G°_{298.15}$, $S°$, $V°$, $Cp°$) and their HKF equation of state parameters ($a_1$ to $a_4$, $c_1$, $c_2$, and $\omega_i$). Owing to a lack of data for the Ga aqueous species, some of these parameters were adjusted to the experimental results. Also, the standard partial molal heat capacity and volume of aqueous Ga species are not well constrained by our experimental results and had to be estimated separately.

### 4.1. Calculation of the Standard Molal Heat Capacity and Volume of $Ga(OH)^{2+}$, $Ga(OH)_2^+$, and $Ga(OH)_3^0$ at 25°C

The heat capacity and volume of hydrolyzed Ga species were generated using the correlations proposed by Hovey (1988) between the nonsolvation contribution of the thermo-
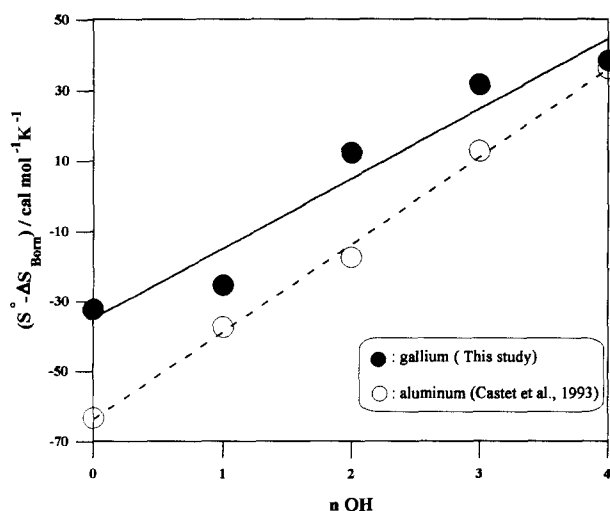
**Table 10:** α–GaOOH dissociation constants (a) and Ga hydrolysis constants (b) deduced from the HKF model

(a)

| t / °C | pK$^\bullet_{s0}$ | pK$^\bullet_{s1}$ | pK$^\bullet_{s2}$ | pK$^\bullet_{s3}$ |
|--------|------|------|------|-------|
| 25  | -1.50 | 1.35 | 5.78 | 10.44 |
| 50  | -0.93 | 1.67 | 5.34 | 9.59 |
| 100 | -0.02 | 2.18 | 4.63 | 8.27 |
| 150 | 0.70  | 2.56 | 4.06 | 7.29 |
| 200 | 1.32  | 2.86 | 3.63 | 6.56 |
| 250 | 1.91  | 3.13 | 3.27 | 6.01 |
| 300 | 2.53  | 3.41 | 2.98 | 5.58 |
| 350 | 2.90  | 3.69 | 2.72 | 5.25 |

(b)

| t / °C | pK$_{11}$ | pK$_{12}$ | pK$_{13}$ | pK$_{14}$ |
|--------|------|------|-------|-------|
| 25  | 2.85 | 7.28  | 11.94 | 15.66 |
| 50  | 2.60 | 6.27  | 10.52 | 14.30 |
| 100 | 2.19 | 4.64  | 8.27  | 12.02 |
| 150 | 1.86 | 3.36  | 6.59  | 10.44 |
| 200 | 1.54 | 2.31  | 5.25  | 9.24  |
| 250 | 1.22 | 1.36  | 4.10  | 8.30  |
| 300 | 0.88 | 0.45  | 3.05  | 7.58  |
| 350 | 0.79 | -0.17 | 2.36  | 7.53  |

dynamic properties of hydrolyzed species and their respective OH$^-$ ligand number. Details on the principle of these correlations and the assumptions used for Ga aqueous species are presented in Diakonov et al. (1997). The calculation of the standard partial molal heat capacity and volume of Ga(OH)$^{2+}$, Ga(OH)$^+_2$, and Ga(OH)$^0_3$ was based on the values of $Cp^0$ and $V^0$ for Ga$^{3+}$ measured by Van Gaans (1990), together with the assumption that the linear relationship between the nonsolvation contribution of $Cp^0$ and $V^0$ and the OH ligand number holds for the aqueous Ga hydroxide species with a slope similar to that for the Al-hydrolyzed species. The values of $Cp^0$ and $V^0$ of the hydrolyzed Ga species are then calculated as the sum of the extrapolated values of the nonsolvation contribution and the Born contribution deduced from

$$Cp^0_{Born} = \omega_i TX \tag{22}$$

$$V^0_{Born} = -\omega_i Q \tag{23}$$

where $T$ stands for the absolute temperature, $X$ and $Q$ are functions of the dielectric constant of water (tabulated in Shock et al., 1992), and $\omega_i$, the conventional Born coefficient, is defined for the $i$th ionic species by (Shock and Helgeson, 1988)

$$\omega_i = \omega_i^{abs} - Z_i \cdot \omega_{H^+}^{abs}$$

$$= (1.6627 \times 10^5 \cdot Z_i^2)/r_{e,i} - Z_i \cdot 53870 \tag{24}$$

where $\omega_{H^+}^{abs}$ denotes the absolute Born coefficient of the hydrogen ion and $Z_i$ and $r_{e,i}$ refer to the charge and the effective radius of the $i$th species. The effective radius used in this calculation is the same for all the species and equal to the value for Ga$^{3+}$ (3.44 Å; Shock and Helgeson, 1988). A value of zero was assigned to the Ga(OH)$^0_3$ conventional Born coefficient in agreement with the Born equation for neutral species. The $Cp^0$ and $V^0$ values obtained for the Ga hydrolyzed species are listed in Table 9.

## 4.2. Calculation of the Apparent Gibbs Free Energy, Entropy, and Equations of State Parameters for Aqueous Ga Hydrolyzed Species

### 4.2.1. Ga$^{3+}$ and Ga(OH)$^{2+}$ species

The apparent standard partial Gibbs free energy for Ga$^{3+}$ was determined from the Saltman and Nachtrieb (1953) data. For Ga(OH)$^{2+}$ it was derived from the $\Delta_f G^0_{298.15}$(Ga$^{3+}$) value together with the selected pK$_{11}$ value (2.84) deduced from the literature. The entropy and the revised HKF equations of state parameters for these two species were obtained by calculating the apparent Gibbs free energies values of Ga$^{3+}$ and Ga(OH)$^{2+}$ at experimental temperatures using the dissociation constants generated in this study (Table 3) together with the thermodynamic data for $\alpha$-GaOOH (Pokrovski et al., 1997, Table 8) and water (Johnson et al., 1992). The apparent Gibbs free energy values were then regressed to the experimental data by specifying at 25°C the partial molal Gibbs free energy of formation ($\Delta_f G^0_{298.15}$), heat capacity ($Cp^0$), volume ($V^0$), and Born parameter ($\omega_i$) reported in Table 9 to generate the best value of the standard partial molal entropy at 25°C ($S^0$) and the HKF equation of state parameters. These calculations were realized with the help of UT-HEL computer code (Shvarov, 1997) which is consistent with the revised HKF equation of state (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1992). The standard state properties and HKF equation of state parameters for Ga$^{3+}$ and Ga(OH)$^{2+}$ thus obtained are reported in Table 9.

### 4.2.2. Ga(OH)$^+_2$ and Ga(OH)$^0_3$ species

The standard partial Gibbs free energies and entropies of Ga(OH)$^+_2$ and Ga(OH)$^0_3$ are unknown. Moreover, the dissociation constants $K^*_{s2}$ and $K^*_{s3}$ cannot be derived from the literature hydrolysis constants owing to their inconsistency. This makes the extrapolation from only the value we obtained at high temperature problematic. Thus, the dissociation constants $K^*_{s2}$ and $K^*_{s3}$ were calculated at 25°C from all the available literature hydrolysis constants using Eqn. 18 in order to constrain the fit, although the obtained values at 25°C are scattered as shown in Fig. 4c and 4d for $K^*_{s2}$ and $K^*_{s3}$, respectively. Both our experimental values and the 25°C literature values were used to adjust the unknown thermodynamic parameters of the HKF model. The standard state properties and HKF equation of state parameters obtained for Ga(OH)$^+_2$ and Ga(OH)$^0_3$ are reported in Table 9.

### 4.2.3. Check of the correlation between the nonsolvation entropy contribution and the hydrolyzed species OH ligand number

From the entropy values at 25°C generated for the different hydrolyzed Ga species (Table 9), we have computed the nonsolvation entropy contribution: $S^0 - \Delta S^0_{Born}$ where $\Delta S^0_{Born} = \omega Y$ (the value of $Y$ is tabulated in Shock et al., 1992). Figure 3 compares the variations of $(S^0 - \Delta S^0_{Born})$ as a function of the OH ligand number ($n_{OH^-}$) for Ga and Al (Castet et al., 1993) hydrolyzed species. The obtained relation for Ga is roughly linear and its slope is close to
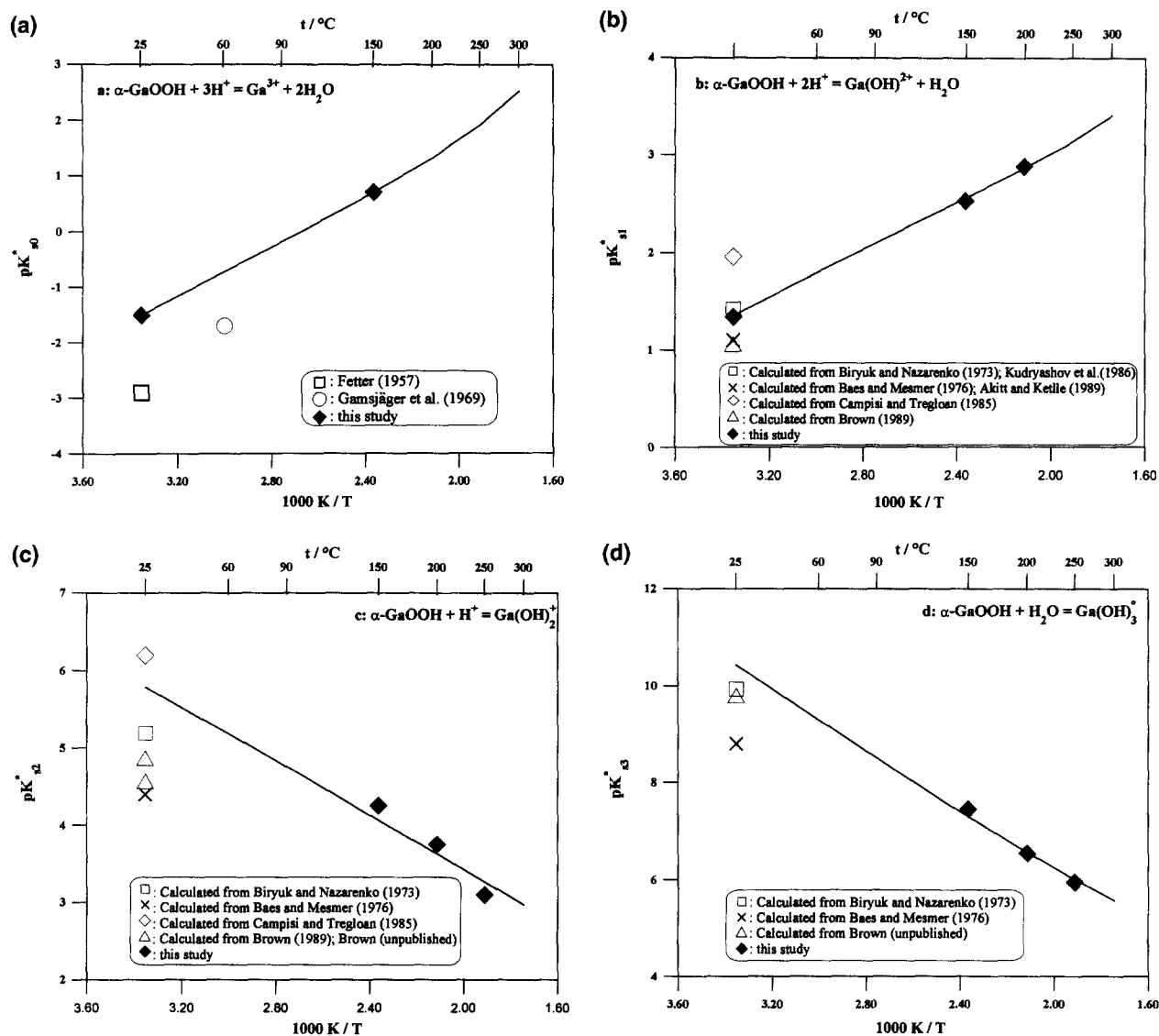
Fig. 4. Negative logarithm of $\alpha$-GaOOH dissociation constants as a function of reciprocal absolute temperature. The symbols depicted are the calculated values from the literature and the experimental values generated in the present study. The solid lines are calculated using the revised HKF equations of state and the parameters given in Table 9 together with the properties of $\alpha$-GaOOH from Pokrovski et al. (1997) (Table 8).

that for Al, which gives confidence to the entropy values determined from the revised HKF equation of state.

The standard partial molal properties of aqueous gallium species at 25°C, 1 bar generated in this study are listed in Table 9, together with parameters for the revised HKF equation of state. These data were associated with the thermodynamic properties of $\alpha$-GaOOH (Table 8) to calculate $\alpha$-GaOOH dissociation constants and Ga hydrolysis constants as a function of temperature. These constants are reported in Table 10 for temperatures from 25 to 350°C. The dissociation constants of $\alpha$-GaOOH are represented as a function of the reciprocal temperature in Fig. 4. The close agreement between the computed curve and the experimental results, depicted as symbols in Fig. 4, attest to the consistency of the HKF model.

Figure 5a–c present, as a function of the pH, the distribution of aqueous Ga species calculated using the data generated in this study at 25, 150, and 250°C. At 25°C (Fig. 5a), Ga speciation is strongly dominated by the negatively-charged species, $Ga(OH)_4^-$ in the pH range of natural waters. Also, it can be seen that the maximum amount of $Ga(OH)_2^+$ and $Ga(OH)_3^0$ increases with temperature. This can be explained by the decrease of the dielectric constant of water with increasing temperature (for example, $\epsilon_{H20}$ decreases from 78.5 at 25°C to 26.5 at 250°C and saturated vapor pressure). This leads to the stabilization of less charged species due to ionic association. We also note a shift of hydrolyzed species maximum stability range to acidic pH with increasing temperatures. Consequently, only $Ga(OH)_2^+$, $Ga(OH)_3^0$, and $Ga(OH)_4^-$ dominate Ga aqueous
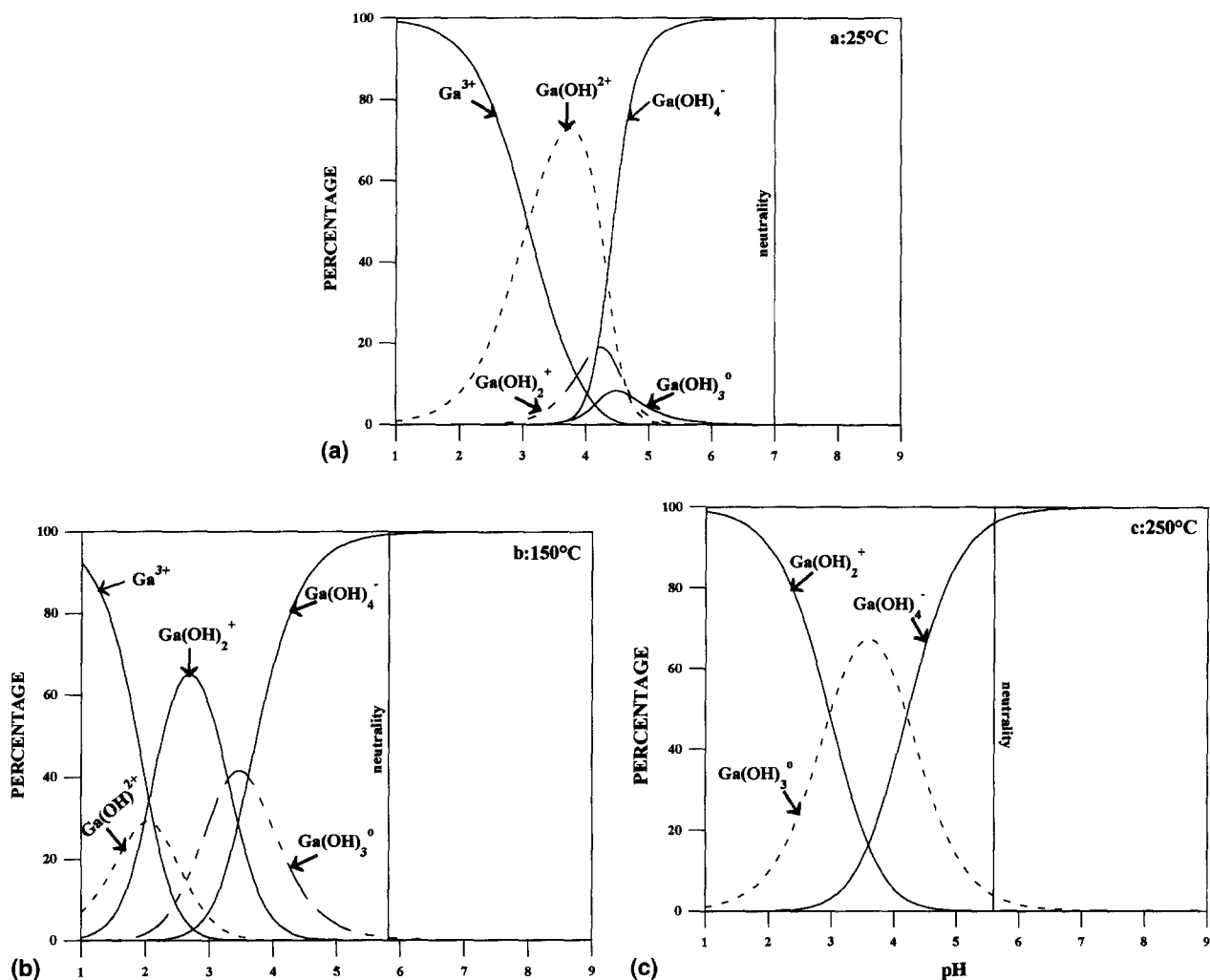
Fig. 5. Distribution of Ga aqueous species as a function of pH at different temperatures: (a) 25°C; (b) 150°C; (c) 250°C. Percentages are expressed in activity unit. The vertical lines show the neutral pH.

speciation above pH 1 at 250°C. As for Al, the neutral species only exists at a pH range more acidic than neutral regardless of the temperature in the range 25–250°C.

## 5. COMPARISON OF GALLIUM AND ALUMINUM BEHAVIOR IN NATURAL FLUIDS

Belonging to the same column in the periodic table of elements, it could be expected that Ga should exhibit a chemical behavior similar to that of Al and other readily-hydrolyzed elements (Fe, Th, Bi, and so on). Nevertheless, analysis of trace element compositions in seawater, rivers, and streams show the different behavior of Ga and Al. For example, the mean Ga/Al concentration ratio in seawater $(0.8 \times 10^{-3}$ to $2.3 \times 10^{-3}$, Shiller, 1988) is higher than the continental crust Ga/Al ratio $(0.1 \ 10^{-3}$, Horn and Adams, 1966), whereas the Ga/Al ratio in rivers $(0.03 \ 10^{-3}$ to $1.06 \ 10^{-3}$, Shiller, 1988) encompasses the continental crust ratio. Elucidation of the enrichment of Ga relative to Al in some rivers and in seawater is under debate. Some authors assume anthropogenic Ga input to seawater. For example, Bertine

and Goldberg (1971) evoked a potential Ga release of $10^9$ g per year from coal burning. If this release were to dissolve in the mixed layer (assumed to be 100 m deep), a Ga residence time in the mixed layer on the order of 50 years would be required to produce the observed enrichment (Shiller, 1988). However, it has been estimated that the dissolved Al residence time in open ocean surface waters ranges between 2 and 6 years (Maring and Duce, 1987; Orians and Bruland, 1988b). Thus, Shiller (1988) considered the anthropogenic source of Ga too low to account for its enrichment in seawater and explained the high Ga/Al ratio by the preferential dissolution of Ga contained in solid phases and preferential removal of dissolved Al. It should be noted, however, that in all the previous analytical studies, the dissolved Ga and Al refer to their content in the 0.4 $\mu$m filtrated fraction (Orians and Bruland, 1988a,b; Shiller, 1988; Shiller and Frilot, 1996). The concentration of the true dissolved Ga and Al fraction can be much lower because of the presence, in the 0.4 $\mu$m filtrate, of small particles of clays and iron hydroxide containing these metals. The greater ionic radius
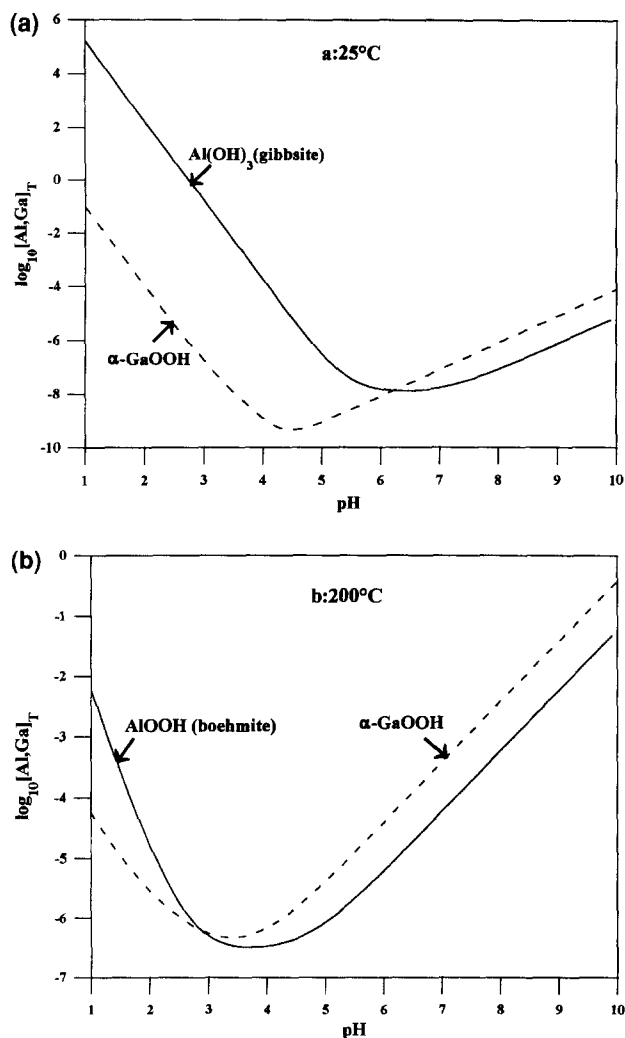
**(a)**



**(b)**



Fig. 6. Comparison of $\alpha$-GaOOH and $\gamma$-AlOOH or gibbsite ($Al(OH)_3$) solubilities at 25°C (a) and 200°C (b) as a function of pH for a constant ionic strength ($I = 0.025$ mol $kg^{-1}$).

of trivalent Ga should result in its more easily solubilization than Al from solid phases in which Ga substitutes for Al (Goldschmidt, 1954). Although both Ga and Al are enriched in weathering products, the Ga/Al ratio tends indeed to decrease in the residual materials (Burton and Culkin, 1972). Removal of Ga and Al from the surface ocean may involve several processes including precipitation of solid phases, adsorption on oxide surfaces, and complexation and/or adsorption by organic matter. During precipitation and following the Goldschmidt (1954) rule, Al should be incorporated preferentially to Ga in solid phases, owing to its smaller ionic radius. Additionally, the Ga-O bond is longer and more covalent than the Al-O bond (Ga-O = 2.02 Å, Al-O = 1.93 Å; Shannon and Prewitt, 1969) suggesting relative exclusion of Ga in the competition with Al for structural sites (Burton and Culkin, 1972). However, Martin (1994) showed that Ga could largely substitute for Al in synthetic kaolinite and bedeillite. The distribution coefficient of Ga/Al between clay and solution is close to 1 for kaolinite and 12 for smectites.

Hence, Ga will be easily incorporated in the phyllosilicate lattice with a great affinity for smectites.

Thermodynamic properties of aqueous Ga species determined in this study and Diakonov et al. (1997), as well as those recently acquired by Castet et al. (1993), Palmer and Wesolowski (1992, 1993), and Wesolowski and Palmer (1994) on Al, allow the comparison of Al and Ga speciation as a function of pH and temperature. Figure 6 compares $\alpha$-GaOOH solubility to that of gibbsite at 25°C (Fig. 6a) and boehmite at 200°C (Fig. 6b). At 200°C, the solubility curves, and thus Ga and Al speciation tend to converge. In particular, at pH's commonly encountered in natural dilute fluids (5 < pH < 8), both Al and Ga are present as negatively-charged species. This accounts for their similar behavior in hydrothermal fluids in the absence of sulfide minerals which can selectively concentrate Ga (Goldschmidt, 1954; Burton and Culkin, 1972). In contrast, at 25°C (Fig. 6a), Ga and Al behaviors differ significantly in the pH range of natural dilute solutions, $Ga(OH)_4^-$ being the dominant Ga hydrolyzed species, whereas $Al(OH)_3^0$ dominates Al speciation. This accounts for the fractionation of Ga from Al in near surface aqueous systems by adsorption onto solid oxides and/or hydroxides surfaces. For example, at 25°C, goethite surfaces are positively charged up to pH 7.8 (Stumm and Morgan, 1981). Above pH 4.5, negatively-charged aqueous Ga species could be adsorbed on the goethite surface in the pH range 4.5-7.8, whereas the pH range for possible Al adsorption is very narrow (7.2-7.8). This process is reversed for the adsorption on kaolinite surfaces that are negatively charged above pH 4.6. Thus, positively charged Al species could be adsorbed between pH 4.6 and 6.0 on kaolinite surfaces, whereas negatively charged kaolinite surfaces do not coexist with positively charged aqueous Ga species. This results in the preferential adsorption of $Ga(OH)_4^-$ on iron oxide and hydroxide surfaces which could explain some recent Ga and Al analyses in weathering products. Indeed, Hieronymus et al. (1990) shows that during ferralitic and bauxitic alteration of basalts and sedimentary rocks from eastern Amazonia, Ga vs. Al correlations are strongly negative while positive correlations occur between Ga and Fe, suggesting Ga retention phenomena by iron oxides and hydroxides. Besides pH, which can affect Ga and Al adsorbing properties, the complexation by organic ligands, such as humic and fulvic acids, is also likely to influence the geochemistry of Ga relative to Al in surface waters. Recently, Viers et al. (1997) in their extensive study of weathering processes in a tropical watershed (Nsimi-Zoetele, Cameroon) showed that the Ga/Al ratios measured in slightly acidic organic-rich waters (pH = 5.6, 10 mg/L < $m_{DOC}$ < 25 mg/L) are about one order of magnitude lower (typically Ga/Al = 0.5–0.7 $10^{-3}$) than those measured in organic-free waters (Ga/Al = $8.10^{-3}$). Both Al and Ga are complexed by organic matter as demonstrated by positive correlation between the decrease of dissolved Al, Ga, and DOC upon ultrafiltration (from 0.2 $\mu$m to 3 nm). Nevertheless, Al concentration is controlled by equilibrium with kaolinite, while Ga is not controlled by any solid phase, and organic acids only modify aqueous Ga speciation without changing its total concentration.

## 6. CONCLUSION

Solubility measurements of $\alpha$-GaOOH in acidic to neutral aqueous solutions at 150, 200, and 250°C and constant ionic strength have been used to generate the $K_{s0}^*$ to $K_{s3}^*$ dissociation constants at the corresponding temperature. These values, associated with available selected literature data at 25°C and thermodynamic properties of $\alpha$-GaOOH (Pokrovski et al., 1997), allowed the calculation of the standard partial molal thermodynamic properties at 25°C, 1 bar and the equation of state parameters for $Ga^{3+}$, $Ga(OH)^{2+}$, $Ga(OH)_2^+$, and $Ga(OH)_3^0$ using the revised HKF model. Together with the corresponding values for $Ga(OH)_4^-$, determined by Diakonov et al. (1997), this results in the first consistent set of thermodynamic properties for aqueous Ga species. Species distribution, calculated using these data, indicates that gallium hydrolysis is important. Indeed, $Ga(OH)_4^-$ is the major species in the pH range of natural solutions. These results, along with Al hydrolysis constants available in the literature, allow comparison of the geochemical behavior of these elements in natural fluids. Even though their solubility and speciation are similar at high temperature, their behavior differs at low temperature. At 25°C and in the pH range of natural solution, $Ga(OH)_4^-$ is the major Ga aqueous species, whereas $Al(OH)_3^0$ dominates the aluminum speciation up to pH 7 at low ionic strength. This accounts for selective Ga removal from natural solutions by adsorption onto oxide or hydroxide surfaces, positively charged up to pH 8, whereas Al could be adsorbed on negatively charged surfaces or complexed with organic matter.

## REFERENCES

Akitt J. W. and Kettle D. (1989) [71]Gallium nuclear magnetic resonance investigation of aqueous gallium(III) and its hydrolysis. *Magn. Reson. Chem.* **27**, 377–379.

Baes C. F., Jr, and Mesmer R. E. (1976) *The Hydrolysis of Cations.* Wiley.

Bertine K. K. and Goldberg E. A. (1971) Fossil fuel combustion and the major sedimentary cycle. *Science* **173**, 233–235.

Biryuk E. A. and Nazarenko V. A. (1973) Determination of hydrolysis constants of monomeric gallium ions in solutions with ionic strength 0.1–1.0. *Russ. J. Inorg. Chem.* **18**, 1576–1578.

Brown P. L. (1989) The hydrolysis of metals ions. Part 11. The ionic strength dependence of gallium(III). *J. Chem. Soc. Dalton. Trans.*, 399–402.

Burton J. D. and Culkin F. (1972) Gallium. In *Handbook of Geochemistry* (ed. K. H. Wedepohl), parts 31B–310. Springer-Verlag.

Campisi A. and Tregloan P. A. (1985) Kinetics and equilibria of Ga(III)-Thiocyanate complex formation. Mechanism of ligand substitution reactions of Ga(III) in aqueous solution. *Inorg. Chim. Acta* **100**, 251–259.

Castet S., Dandurand J. L., Schott J., and Gout R. (1993) Boehmite solubility and aqueous aluminum speciation in hydrothermal solutions (90–350°C). Experimental study and modeling. *Geochim. Cosmochim. Acta* **57**, 4869–4884.

Devidal J. L. (1994) Solubilité et cinétique de dissolution/précipitation de la kaolinite en milieu hydrothermal. Approche expérimentale et modélisation. Thèse de l'Univ. Paul-Sabatier, Toulouse.

Diakonov I. I., Pokrovski G. S., Bénézeth P., Schott J., Dandurand J.-L., and Escalier J. (1997) Gallium speciation in aqueous solution. Experimental study and modeling: Part 1. Thermodynamic properties of Ga(OH)$_4^-$ to 300°C. *Geochim. Cosmochim. Acta.* (this issue).

Feitknecht W. and Schindler P. (1963) Solubility constants of metal oxides, metal hydroxides, and metal hydroxide salts in aqueous solution. *Pure Appl. Chem.* **6**, 130–199.

Fetter N. R. (1957) The equilibria of crystalline gallium oxide monohydrate in dilute solutions of perchloric acid and sodium hydroxide at 25°C. Ph.D. Thesis, Univ. Oregon.

Fricke R. and Blencke (1925) Beiträge zur Chemie des Galliums. *Z. Anorg. Allgem. Chem.* **143**, 183–200.

Fricke R. and Meyring K. (1928) Beiträge zur Chemie des Galliums. II. *Z. Anorg. Allgem. Chem.* **176**, 325–348.

Gamsjäger H. and Schindler P. (1967) Die Löslichkeit von $\alpha$-GaO(OH) bei 60°C in perchlorsauren Lösungen konstanter Ionenstärke. *Helv. Chim. Acta* **50**, 2053–2057.

Gamsjäger H., Aeberhard K., and Schindler P. (1969) Die Hydrolyse des Ga$^{3+}$-ions; potentiometrische Untersuchungen in 3m NaClO$_4$ bei 60°C. *Helv. Chim. Acta* **52**, 2315–2327.

Gimblett F. G. R. (1971) Particle growth and precipitation in hydrolyzed gallium (III) perchlorate solutions. *J. Inorg. Nucl. Chem.* **33**, 2887–2903.

Goldschmidt V. M. (1954) *Geochemistry.* Oxford Univ. Press.

Haladjian J. and Carpeni G. (1967) Recherches sur le point isohydrique et les phénomènes de condensation ou d'association (xxiv). Etude électrométrique de l'isopolycondensation du cation hydraté [Ga aq]$^{3+}$, à 25°C en milieu KCl ($C_{Cl^-}$ = 3M). *J. Chim. Phys. Physiochim. Biol.* **64**, 1338.

Helgeson H. C. and Kirkham D. H. (1974) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: II. Debye-Hückel parameters for activity coefficients and relative partial molal properties. *Amer. J. Sci.* **274**, 1199–1261.

Hieronymus B., Boulegue J., and Kotschoubey B. (1990) Gallium behavior in some intertropical environment alterations. *Geochem. Earth's Surf. Min. Form. 2nd Intl. Symp., Aix en Provence, France, Chem. Geol.* **84**, 78–82.

Horn M. K. and Adams J. A. S. (1966) Computer-derived geochemical balances and element abundances. *Geochim. Cosmochim. Acta* **30**, 279–297.

Hovey J. K. (1988) Thermodynamics of aqueous solutions. Ph.D. Thesis, Univ. Alberta.

Ivanov-Emin B. N., Nisel'son L. A., and Larionova L. E. (1962) Alkali metal gallate solutions. *Russ. J. Inorg. Chem.* **7**, 266–268.

Johnson J. W., Oelkers H. E., and Helgeson H. C. (1992) SUPCRT92. A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Comput. Geosci.* **18**, 899–947.

Kopeykin V. A. (1984) Geochemical features of the behavior of gallium in laterization. *Geochem. Intl.* **14**, 16–20.

Kudryashov B., Davidov Yu., and Mironov B. (1986) 2ème conférence de la chimie analytique de solutions d'électrolytes, Moscou, 2–4 décembre, p20.

Lacroix S. (1948) *Etude de quelques complexes et composés peu solubles des ions Al$^{3+}$, Ga$^{3+}$, In$^{3+}$.* Masson.

Laubengayer A. W. and Engle H. R. (1939) The sesquioxide and hydroxides of gallium. *J. Amer. Chem. Soc.* **61**, 1210–1214.

Maring H. R. and Duce R. A. (1987) The impact of atmospheric

aerosols on trace metal chemistry in open ocean surface seawater. 1. Aluminum. *Earth Planet. Sci. Lett.* **84**, 381–392.

Martin F. (1994) Etude cristallographique et cristallochimique de l'incorporation du germanium et du gallium dans les phyllosilicates. Approche par synthèse minérale. Thèse de l'Univ. Aix, Marseille.

Moeller T. and King G. L. (1950) Some physicochemical studies on Gallium(III) salt solutions. *J. Phys. Colloid Chem.* **54**, 999–1011.

Nazarenko V. A., Antonovich V. P., and Nevskaya E. M. (1968) Spectrophotometric determination of the hydrolysis constants of gallium ions. *Russ. J. Inorg. Chem.* **13**, 825–828.

Oka Y. (1938) The fundamental reactions in analytical chemistry. IX. Summary. *J. Chem. Soc. Japan* **59**, 971.

Orians K. J. and Bruland K. W. (1988a) Dissolved gallium in the open ocean. *Nature* **21**, 717–719.

Orians K. J. and Bruland K. W. (1988b) The marine geochemistry of dissolved gallium. A comparison with dissolved aluminum. *Geochim. Cosmochim. Acta* **52**, 2955–2962.

Palmer D. A. and Wesolowski D. J. (1992) Aluminum speciation and equilibria in aqueous solution: II. The solubility of gibbsite in acidic sodium chloride solutions from 30 to 70°C. *Geochim. Cosmochim. Acta* **56**, 1093–1111.

Palmer D. A. and Wesolowski (1993) Aluminum speciation and equilibria in aqueous solution: III. Potentiometric determination of the first hydrolysis constant of aluminum (III) in sodium chloride solutions to 125°C. *Geochim. Cosmochim. Acta* **57**, 2929–2938.

Pokrovski G. et al. (1996) Thermodynamic properties of gallium hydroxide ($\alpha$GaOOH) at temperatures to 700K. Submitted to *Eur. J. Miner.*

Ruaya J. R. and Seward T. M. (1987) The ion-pair constant and other thermodynamic properties of HCl up to 350°C. *Geochim. Cosmochim. Acta* **51**, 121–130.

Saltman W. M. and Nachtrieb N. H. (1953) The electrochemistry of gallium. *J. Electrochem. Soc.* **100**, 126–130.

Shan X. Q., Yuan Z. N., and Ni Z. M. (1985) Determination of gallium in sediment, coal, coal fly ash, and botanical samples by Graphite Furnace Atomic Absorption Spectrometry using nickel matrix modification. *Anal. Chem.* **57**, 857–861.

Shannon R. D. and Prewitt C. D. (1969) Effective ionic radii in oxides and fluorides. *Acta Cryst.* **B25**, 925–946.

Shiller A. M. (1988) Enrichment of dissolved gallium relative to aluminum in natural waters. *Geochim. Cosmochim. Acta* **52**, 1879–1882.

Shiller A. M. and Frilot D. M. (1996) The geochemistry of gallium relative to aluminum in California streams. *Geochim. Cosmochim. Acta* **60**, 1323–1328.

Shock E. L. and Helgeson H. C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high temperatures and pressures: Correlation algorithms for ionic species and equation of state predictions to 5 kbar and 1000°C. *Geochim. Cosmochim. Acta* **52**, 2009–2036.

Shock E. L., Oelkers E. H., Johnson J. W., Sverjensky D. A., and Helgeson H. C. (1992) Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures: Effective electrostatic radii, dissociation constants and standard partial molal properties to 1000°C and 5 kbar. *J. Chem. Soc. Faraday Trans.* **88**, 803–826.

Shvarov Y. V. (1997) "UT-HEL": A BASIC computer code for calculating the revised HKF equations of state parameters for aqueous species. Version 2-0. *Submitted to Software Notice,* Amer. Miner.

Stoch L. (1984) Significance of structural factors in dehydroxylation of kaolinite polytypes. *J. Therm. Anal.* **29**, 161–166.

Stumm W. and Morgan J. J. (1981) *Aquatic Surface Chemistry.* 2nd edition. Wiley.

Tanger J. C. and Helgeson H. C. (1988) Revised equation of state for the standard partial molal properties of ions and electrolytes. *Amer. J. Sci.* **288**, 19–98.

Van Gaans P. F. M. (1990) The Pitzer model applied to aqueous GaCl$_3$ solutions with evaluation of regression methods. Ph.D. Thesis, Univ. Utrecht.

Viers J., Dupre B., Polve M., Schott J., Dandurand J. L., and Braun J. J. (1996) Geochemistry of major, trace elements and dissolved organic carbon in waters (ground and river water) draining lateritic soils in a tropical area: Nsimi-Zoetele (Cameroon, Central Africa). Submitted to *Chem. Geol.*

Wagman D. D. et al. (1982) The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C$_1$ and C$_2$ organic substances in SI units. *J. Phys. Chem. Ref. Data* **11** (suppl. 2), pp. 131–132.

Wesolowski D. J. and Palmer D. A. (1994) Aluminum speciation and equilibria in aqueous solution: V. Gibbsite solubility at 50°C and pH 3 to 9 in 0.1 molal NaCl solutions (a general model for aluminum speciation; analytical methods). *Geochim. Cosmochim. Acta* **58**, 2947–2969.