

## Hydration change reaction of light REE<sup>3+</sup>(aq) series-I: An important constraint on REE(III) partitioning and complex formation reactions in low-temperature to hydrothermal condition

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### ABSTRACT

The hydration state of light REE<sup>3+</sup>(aq) is changing across the series, and each light REE<sup>3+</sup>(aq) is a mixture of two distinguishable species of nonhydrate and octahydrate in equilibrium with respect to the hydration change reaction of light REE<sup>3+</sup>(aq). Two sets of thermodynamic data for the hydration change of light REE<sup>3+</sup>(aq) at 25°C and 1 atm have been reported: one is the data set for the reaction  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = [\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  evaluated by Miyagawa *et al.* (1988) on the basis of the hydration enthalpies and free energies for the two hydrate series calculated from electrostatic bonding energies and Born's hydration theory. The other is the data set for the conventional reaction that octahydrate REE<sup>3+</sup>(aq) = REE<sup>3+</sup>(aq), which was evaluated by Kawabe (1999a) from the thermodynamic data for solution of the fully isomorphous series of  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$  ( $\text{ES} = \text{C}_2\text{H}_3\text{SO}_4^-$ ) and the partly isomorphous ones of  $\text{REECl}_3 \cdot n\text{H}_2\text{O}$  ( $n = 7$  for La – Pr and  $n = 6$  for Nd – Lu) and their least-squares fittings to the improved RSPET (refined spin-pairing energy theory) equation. Here is shown that the thermodynamic parameters for the two reactions are readily convertible, and that the standard-state  $\Delta G_r^0$  values for  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = [\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  from Kawabe (1999a) are more acceptable than those calculations by Miyakawa *et al.* (1988) when referred to the X-ray diffraction studies of hydrated REE<sup>3+</sup> in REE(III) chloride solutions. The  $\Delta G_r^0$  values at elevated temperatures up to 250°C have been calculated using the standard-state  $\Delta H_r^0$  and  $\Delta S_r^0$  for the reaction and the equation by Helgeson (1967 and 1969). The theoretical estimates are compatible with our recent experimental results of REE(III) partition coefficients between Fe(III) oxyhydroxide and aqueous solution in hydrothermal conditions. The series variations of logarithmic equilibrium constants for all the geochemical reactions involving REE<sup>3+</sup>(aq) are affected by the hydration change of REE<sup>3+</sup>(aq), but the hydration change effect can be separated from the over-all series variations using the thermodynamic parameters calculated in this study.

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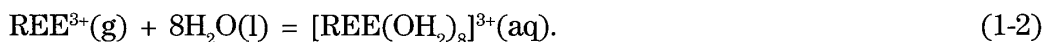
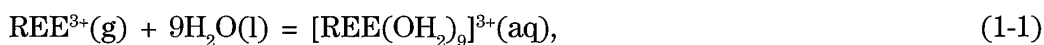
## INTRODUCTION

The hydration number of  $\text{REE}^{3+}(\text{aq})$  is not constant across the series according to X-ray and neutron diffraction studies of  $\text{REE}(\text{III})$  chloride or perchlorate solutions at normal temperature and pressure (Habenschuss and Spedding, 1980; Rizkalla and Choppin, 1991; Ohataki and Radnai, 1993). The hydration number of light  $\text{REE}^{3+}(\text{aq})$  like  $\text{La}^{3+}(\text{aq})$  or  $\text{Pr}^{3+}(\text{aq})$  is closer to 9, suggesting a nonahydrate of  $[\text{REE}(\text{OH}_2)_9]^{3+}(\text{aq})$ , but the hydration number of light  $\text{REE}^{3+}(\text{aq})$  gradually decreases from 9 to 8 with going from La to Gd, and then the heavy  $\text{REE}^{3+}(\text{aq})$  from Tb to Lu has the hydration number of 8 as the octahydrate of  $[\text{REE}(\text{OH}_2)_8]^{3+}(\text{aq})$ . Referring to Raman and EXAFS measurements of the hydrated  $\text{REE}^{3+}$  in water and in the aqueous glassy state, Ohataki and Radnai (1993) concluded that the intermediate  $\text{REE}^{3+}(\text{aq})$  like  $\text{Sm}^{3+}(\text{aq})$  or  $\text{Eu}^{3+}(\text{aq})$  is likely to be a mixture of nona- and octahydrates which are in equilibrium with each other.

Miyakawa *et al.* (1988) and Kawabe (1999a) independently presented the thermodynamic discussion that light  $\text{REE}^{3+}(\text{aq})$  is a mixture of  $[\text{REE}(\text{OH}_2)_9]^{3+}(\text{aq})$  and  $[\text{REE}(\text{OH}_2)_8]^{3+}(\text{aq})$ . Miyakawa *et al.* (1988) calculated the hydration enthalpies and free energies for  $[\text{REE}(\text{OH}_2)_9]^{3+}$  and  $[\text{REE}(\text{OH}_2)_8]^{3+}$  on the basis of the electrostatic bonding model for the two complexes and Born's hydration model for ions, and they supplemented the model calculations with the temperature variation of ultra-violet (4f→5d) absorption spectra of aqueous  $\text{Ce}(\text{III})(\text{ES})_3$  ( $\text{ES} = \text{C}_2\text{H}_5\text{SO}_4^-$ ) solution. They distinguished the absorption bands of octahydrate  $\text{Ce}^{3+}(\text{aq})$  and nonahydrate  $\text{Ce}^{3+}(\text{aq})$  in aqueous  $\text{Ce}(\text{ES})_3$  solution in reference to the absorption spectra of crystalline  $\text{Ce}(\text{III})$ -doped  $\text{La}(\text{ES})_3 \cdot (\text{H}_2\text{O})_9$ . They confirmed the suggestion by Jørgensen and Brinen (1963) that a small amount of octahydrate  $\text{Ce}^{3+}(\text{aq})$  is present with dominant nonahydrate  $\text{Ce}^{3+}(\text{aq})$  in aqueous  $\text{Ce}(\text{III})$  solutions. They estimated thermodynamic parameters for the following hydration change reaction of  $\text{REE}^{3+}(\text{aq})$  at 25°C and 1 atm pressure:



They can be given as the differences of calculated hydration enthalpies and free energies for  $[\text{REE}(\text{OH}_2)_9]^{3+}$  and  $[\text{REE}(\text{OH}_2)_8]^{3+}$  in reference to the following reactions:



Originally Miyagawa *et al.* (1988) evaluated the thermodynamic parameters for the reverse reaction of (1), but here is cited their results as those for (1) in order to make an immediate comparison with the results by Kawabe (1999a) as below.

For the purpose of elimination of the hydration change effect in light  $\text{REE}^{3+}(\text{aq})$  relative to heavy  $\text{REE}^{3+}(\text{aq})$  on the equilibrium constants for the reactions involving  $\text{REE}^{3+}(\text{aq})$ , Kawabe (1999a) estimated the thermodynamic parameters ( $\Delta H_h^*$ ,  $\Delta S_h^*$ , and  $\Delta G_h^* = \Delta H_h^* - T\Delta S_h^*$ ) for the hypothetical reaction for  $\text{REE} = \text{La} - \text{Gd}$  at 25°C and 1 atm pressure;



They represent the deviations of the thermodynamic quantities for real  $\text{REE}^{3+}(\text{aq})$

relative to those for hypothetical octahydrate REE<sup>3+</sup>(aq) in the light REE series. The values of  $\Delta H_h^*$ ,  $\Delta S_h^*$  and  $\Delta G_h^*$  by Kawabe (1999a) were determined from the thermodynamic data for solution of the fully isomorphous series of  $REE(ES)_3 \cdot 9H_2O$  ( $ES = C_2H_5SO_4^-$ ) and the partly isomorphous series of  $REECl_3 \cdot nH_2O$  ( $n = 7$  for La – Pr and  $n = 6$  for Nd – Lu) at 25°C and 1 atm, and their least-squares fittings to the improved RSPET (refined spin-pairing energy theory) equation by Kawabe (1992). The values of  $\Delta G_h^* = \Delta H_h^* - T\Delta S_h^*$  have been applied to elimination of the hydration change effect in light REE<sup>3+</sup>(aq) from the experimental data of logarithmic REE(III) partition coefficients between Fe(III) oxyhydroxide and aqueous solution, and from logarithmic stability constants for REE(III)-carbonate complexes (Kawabe, 1999b; Kawabe *et al.*, 1999; Ohta and Kawabe, 2000a, b and 2001).

Unfortunately, however, little attention has been paid to the hydration change in light REE<sup>3+</sup>(aq) series in the studies of REE geochemistry dealing with aqueous solutions (Wood, 1990a, b; Hass *et al.*, 1995) except ours. As long as the hydration change of light REE<sup>3+</sup>(aq) is ignored, it is almost impossible to make proper discussion on the series variations of logarithmic REE partition coefficients and stability constants of aqueous REE(III) complexes determined experimentally, because they are the thermodynamic data for the reactions involving REE<sup>3+</sup>(aq). Our recent study of REE partitioning between Fe(III) oxyhydroxide precipitate and hydrothermal solutions (Takahashi and Kawabe, 2004) has revealed that the characteristics of light REE<sup>3+</sup>(aq) as a mixture of nonahydrate and octahydrate is undoubtedly significant even under hydrothermal conditions up to 170°C.

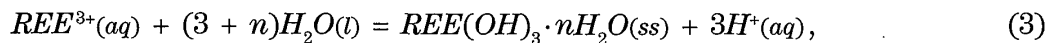
The aims of the present study are twofold: Firstly, we will demonstrate how the thermodynamic parameters for the reaction (2) are expressed in terms of those for the reaction (1), and discuss the thermodynamic parameters for the hydration change reaction for light REE<sup>3+</sup>(aq) series. Secondly, we will present theoretical estimates of  $\Delta G_r^0$  and  $\Delta G_h^*$  for the respective reactions of (1) and (2) at hydrothermal conditions up to 250°C. It has been found that the theoretical estimates at hydrothermal conditions are compatible with our recent experimental results of REE(III) partition coefficients between Fe(III) oxyhydroxide and aqueous solution and stability constants of REE(III)-carbonate complexes in hydrothermal conditions (Takahashi and Kawabe, 2004), although the detailed comparisons between the theoretical calculations and experimental data will be presented in separate papers, together with the experimental data. The nephelauxetic effects of octahydrate and nonahydrate series of REE<sup>3+</sup>(aq) and tetrad effects of hydration enthalpies and the reciprocals of REE-OH<sub>2</sub> distances of octahydrate REE<sup>3+</sup>(aq) series will be discussed in the part-II (Kawabe *et al.*, 2006).

## RESULTS AND DISCUSSION

### 1) Reactions involving $[REE(OH_2)_9]^{3+}(aq)$ and $[REE(OH_2)_8]^{3+}(aq)$

Here is described the thermodynamic treatment for light REE<sup>3+</sup>(aq) as a mixture of  $[REE(OH_2)_9]^{3+}(aq)$  and  $[REE(OH_2)_8]^{3+}(aq)$  using the reaction to define REE partition coefficients,  $K_d = X(REE)_{ppt}/m(REE)_{sol}$  between Fe(III) oxyhydroxide precipitate and aqueous solution without carbonate ion (Kawabe *et al.*, 1999b; Ohta and Kawabe, 2000a, b and 2001).  $X(REE)_{ppt}$  is the mole fraction of each REE in the precipitate, and

$m(REE)_{sol}$  is the molal concentration of  $REE^{3+}(aq)$  in solution. The thermodynamic significance of  $\log K_d(REE)$  or  $[\log K_d(REE) - 3pH]$  can be illustrated by the reaction below,



where REE precipitated with Fe(III) oxyhydroxide is written conventionally as  $REE(OH)_3 \cdot nH_2O$ . The equilibrium constant  $K$  for (3) is written as,

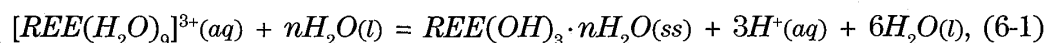
$$\begin{aligned} K &= \frac{a(REE(OH)_3 \cdot nH_2O) \cdot a^3(H^+)}{a(REE^{3+}, aq) \cdot a_w^{(n+3)}} = \frac{a(REE(OH)_3 \cdot nH_2O) \cdot a^3(H^+)}{\gamma(REE^{3+}, aq) \cdot m(REE^{3+}, aq) \cdot a_w^{(n+3)}} \\ &= \frac{X(REE(OH)_3 \cdot nH_2O) \cdot a^3(H^+)}{m(REE^{3+}, aq)} \cdot \left[ \frac{\lambda(REE(OH)_3 \cdot nH_2O)}{\gamma(REE^{3+}, aq) \cdot a_w^{(n+3)}} \right] \\ &= K_d \cdot a^3(H^+) \cdot \left[ \frac{\lambda(REE(OH)_3 \cdot nH_2O)}{\gamma(REE^{3+}, aq) \cdot a_w^{(n+3)}} \right]. \end{aligned} \quad (4)$$

Hence it follows that

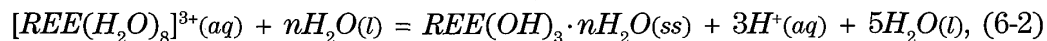
$$\log K = [\log K_d - 3pH] + \log \left[ \frac{\lambda(REE(OH)_3 \cdot nH_2O)}{\gamma(REE^{3+}, aq) \cdot a_w^{(n+3)}} \right]. \quad (5)$$

However, we are now accepting that light  $REE^{3+}(aq)$  is a mixture of  $[REE(OH_2)_9]^{3+}(aq)$  and  $[REE(OH_2)_8]^{3+}(aq)$ , so that  $REE^{3+}(aq)$  in (3) is to be written in terms of the two distinguishable species, and  $a(REE^{3+}, aq)$  in (4) is also to be expressed in terms of the activities of the two species. Eventually the thermodynamic meaning of experimental values of  $\log K_d$  or  $[\log K_d - 3pH]$  is to be modified.

For each of  $[REE(OH_2)_9]^{3+}(aq)$  and  $[REE(OH_2)_8]^{3+}(aq)$ , the reaction corresponding to (3) is written as below,



and



Here is assumed that  $REE(OH)_3 \cdot nH_2O$  is a single species at least in light REE. The relations that  $RT \ln K = -\Delta G_r^0$ , for (6-1) and (6-2) are given by

$$RT \ln K(nona) = -\Delta G_r^0(nona) = -\{\mu_{ppt}^0 - \mu_9^0 - (n-6)\mu_w^0\} \quad (7-1)$$

and

$$RT \ln K(octa) = -\Delta G_r^0(octa) = -\{\mu_{ppt}^0 - \mu_8^0 - (n-5)\mu_w^0\}, \quad (7-2)$$

where  $\mu_{ppt}^0$ ,  $\mu_9^0$ ,  $\mu_8^0$ , and  $\mu_w^0$  stand for the standard-state chemical potentials for  $REE(OH)_3 \cdot nH_2O(c)$ ,  $[REE(H_2O)_9]^{3+}(aq)$ ,  $[REE(H_2O)_8]^{3+}(aq)$  and  $H_2O(l)$ , respectively. At any temperatures,  $\mu_{H^+}^0(aq) = 0$  because of the thermodynamic convention for  $H^+(aq)$  (Denbigh, 1981). The difference of between (6-2) and (6-1) gives the hydration change

reaction of REE<sup>3+</sup>(aq) already mentioned as (1). The relationship that  $RT \ln K = -\Delta G_r^0$  for (1) is given as

$$RT \ln K_{hc}(REE^{3+}, aq) = -\Delta G_{hc}^0(REE^{3+}, aq) = -(\mu_9^0 - \mu_8^0 - \mu_w^0). \quad (8)$$

Because the reaction (1) is the difference between (6-2) and (6-1), it holds also that

$$RT \ln K_{hc}(REE^{3+}, aq) = RT \ln [K(octa)/K(nona)] \quad (9)$$

The distribution of two light REE<sup>3+</sup>(aq) species is constrained by the equilibrium of the hydration change reaction of (1).

## 2) Chemical potential of light REE<sup>3+</sup>(aq)

The molal concentration of light REE<sup>3+</sup>(aq) used in (4) is the sum of molal concentrations of the two species in our present understanding,

$$m(REE^{3+}, aq) = m(REE(OH_2)_9]^{3+}, aq) + m(REE(OH_2)_8]^{3+}, aq). \quad (10)$$

The respective molar fractions of [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup>(aq) and [REE(OH<sub>2</sub>)<sub>8</sub>]<sup>3+</sup>(aq) to their sum are written as

$$x_9 = \frac{m([REE(OH_2)_9]^{3+}, aq)}{m(REE^{3+}, aq)} \quad \text{and} \quad x_8 = \frac{m([REE(OH_2)_8]^{3+}, aq)}{m(REE^{3+}, aq)}. \quad (11)$$

It holds always that  $x_9 + x_8 = 1$ . Hence the chemical potential of REE<sup>3+</sup>(aq) can be expressed in terms of the chemical potentials of the two species because it is a mixture of them,

$$\begin{aligned} \mu(REE^{3+}, aq) &= x_9 \cdot \mu_{nona} + x_8 \cdot \mu_{octa} = x_9(\mu_{nona}^0 + RT \ln a_{nona}) + x_8(\mu_{octa}^0 + RT \ln a_{octa}) \\ &= x_9 \cdot \mu_{nona}^0 + x_8 \cdot \mu_{octa}^0 + RT \ln [(a_{nona})^{x_9} \cdot (a_{octa})^{x_8}]. \end{aligned} \quad (12)$$

The last term in (12) is rewritten by using  $a_i = \gamma_i \cdot m_i$  in the form,

$$\begin{aligned} (a_{nona})^{x_9} \cdot (a_{octa})^{x_8} &= (\gamma_{nona})^{x_9} \cdot (\gamma_{octa})^{x_8} \cdot (m_{nona})^{x_9} \cdot (m_{octa})^{x_8} \\ &= (\gamma_{nona})^{x_9} \cdot (\gamma_{octa})^{x_8} \cdot m(REE^{3+}, aq) \cdot (x_9)^{x_9} \cdot (x_8)^{x_8} \\ &= \gamma(REE^{3+}, aq) \cdot m(REE^{3+}, aq) \cdot (x_9)^{x_9} \cdot (x_8)^{x_8}, \end{aligned} \quad (13)$$

where the following relation among the activity coefficients has been assumed in the last equation of (13):

$$\gamma_{nona} = \gamma_{octa} = \gamma(REE^{3+}, aq). \quad (14)$$

Hence eq. (12) is given as below,

$$\begin{aligned} \mu(REE^{3+}, aq) &= x_9 \cdot \mu_{nona}^0 + x_8 \cdot \mu_{octa}^0 + RT \ln [(x_9)^{x_9} \cdot (x_8)^{x_8}] \\ &\quad + RT \ln [\gamma(REE^{3+}, aq) \cdot m(REE^{3+}, aq)]. \end{aligned} \quad (15)$$

Even when REE<sup>3+</sup>(aq) is a mixture of nonahydrate [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup>(aq) and octahydrate [REE(OH<sub>2</sub>)<sub>8</sub>]<sup>3+</sup>(aq), the first two terms of (15) could be written nominally as

$$x_9 \cdot \mu_{nona}^0 + x_8 \cdot \mu_{octa}^0 + RT \ln [(x_9)^{x_9} \cdot (x_8)^{x_8}] = \text{“}\mu(REE^{3+}, aq)\text{”}. \quad (16)$$

Hence eq. (15) can be written in the usual way that,

$$\mu(\text{REE}^{3+}, aq) = \text{“}\mu^0(\text{REE}^{3+}, aq)\text{”} + RT \ln [\gamma(\text{REE}^{3+}, aq) \cdot m(\text{REE}^{3+}, aq)]. \quad (15')$$

The equations (4) and (5) for the reaction (3) implicitly assume the expression of (15'), but the term of “ $\mu^0(\text{REE}^{3+}, aq)$ ” is by no means the chemical potential for a single species at the standard state. This is given by the equilibrium condition of (8) for the hydration change reaction (1), namely,

$$RT \ln [a_{\text{nona}} / (a_{\text{octa}} \cdot a_w)] = -\Delta G_{hc}^0(\text{REE}^{3+}, aq). \quad (17)$$

Using the condition of (14) and the assumption that  $a_w = 1$ , eq. (17) is further simplified into  $RT \ln [x_9 / x_8] = -\Delta G_{hc}^0(\text{REE}^{3+}, aq)$ , and then this can be solved with respect to  $x_9 (= 1 - x_8)$ :

$$x_9 = \exp [-\Delta G_{hc}^0 / (RT)] / \{1 + \exp [-\Delta G_{hc}^0 / (RT)]\} = 1 - x_8. \quad (18)$$

The equations of (16) and (18) are the constraint originating from the situation that light  $\text{REE}^{3+}(aq)$  is a mixture of nonahydrate and octahaydrate. The importance of (15) or (16), instead of the conventional one of (15'), can be illustrated further when considering the three different cases as below,

$$(i) \quad \Delta G_{hc}^0 / (RT) < -4.6: x_9 \approx 1, x_8 < 0.01, \text{“}\mu^0(\text{REE}^{3+}, aq)\text{”} \approx \mu_{\text{nona}}^0 \quad (19-1)$$

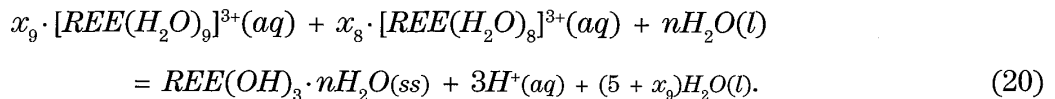
$$(ii) \quad \Delta G_{hc}^0 / (RT) = 0: \quad x_9 = x_8 = 1/2, \quad \text{“}\mu^0(\text{REE}^{3+}, aq)\text{”} \\ = (1/2)(\mu_{\text{nona}}^0 + \mu_{\text{octa}}^0) - RT \ln 2 \quad (19-2)$$

$$(iii) \quad \Delta G_{hc}^0 / (RT) > 4.6: x_9 < 0.01, x_8 \approx 1, \text{“}\mu^0(\text{REE}^{3+}, aq)\text{”} \approx \mu_{\text{octa}}^0 \quad (19-3)$$

When  $|\Delta G_{hc}^0 / (RT)| > 4.6$ ,  $\text{REE}^{3+}(aq)$  can be regarded actually as a single species of nona- or octatahydrate  $\text{REE}^{3+}(aq)$  as in (19-1) or (19-3). The hydration change is significant under the condition that  $|\Delta G_{hc}^0 / (RT)| \leq 4.6$ . The term of  $RT \ln 2$  in (19-2) corresponds to the maximum value of ideal mixing entropy ( $R \ln 2$ ) in binary systems, which is expressing the situation that the two distinct species are coexisting with the equal abundances.

### 3) Correction of experimental $[\log K_d - 3pH]$ for hydration change in light $\text{REE}^{3+}(aq)$

Here is considered how the correction of hydration change in light  $\text{REE}^{3+}(aq)$  is made to the experimental data of  $K_d$  for the conventional reaction (3). The reaction (3) must be replaced by the linear combination of  $\{x_9 \cdot (6-1) + x_8 \cdot (6-2)\}$  as below,



We will use  $K^*$  in  $RT \ln K = -\Delta G_r^0$  for (20) in order to distinguish it from  $K$  for (3),

$$RT \ln K^* = RT \ln \left[ \frac{a(\text{REE}(\text{OH})_3 \cdot n\text{H}_2\text{O}) \cdot a^3(\text{H}^+)}{(a_{\text{nona}})^{x_9} \cdot (a_{\text{octa}})^{x_8} \cdot (a_w)^{(n-5-x_9)}} \right] \\ = -\{ \mu_{\text{ppt}}^0 - x_9 \cdot (\mu_9^0 - \mu_8^0 - \mu_w^0) - \mu_8^0 - (n-5) \cdot \mu_w^0 \}. \quad (21)$$

The experimental data of  $K_d$  are based on  $K$  for (3) as shown in (5), but they can be expressed in terms of  $K^*$  for (21). By using the relation that  $(a_{nona})^{x_9} \cdot (a_{acta})^{x_8} = \gamma(REE^{3+}, aq) \cdot m(REE^{3+}, aq) \cdot (x_9)^{x_9} \cdot (x_8)^{x_8}$  of (13),  $K^*$  can be modified into the following form compatible with the experimental  $K$  for the conventional reaction (3):

$$\begin{aligned} \ln K^* &= \ln \left[ \frac{a(REE(OH)_3 \cdot nH_2O) \cdot a^3(H^+)}{(a_{nona})^{x_9} \cdot (a_{acta})^{x_8} \cdot (a_w)^{(n-5-x_9)}} \right] \\ &= \ln \left[ \frac{a(REE(OH)_3 \cdot nH_2O) \cdot a^3(H^+)}{\gamma(REE^{3+}, aq) \cdot m(REE^{3+}, aq) \cdot (a_w)^{(n-5-x_9)}} \right] - \ln [(x_9)^{x_9} \cdot (x_8)^{x_8}]. \end{aligned} \quad (22)$$

Since we are assuming that  $a_w = 1$ , eq. (22) gives the relationship between  $K$  for (3) and  $K^*$  for (20):

$$\begin{aligned} RT \ln K^* &= RT \ln K - RT \ln [(x_9)^{x_9} \cdot (x_8)^{x_8}] \\ &= -\{\mu_{ppt}^0 - x_9 \cdot (\mu_9^0 - \mu_8^0 - \mu_w^0) - \mu_8^0 - (n-5) \cdot \mu_w^0\}. \end{aligned}$$

Hence, it follows that

$$\begin{aligned} RT \ln K &= -\{\mu_{ppt}^0 - x_9 \cdot (\mu_9^0 - \mu_8^0 - \mu_w^0) \\ &\quad - RT \ln [(x_9)^{x_9} \cdot (x_8)^{x_8}] - \mu_8^0 - (n-5) \cdot \mu_w^0\} \end{aligned} \quad (23)$$

Taking the difference between  $RT \ln K$  of (23) and  $RT \ln K(octa)$  of (7-2) and putting (8) into it, we have the expression that

$$\begin{aligned} RT \ln K - RT \ln K(octa) &= x_9 \cdot (\mu_9^0 - \mu_8^0 - \mu_w^0) + RT \ln [(x_9)^{x_9} \cdot (x_8)^{x_8}] \\ &= x_9 \cdot \Delta G_{hc}^0(REE^{3+}, aq) + RT \ln [(x_9)^{x_9} \cdot (1-x_9)^{x_9}] \\ &= \Delta G_{hyd}^0(REE^{3+}, aq) \end{aligned} \quad (24)$$

This is the thermodynamic parameter which Kawabe (1999a) put forward. Equation (24) means that the experimental values of  $\log K$  are converted into those of  $\log K(octa)$  for the reaction involving only  $[REE(OH)_2]_8^{3+}(aq)$ . That is

$$\log K(octa) = \log K - \Delta G_{hyd}^*(REE^{3+}, aq)/(2.303RT). \quad (25)$$

Putting the condition that  $x_9 = 0$  and  $x_8 = 1$  into (22), we have the expression of  $K(octa)$ ,

$$\begin{aligned} \log K(octa) &= \log \left[ \frac{a(REE(OH)_3 \cdot nH_2O) \cdot a^3(H^+)}{\gamma(REE^{3+}, aq) \cdot m(REE^{3+}, aq) \cdot (a_w)^{(n-5)}} \right] \\ &= [\log K_d - 3pH]_{(octa)} + \log \left[ \frac{\lambda(REE(OH)_3 \cdot nH_2O)}{\gamma(REE^{3+}, aq) \cdot (a_w)^{(n-5)}} \right]. \end{aligned} \quad (26)$$

The expression of  $K$  for the reaction (3) has already been given in (5). The second term on the right-hand side is the same between (26) and (5) because we are assuming

that  $\alpha_w = 1$ . Therefore, it follows that

$$[\log K_d - 3pH]_{(octa)} = [\log K_d - 3pH] - \Delta G_{hyd}^*(REE^{3+}, aq)/(2.303RT). \quad (27)$$

The second term of (27) is the necessary correction when we convert the experimental values of  $[\log K_d - 3pH]$  for (3) into those of  $[\log K_d - 3pH]_{(octa)}$  for (6-2) involving only octahydrate  $REE^{3+}(aq)$ . As described already in (24),

$$\Delta G_{hyd}^*(REE^{3+}, aq) = x_9 \cdot \Delta G_{hc}^0(REE^{3+}, aq) + RT \ln [(x_9)^{x_9} \cdot (x_8)^{x_8}]. \quad (28)$$

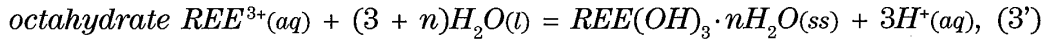
From the relations of  $\Delta G_{hyd}^* = \Delta H_{hyd}^* - T\Delta S_{hyd}^*$ ,  $\Delta G_{hc}^0 = \Delta H_{hc}^0 - T\Delta S_{hc}^0$  and (28), it follows that

$$\Delta H_{hyd}^*(REE^{3+}, aq) = x_9 \cdot \Delta H_{hc}^0(REE^{3+}, aq) \quad (29)$$

and that

$$\Delta S_{hyd}^*(REE^{3+}, aq) = x_9 \cdot \Delta S_{hc}^0(REE^{3+}, aq) - RT \ln [(x_9)^{x_9} \cdot (1 - x_9)^{(1-x_9)}]. \quad (30)$$

Equations (28), (20) and (30) give the relationship between the thermodynamic parameters given by Kawabe (1999a) and those for the hydration change reaction of (1) for light  $REE^{3+}(aq)$ . When we write the precipitation reaction of octahydrate  $REE^{3+}(aq)$  in the following form analogous to (3),



and then make the difference between (3') and (3), we obtain the reaction (2) given by Kawabe (1999a). Originally  $\Delta G_{hyd}^*(REE^{3+}, aq)$  was defined in the following manner:

$$\begin{aligned} \Delta G_{hyd}^*(REE^{3+}, aq) &= \mu^0(REE^{3+}, aq) - \mu^0(\text{octahydrate } REE^{3+}, aq) \\ &= RT \ln K - RT \ln K(\text{octa}), \end{aligned} \quad (31)$$

where  $K(\text{octa})$  in (31) is interpreted in reference to the reaction (3'). The expressions of (28) and (31) for  $\Delta G_{hyd}^*(REE^{3+}, aq)$  correspond to the different expressions of (6-2) and (3') for the precipitation reaction of octahydrate  $REE^{3+}(aq)$ , respectively. Whatever the same change of states is expressed by different reactions, the treatments are valid as long as the experimental data are uniquely specified as in (24) and (31) and they are the same.

Kawabe (1999a) presented the values of left-hand sides of eqs. (18), (29) and (30) at 25°C and 1 atm by referring to the straightforward expression of (2) derived from (3) and (3'). The use of  $\Delta G_{hyd}^*(REE^{3+}, aq)$  has an immediate merit when the experimental data of  $[\log K_d - 3pH]$  are corrected into those of  $[\log K_d - 3pH]_{(octa)}$  as is indicated by (27). The use of  $\Delta G_{hc}^0(REE^{3+}, aq)$  given by the reactions (6-2) and (1) is also important from the following two reasons: (i) the reactions (6-2) and (1) express explicitly the two distinct hydrate species in equilibrium with respect to the hydration change reaction of (1), and (ii) when we will discuss how the hydration state of light  $REE^{3+}(aq)$  is altered at elevated temperatures, it is more suitable to refer to the reaction (1) as will be described in the next subsection.

Kawabe (1999a) presented the values of  $\Delta G_{hyd}^*(REE^{3+}, aq)$ ,  $\Delta H_{hyd}^*(REE^{3+}, aq)$ , and  $\Delta S_{hyd}^*(REE^{3+}, aq)$  at 25°C and 1 atm for REE (=La–Gd) from his estimates of



$\Delta G_{hc}^0(REE^{3+},aq)$ ,  $\Delta H_{hc}^0(REE^{3+},aq)$  and  $\Delta S_{hc}^0(REE^{3+},aq)$  at 25°C and 1 atm. Miyakawa *et al.* (1988) reported that  $\Delta G_{hc}^0(Ce^{3+},aq) = -3$  (kJ/mol) from the temperature variation of absorption spectra of aqueous Ce(ES)<sub>3</sub> solution. In addition they also estimated  $\Delta G_{hc}^0(REE^{3+},aq)$ ,  $\Delta H_{hc}^0(REE^{3+},aq)$  and  $\Delta S_{hc}^0(REE^{3+},aq)$  at 25°C and 1 atm pressure based on the calculations of hydration enthalpies and free energies for nona- and cotahydrate complexes of REE<sup>3+</sup>. The two sets of thermodynamic parameters for hydration change reaction (1) for light REE<sup>3+</sup>(aq) are roughly comparable with each other in spite of the totally different data sets and theoretical bases between Kawabe (1999a) and Miyagawa *et al.* (1988). Table 1-A lists  $\Delta G_{hc}^0(REE^{3+},aq)$ ,  $\Delta H_{hc}^0(REE^{3+},aq)$  and  $\Delta S_{hc}^0(REE^{3+},aq)$  at 25°C and 1 atm which are consistent with  $\Delta G_{hyd}^*(REE^{3+},aq)$ ,  $\Delta H_{hyd}^*(REE^{3+},aq)$ , and  $\Delta S_{hyd}^*(REE^{3+},aq)$  by Kawabe (1999a) and the estimates of  $\Delta G_{hc}^0(REE^{3+},aq)$  by Miyakawa *et al.* (1988).  $\Delta G_{hyd}^*(REE^{3+},aq)$ ,  $\Delta H_{hyd}^*(REE^{3+},aq)$ , and  $\Delta S_{hyd}^*(REE^{3+},aq)$  by Kawabe (1999a) are cited in Table 1-B.

In order to see the small differences between the two sets of  $\Delta G_{hc}^0(REE^{3+},aq)$ , their series variations are compared in Fig. 1. The datum of  $\Delta G_{hc}^0(Ce^{3+},aq) = -3$  (kJ/mol) estimated from the temperature variation of absorption spectra of aqueous Ce(ES)<sub>3</sub> solution (Miyakawa *et al.*, 1988) is also plotted in Fig. 1. The conditions of  $\Delta G_{hc}^0/(RT) = \pm 4.6$ , namely,  $\Delta G_{hc}^0 = \pm 11.4$  (kJ/mol) at 25°C, to distinguish the cases of (19-1) and (19-3) are also indicated in Fig. 1. Obviously the data of  $\Delta G_{hc}^0(REE^{3+},aq)$  for Tb, Dy and Ho by Miyakawa *et al.* (1988) signify that fairly large amounts of [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup>(aq) are coexisting with respective [REE(OH<sub>2</sub>)<sub>8</sub>]<sup>3+</sup>(aq) even in the cases of heavy REE<sup>3+</sup>(aq) according to eq. (18), but this situation is definitely incompatible with the experimental evidence provided by X-ray diffraction studies that REE<sup>3+</sup>(aq) not lighter than Tb is actually a single species of [REE(OH<sub>2</sub>)<sub>8</sub>]<sup>3+</sup>(aq) (Habenschuss and Spedding, 1980; Rizkalla and Choppin, 1991; Ohataki and Radnai, 1993). On the other hand,  $\Delta G_{hc}^0(REE^{3+},aq)$  values derived from  $\Delta G_{hyd}^*(REE^{3+},aq)$  by Kawabe (1999a) are compatible with the experimental evidence in X-ray diffraction studies. Hence the set of  $\Delta G_{hc}^0(REE^{3+},aq)$ ,  $\Delta H_{hc}^0(REE^{3+},aq)$  and  $\Delta S_{hc}^0(REE^{3+},aq)$  data from  $\Delta G_{hyd}^*(REE^{3+},aq)$ ,  $\Delta H_{hyd}^*(REE^{3+},aq)$  and  $\Delta S_{hyd}^*(REE^{3+},aq)$  by Kawabe (1999a) are preferred to in Table 1-A.

The preference is inevitable from the difference of the two methods. Kawabe (1999a) dealt with  $\Delta G_{hyd}^*(REE^{3+},aq)$ ,  $\Delta H_{hyd}^*(REE^{3+},aq)$  and  $\Delta S_{hyd}^*(REE^{3+},aq)$  which can be estimated almost directly from the series variations of experimental data for solution of the fully isomorphous  $REE(ES)_3 \cdot 9H_2O$  and partly isomorphous series of  $REECl_3 \cdot nH_2O$ . In contrast, Miyakawa *et al.* (1988) calculated the absolute hydration enthalpies of [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup> and [REE(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup> with large negative values of about  $-3 \times 10^3$  kJ/mol, and then evaluated small value of  $\Delta H_{hc}^0(REE^{3+},aq)$  within  $\pm 10$  kJ/mol by their differences. Uncertainties associating with the calculations of absolute hydration enthalpies are much greater than the  $\Delta H_{hc}^0(REE^{3+},aq)$  values given as their differences.

The temperature variation of absorption spectra of aqueous Ce(ES)<sub>3</sub> solution (Miyakawa *et al.*, 1988), however, is the spectroscopic evidence for the presence of [Ce(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup> even in Ce<sup>3+</sup>(aq) as a typical light REE. The estimate of  $\Delta G_{hc}^0(Ce^{3+},aq) = -3$  kJ/mol from the temperature change of absorption spectra and the estimates of  $\Delta H_{hc}^0(Ce^{3+},aq) = -13$  kJ/mol and  $\Delta S_{hc}^0(Ce^{3+},aq) = -33$  J/mol/K as temperature-independent parameters are not so different from  $\Delta G_{hc}^0(Ce^{3+},aq) = -5$  kJ/mol,  $\Delta H_{hc}^0(Ce^{3+},aq) = -14$  kJ/mol and  $\Delta S_{hc}^0(Ce^{3+},aq) = -31$  J/mol/K by Kawabe (1999a).

**Table 1-A**  $\Delta G_{hc}^0(REE^{3+},aq)$ ,  $\Delta H_{hc}^0(REE^{3+},aq)$  and  $\Delta S_{hc}^0(REE^{3+},aq)$  at 25°C and 1 atm for the hydration reactions of (1) derived from  $\Delta G_{hyd}^*(REE^{3+},aq)$ ,  $\Delta H_{hyd}^*(REE^{3+},aq)$ , and  $\Delta S_{hyd}^*(REE^{3+},aq)$  by Kawabe (1999a) and the comparison with the estimates of  $\Delta G_{hc}^0(REE^{3+},aq)$  by Miyakawa *et al.* (1988)\*.

	Kawabe (1999a)**			Miyakawa <i>et al.</i> (1988)
	$\Delta G_{hc}^0(REE^{3+},aq)$ (kJ/mol)	$\Delta H_{hc}^0(REE^{3+},aq)$ (kJ/mol)	$\Delta S_{hc}^0(REE^{3+},aq)$ (kJ/mol)	$\Delta G_{hc}^0(REE^{3+},aq)$ (kJ/mol)
La	-7.02	-17.89	-36.46	-4.1
Ce	-4.96	-14.08	-30.59	-4.1
Pr	-3.56	-11.70	-27.30	-3.1
Nd	-2.15	-10.85	-29.18	-2.1
Pm	+0.50	-9.30	-32.87	-1.1
Sm	+3.50	-6.19	-32.50	+0.9
Eu	+6.50	-3.50	-33.54	+1.9
Gd	+9.20	-2.50	-39.24	+1.9
Tb	-	-	-	+3.9
Dy	-	-	-	+6.9
Ho	-	-	-	+7.9
Er	-	-	-	+9.9
Tm	-	-	-	+9.9
Yb	-	-	-	+10.9
Lu	-	-	-	+11.9

\*)  $\Delta G_{hyd}^*(REE^{3+},aq)$ ,  $\Delta H_{hyd}^*(REE^{3+},aq)$ , and  $\Delta S_{hyd}^*(REE^{3+},aq)$  by Kawabe (1999a) are cited in Table 1-B. Graphical comparison of  $\Delta G_{hc}^0(REE^{3+},aq)$  in this study with those by Miyakawa *et al.* (1988) are presented in Fig. 1.

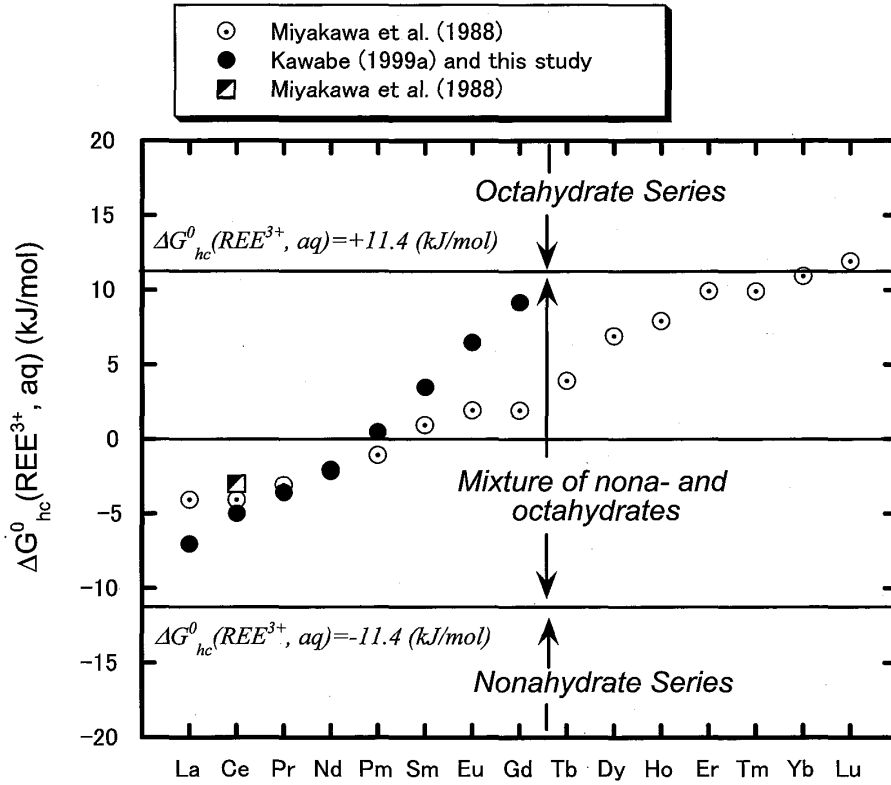
\*\*) The estimated values for Pm are supplemented in this study.

**Table 1-B**  $\Delta G_{hyd}^*(REE^{3+},aq)$ ,  $\Delta H_{hyd}^*(REE^{3+},aq)$ , and  $\Delta S_{hyd}^*(REE^{3+},aq)$  at 25°C and 1 atm for the reaction of (2) by Kawabe (1999a).

	$\Delta G_{hyd}^*(REE^{3+},aq)$ (kJ/mol)	$\Delta H_{hyd}^*(REE^{3+},aq)$ (kJ/mol)	$\Delta S_{hyd}^*(REE^{3+},aq)$ (kJ/mol)
La	-7.16	-16.9	-32.67
Ce	-5.27	-12.4	-23.91
Pr	-4.09	-9.45	-17.98
Nd	-3.02	-7.64	-15.50
Pm*	-1.45	-4.18	-9.06
Sm	-0.541	-1.21	-2.24
Eu	-0.174	-0.238	-0.214
Gd	-0.06	-0.060	0.00

\*) The estimated values for Pm are supplemented in this study.

In the next subsection, we will extend our discussion on hydration change in  $REE^{3+}(aq)$  series into the hydrothermal condition. Additional comments on the differences between the two sets of thermodynamic parameters in Table 1-A will be given in the later subsection as well as other suggestions derived from the thermochemical data in Table 1-A.



**Fig. 1**  $\Delta G_{hc}^0(REE^{3+}, aq)$  at 25°C and 1 atm (filled circles) compatible with  $\Delta G_{hyd}^*(REE^{3+}, aq)$  by Kawabe (1999a) compared with those calculated by Miyakawa *et al.* (1988) (open circles). The spectroscopic estimate of  $\Delta G_{hc}^0(Ce^{3+}, aq) = -3$  (kJ/mol) by Miyakawa *et al.* (1988) is also plotted (a half-filled square). The condition that  $\Delta G_{hc}^0/(RT) = \pm 4.6$ , namely,  $\Delta G_{hc}^0 = \pm 11.4$  (kJ/mol) at 25°C, are also indicated.

#### 4) Hydration change in light REE<sup>3+</sup>(aq) series at hydrothermal conditions

The values of  $\Delta G_{hyd}^*(REE^{3+}, aq)$  at elevated temperatures are given by  $\Delta G_{hc}^0(REE^{3+}, aq)$  for (1) using eq. (28). Both the reactant and product in hydration change reaction (1) are aqueous REE(III) complexes, therefore  $\Delta G_{hc}^0(REE^{3+}, aq)$  at elevated temperatures and saturated water vapor pressures can be evaluated by Helgeson's (1967) equation using only  $\Delta H_{hc}^0(REE^{3+}, aq)$  and  $\Delta S_{hc}^0(REE^{3+}, aq)$  at 25°C and 1 atm listed Table 1-A. The equation is written as below,

$$\log K(T) = -\Delta G_r^0(T)/(2.303RT)$$

$$= \frac{\Delta S_r^0(T_r)}{2.303RT} \cdot [T_r - (\theta/\omega) \cdot \{1 - \exp[\exp(a+bT) - c + (T - T_r)/\theta]\}] - \frac{\Delta H_r^0(T_r)}{2.303RT}, \quad (32)$$

where  $T_r = 298.15$  K and  $R$  is the gas constant.  $(\theta/\omega) = 218.297$ ,  $b = -12.741$ ,  $a = 0.01875$ ,  $\theta = 219$ , and  $c = 7.84 \times 10^{-4}$  (Helgeson, 1967 and 1969).  $\Delta H_r^0(T_r)$  and  $\Delta S_r^0(T_r)$  correspond to  $\Delta H_{hc}^0(REE^{3+}, aq)$  and  $\Delta S_{hc}^0(REE^{3+}, aq)$  at 25°C and 1 atm in the present case.  $\Delta G_r^0(T)$  in (32) gives estimates of  $\Delta G_{hc}^0(REE^{3+}, aq)$  at elevated temperatures and saturated water vapor pressure up to 250°C.

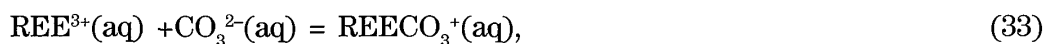
Table 2 summarizes the calculated values of  $\Delta G_{hc}^0(REE^{3+}, aq)$  and  $\Delta G_{hyd}^*(REE^{3+}, aq)$

**Table 2** The calculated thermodynamic parameters for hydration change reactions in light REE<sup>3+</sup>(aq) series as a function of temperature.

$\Delta G_{hc}^0(REE^{3+},aq)$ (kJ/mol)										
	25°C	50°C	75°C	100°C	125°C	150°C	175°C	200°C	225°C	250°C
La	-7.02	-6.05	-4.97	-3.74	-2.36	-0.79	1.00	3.07	5.50	8.42
Ce	-4.96	-4.15	-3.24	-2.21	-1.05	0.27	1.77	3.51	5.54	8.00
Pr	-3.56	-2.84	-2.02	-1.11	-0.07	1.10	2.44	3.99	5.81	8.00
Nd	-2.15	-1.38	-0.51	0.47	1.58	2.83	4.27	5.92	7.87	10.21
Pm	0.50	1.37	2.35	3.45	4.70	6.12	7.73	9.60	11.79	14.42
Sm	3.50	4.36	5.33	6.42	7.65	9.05	10.65	12.49	14.66	17.27
Eu	6.50	7.39	8.39	9.51	10.79	12.23	13.88	15.78	18.02	20.71
Gd	9.20	10.24	11.41	12.73	14.21	15.90	17.83	20.06	22.67	25.82
$\Delta G_{hyd}^*(REE^{3+},aq)$ (kJ/mol)										
	25°C	50°C	75°C	100°C	125°C	150°C	175°C	200°C	225°C	250°C
La	-7.16	-6.32	-5.36	-4.55	-3.82	-2.86	-2.12	-1.48	-0.97	-0.59
Ce	-5.27	-4.67	-3.94	-3.45	-3.01	-2.31	-1.80	-1.35	-0.96	-0.64
Pr	-4.09	-3.64	-3.06	-2.75	-2.49	-1.93	-1.56	-1.22	-0.91	-0.64
Nd	-3.02	-2.64	-2.13	-1.92	-1.75	-1.30	-1.03	-0.79	-0.58	-0.40
Pm	-1.45	-1.26	-0.93	-0.88	-0.83	-0.57	-0.44	-0.33	-0.23	-0.16
Sm	-0.541	-0.48	-0.34	-0.37	-0.38	-0.26	-0.21	-0.16	-0.12	-0.08
Eu	-0.174	-0.17	-0.11	-0.14	-0.16	-0.11	-0.09	-0.07	-0.05	-0.04
Gd	-0.06	-0.06	-0.04	-0.05	-0.06	-0.04	-0.03	-0.02	-0.02	-0.01

for REE=La–Gd at the temperatures from 25° to 250°C by using (28), (32) and the parameters in listed Tables 1-A and -B from Kawabe (1999a). The calculations indicate that light REE satisfying the condition of  $\Delta G_{hc}^0(REE^{3+},aq) = 0$  in (19-2) shifts from Pm to the more lighter REE with increasing temperature from 25° to 160°C (Fig. 2). This means that the reaction (1),  $[REE(OH_2)_8]^{3+}_{(aq)} + H_2O(l) = [REE(OH_2)_9]^{3+}(aq)$ , shifts to the left-hand side with increasing temperature, and that the stability field of octahydrate  $[REE(OH_2)_8]^{3+}(aq)$  relative to nonahydrate  $[REE(OH_2)_9]^{3+}(aq)$  expands in elevated temperatures. Figure 2 indicates that no light REE satisfies the condition that  $\Delta G_{hc}^0(REE^{3+},aq) < 0$  at the temperature higher than 162°C, but this does not mean the absence of  $[REE(OH_2)_9]^{3+}(aq)$  in the high temperature solutions. As emphatically noted in (19-1, -2, and -3) and Fig. 1,  $[REE(OH_2)_8]^{3+}(aq)$  and  $[REE(OH_2)_9]^{3+}(aq)$  in the light REE series are coexisting in the condition of  $|\Delta G_{hc}^0/(RT)| < 4.6$ . Even at 200°C,  $[REE(OH_2)_9]^{3+}(aq)$  are present together with  $[REE(OH_2)_8]^{3+}(aq)$  as long as REE satisfy the condition that  $|\Delta G_{hc}^0| < 18.1$  (kJ/mol).

The discussion as above has been made using the reaction (3) for precipitation of REE<sup>3+</sup>(aq). If the reaction (3) is replaced by the formation reaction of aqueous REE(III) complex like REECO<sup>3+</sup>(aq),



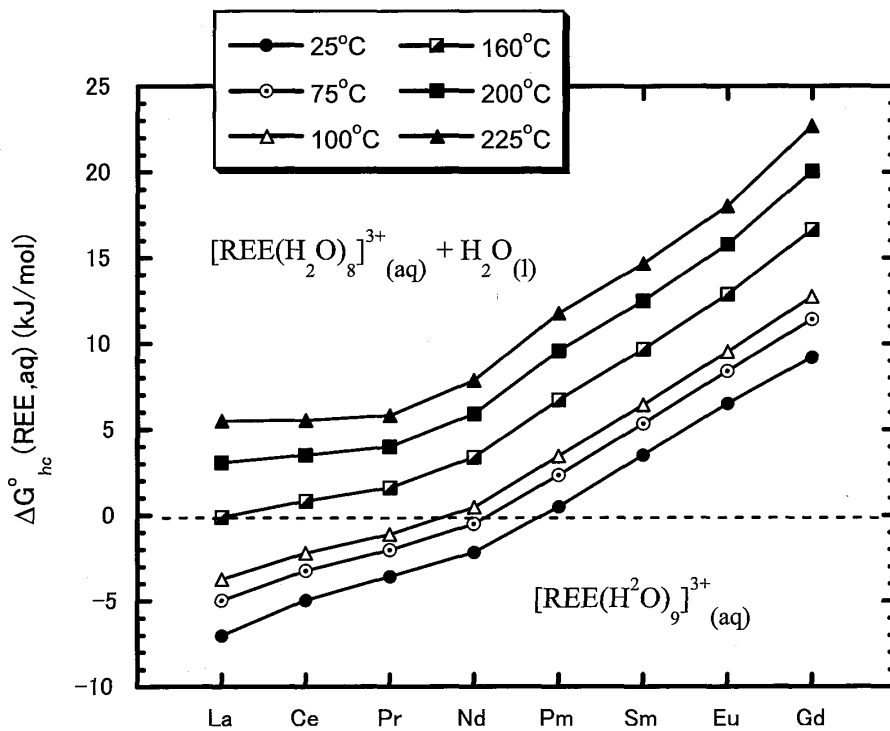
the equation that  $\log K(octa) = \log K - \Delta G_{hyd}^*(REE^{3+},aq)/(2.303RT)$  of (25) can be

derived again after repeating chains of equations described as above. In this case, the equilibrium constant  $K$  in (25) means the complex formation constant defined by (33), and  $K(octa)$  is the complex formation from octahydrate of  $[REE(H_2O)_8]^{3+}(aq)$ :

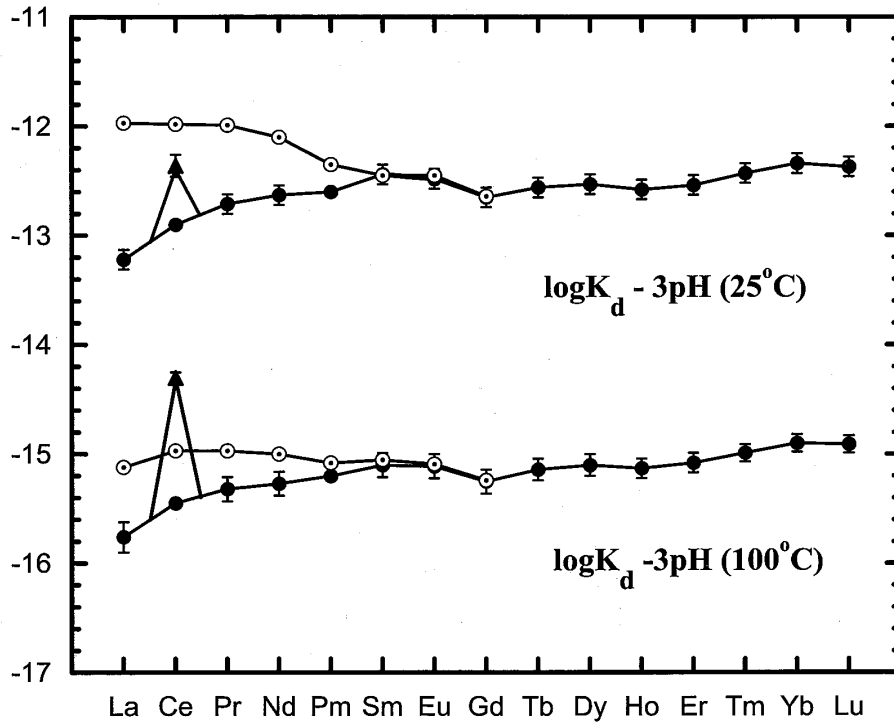


The experimental values of  $\log K$  for the conventional reaction (33) can be corrected into those of  $\log K(octa)$  for (34) by using  $\Delta G_{hyd}^*(REE^{3+},aq)/(2.303RT)$ . The correction of the logarithmic equilibrium constant with respect to the hydration change of light REE<sup>3+</sup>(aq) relative to heavy REE<sup>3+</sup>(aq) is the same between the precipitation reaction of REE<sup>3+</sup>(aq) and the aqueous REE(III) complex formation reaction, since REE<sup>3+</sup>(aq) is the reactant in both the reactions. If we consider the dissolution or dissociation reaction of REE(III) compound or complex in which REE<sup>3+</sup>(aq) is the product, the negative of  $\Delta G_{hyd}^*(REE^{3+},aq)/(2.303RT)$  is to be used.

The results of Table 2 are applicable not only to the equilibrium constants for the precipitation (or dissolution) reaction of REE<sup>3+</sup>(aq) but also to the aqueous REE(III) complex formation (or dissociation) constants defined by conventional reactions in



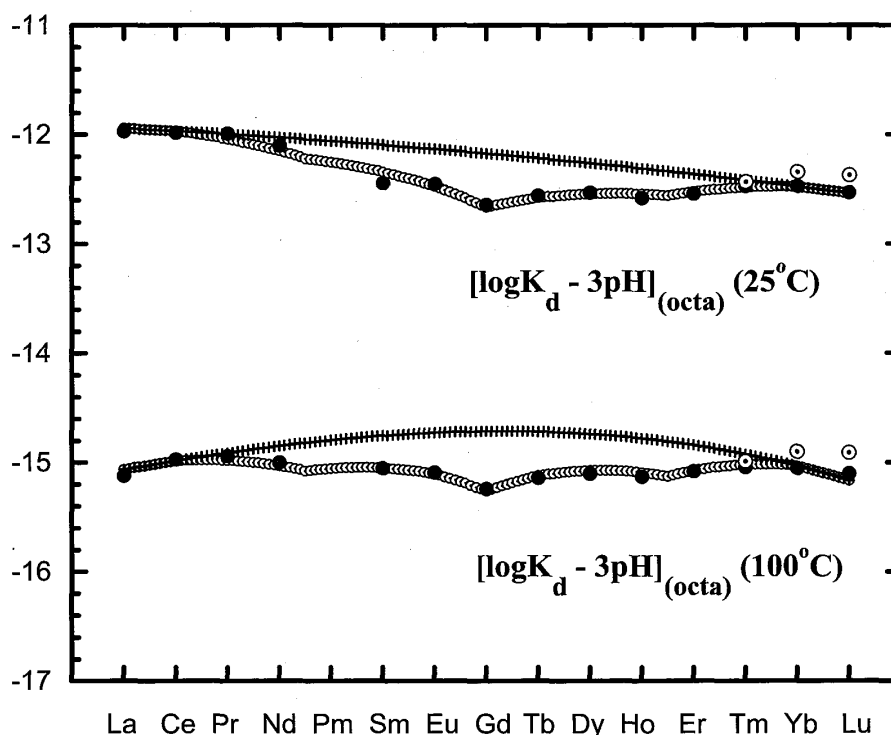
**Fig. 2** The hydration change reaction that  $[REE(OH_2)_8]^{3+}(aq) + H_2O(l) = [REE(OH_2)_9]^{3+}(aq)$  shifts to the left-hand side with increasing temperature, and light REE satisfying the condition of  $\Delta G_{hc}^0(REE^{3+},aq)$  migrates from the position near Pm to the lighter REE as the temperature increases from 25° to 160°C. The octahydrate  $[REE(OH_2)_8]^{3+}(aq)$  becomes stable relative to nonahydrate  $[REE(OH_2)_9]^{3+}(aq)$  even in the light REE series. No light REE satisfies the condition that  $\Delta G_{hc}^0(REE^{3+},aq) \leq 0$  for  $T \geq 162^\circ C$ , but this does not mean the absence of nonahydrate  $[REE(OH_2)_9]^{3+}(aq)$  in the hydrothermal condition (see text).



**Fig. 3** The experimental  $[\log K_d - 3pH]$  values for the REE(III) partitioning system between Fe(III) oxyhydroxide and solution at 25° and 100°C (filled circles and triangles) and the corrected values of  $[\log K_d - 3pH]_{(octa)}$  by using eq. (27) and  $\Delta G_{hyd}^*(REE^{3+}, aq)$  in Table 2 (open circles). The two filled triangles are the experimental data for Ce involving anomalies due to Ce(IV). Filled circles for Ce and Pm are interpolated from the neighboring data. The experimental data at 25°C are the means and  $\sigma(\text{mean})$ 's for 10 runs (pH = 5.33–5.72) of Fe-2 series (Kawabe *et al.*, 1999), and those at 100°C are the means and  $\sigma(\text{mean})$ 's for 11 runs (Takahashi and Kawabe, 2004). The pH values (6.30–6.55) in the runs at 100°C were measured at room temperature after the respective runs. Elimination of the hydration change effect in the light REE makes the series variation symmetric, but there are remaining subtle irregularities of  $[\log K_d - 3pH]$  at heavy REE (Tm, Yb and Lu) due to the coordination change in REE(III) coprecipitated with Fe(III) oxyhydroxide (see Fig. 4).

which light  $REE^{3+}(aq)$  is treated as a single species. The equilibrium constants are corrected into those for the reactions involving only isomorphous series of octahydrate  $[REE(OH_2)_8]^{3+}(aq)$  according to eq. (25).

The experimental values of  $[\log K_d - 3pH]$  for the REE(III) partitioning system between Fe(III) oxyhydroxide and solution at 25°C (Kawabe *et al.*, 1999) and 100°C (Takahashi and Kawabe, 2004) are corrected to the values of  $[\log K_d - 3pH]_{(octa)}$  using eq. (27) and  $\Delta G_{hyd}^*(REE^{3+}, aq)$  in Table 2, which are shown in Fig. 3. The corrected data points of  $[\log K_d - 3pH]_{(octa)}$  for light REE become compatible with the improved RSPET equation (Kawabe, 1992). Subtle irregularities in experimental data of  $[\log K_d - 3pH]$  for heavy REE (Tm, Yb and Lu) are due to the coordination change in REE(III) coprecipitated with Fe(III) oxyhydroxide. The irregularities can be corrected empirically by using  $[\log K_d - 3pH]_{(octa)}$  and the RSPET equation for the experimental data at 25°C and 100°C as shown in Fig. 4. The convex (“M” type) tetrad effects of  $[\log K_d - 3pH]_{(octa)}$  are not so different between 25° and 100°C. This is due to the difference



**Fig. 4** The  $[\log K_d - 3pH]_{(octa)}$  values corrected for the hydration change effect in light REE can be fitted to the improved RSPET equation (Kawabe, 1992) successfully, in which the small irregularities of  $[\log K_d - 3pH]_{(octa)}$  at heavy REE (Tm, Yb and Lu) have also been corrected on the trial-error basis. The three open circles are corrected to the filled ones, and they are used as the input data in the least-squares fittings to the RSPET equation. The corrections for Tm, Yb, and Lu are  $-0.044$ ,  $-0.131$ , and  $0.158$  for the data at  $25^\circ\text{C}$ , and  $-0.050$ ,  $-0.150$ , and  $-0.190$  for those at  $100^\circ\text{C}$ .

in pH of solution between the two systems. The average pH of the runs at  $25^\circ\text{C}$  is about one pH unit smaller than that at  $100^\circ\text{C}$  (see explanation for Fig. 3). The  $[\log K_d - 3pH]_{(octa)}$  values for solutions with the smaller pH indicate the smaller convex tetrad effect as discussed in the  $\delta\text{-MnO}_2/\text{solution}$  system at  $25^\circ\text{C}$  (Ohta and Kawabe, 2001).

It has been found that the calculated values of  $\Delta G_{hc}^0(REE^{3+},aq)$  and  $\Delta G_{hyd}^*(REE^{3+},aq)$  in Table 2 successfully correct the hydration change effect of light REE<sup>3+</sup>(aq) series involved in the experimental values of  $[\log K_d - 3pH]$  in hydrothermal solution up to  $170^\circ\text{C}$  and logarithmic stability constants of REE(III)-carbonate complexes at  $100^\circ\text{C}$  (Takahashi and Kawabe, 2004). The detailed discussion on the application results will be presented in separate papers, together with the original experimental data.

##### 5) Series variation of thermodynamic parameters for hydration change reaction

It has been shown in Fig. 1 that the theoretical estimates of  $\Delta G_{hc}^0(REE^{3+},aq)$  by Miyakawa *et al.* (1988) are not acceptable although their calculations are undoubtedly a theoretical contribution to our understanding of the hydration change of REE<sup>3+</sup>(aq) series. In our view, the main reason why their calculations did not lead to the results compatible with the X-ray studies by Habenschuss and Spedding (1979a, b and 1980) is as follows: They used the REE-OH<sub>2</sub> distances in  $[\text{REE}(\text{OH}_2)_9]^{3+}$  complexes for light

REE like La and Pr, which are significantly smaller than the observed light REE-OH<sub>2</sub> distances in Habenschuss and Spedding (1979a, b and 1980), under the assumption that REE-OH<sub>2</sub> distances in [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup> is expressed as a linear function of the atomic number of REE. Eventually the differences in REE-OH<sub>2</sub> distance between [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup> and [REE(OH<sub>2</sub>)<sub>8</sub>]<sup>3+</sup> are smaller than the acceptable ones, particularly in middle and heavy REE<sup>3+</sup>(aq) series. As long as we accept that light REE<sup>3+</sup>(aq) is a mixture of [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup> (aq) and [REE(OH<sub>2</sub>)<sub>8</sub>]<sup>3+</sup>, the REE-OH<sub>2</sub> distances in [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup> complexes for light REE should be greater than observed light REE-OH<sub>2</sub> distances. The REE-OH<sub>2</sub> distances which we have estimated for [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup> (aq) and [REE(OH<sub>2</sub>)<sub>8</sub>]<sup>3+</sup> will be discussed in the second part of this study (Kawabe *et al.*, 2006).

In addition, their assumption that REE-OH<sub>2</sub> distances in [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup> is expressed as a linear function of the atomic number of REE may be a practical approximation, but such an assumption should be made carefully because of the lanthanide tetrad or double-double effect (Peppard *et al.*, 1969; Nugent, 1970; Jørgensen, 1970 and 1979; Siekierski, 1971; Fidelis and Mioduski, 1981; Kawabe, 1992; Kawabe and Masuda, 2001). When the Racah parameters for REE<sup>3+</sup> with partly-filled (4f)<sup>*n*</sup> electronic configurations are different between the REE(III) complex and gaseous free REE<sup>3+</sup>, tetrad effect variations appear in the series variations of REE-ligand distances as exemplified in REEO<sub>1.5</sub>(cub) discussed in Kawabe (1992). We will present more detailed discussion on the tetrad effect of hydration enthalpies REE<sup>3+</sup>(aq) and REE<sup>3+</sup>-OH<sub>2</sub> distances as well as the nephelauxetic effects of two REE<sup>3+</sup>(aq) series in the second part of this study (Kawabe *et al.*, 2006).

## CONCLUSIONS

- (1) The thermodynamic treatment for the hydration change reaction of light REE<sup>3+</sup>(aq) series has been refined. The thermodynamic parameters for the conventional hydration reaction that octahydrate REE<sup>3+</sup>(aq) = REE<sup>3+</sup>(aq) by Kawabe (1999a) can be readily converted into those for the reaction [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup>(aq) + H<sub>2</sub>O(l) = [REE(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup>(aq) by Miyakawa *et al.* (1988).
- (2) In reference to the X-ray studies of hydration states of REE<sup>3+</sup>(aq) series, the standard-state Δ*G*<sub>*r*</sub><sup>0</sup> values for [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup>(aq) + H<sub>2</sub>O(l) = [REE(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup>(aq) from Kawabe (1999a) are more acceptable than those calculations by Miyakawa *et al.* (1988) on the basis of electrostatic bonding energy calculations and Born's hydration theory.
- (3) The method to eliminate the hydration change effect from experimental REE partition coefficients and REE(III) complex formation constants has been described in details, and then the thermodynamic treatment and correction method have been extended to those for the hydrothermal conditions up to 250°C.
- (4) The theoretical estimates are compatible with the experimental results of REE(III) partition coefficients between Fe(III) oxyhydroxide and hydrothermal solution and stability constants of REE(III)-carbonate complexes in hydrothermal conditions (Takahashi and Kawabe, 2004), although the detailed comparison will be presented elsewhere.



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