Comparison of the experimental and thermodynamic methods of stability constant estimation of the *REE* chloride complexes at elevated temperatures using $NdCl^{2+}$ and $HoCl^{2+}$ as examples

G. R. Kolonin
K. G. Morgunov
S. A. Stepanchikova

Institute of Mineralogy and Petrography, Siberian Dept. RAS,
Novosibirsk 630090, Russia

Different methods of thermodynamic extrapolations have been recently used for calculations of the *REE* stability constants at high temperatures (Wood *et al.*, 1994; Gammons *et al.*, 1996). The HKF equation together with standard thermodynamic data for Nd aqueous species by Haas *et al.* (1995) was used in the last work. Nevertheless, the universal character of a thermodynamic approach has a chance not to take into account some specific features of complex formation reactions, in particular, the influence of the *REE* position in lanthanide group (light, middle, heavy). Now for checking of theoretical models the authors have a possibility to use two sets of experimental constants for first chloride complexes of different *REE*, namely for $NdCl^{2+}$ and $HoCl^{2+}$ as the representatives of the light and heavy *REE* groups respectively. The needed data have been obtained by spectrophotometric method within 100–250°C temperature interval under saturated vapour pressure and treated with help of identical mathematical procedure.

If our results about temperature influence at stability constant of $NdCl^{2+}$ complex were presented elsewhere (Kolonin, Stepanchikova, 1997; Stepanchikova, Kolonin, 1998), the following tentative data of $HoCl^{2+}$ stability constant at infinity dilution is the first publication:

t, °C	100	150	200	250
log β_1	2.14	2.22	2.34	2.66
$\pm$log β_1	0.054	0.036	0.029	0.016

The spectral region 21500–22500 cm^{-1} has been used for these measurements, performed with the help of a special high temperature cell. It is the region where the appearance and the increase of a new band more pronounced as well as the essential decrease of intensity of aqua-ion Ho^{3+} band, when the temperature rises. Owing to respectively high intensity of holmium bands no any excess of chloride ions was necessary in comparison with the previous measurements for neodimium chloride solutions. It means, that the above data belong to 0.02–0.14 mol/kg H_20 concentration, when the main experiments with Nd solutions with the composition of 0.16 mol/kg $NdCl_3$ + 1.58 mol/kg H_2O have been undertaken earlier.

The first comparison of the experimental and calculated data for $NdCl^{+2}$ stability constants was presented by Gammons *et al.* (1996). We repeat them together with our experimental data on log β_1 and the values, calculated after their treatment with the help of a regression equation of exponential type (Table 1).

These data demonstrate as a general regularity the increase of log K_1 for $NdCl^{2+}$ complex between 25 and 300°C over 3.86 ± 0.66 interval of order of magnitude, but the difference at intermediate temperatures of 150 and 200°C is too small (1.52 ± 0.21 and 2.14 ± 0.16 respectively). Due to this reason we prefer the temperature interval 150–200°C for the estimation of enthalpy and entropy of the reaction of $NdCl^{2+}$ formation, realized

TABLE 1. Experimental and calculated values of β_1 for the complex $NdCl^{2+}$

t, °C	25	100	150	200	250	300
Gammons *et al.* (1996) experiment	0.06	0.66	1.31	2.17	3.22	4.48
the same work, calculation	0.31	1.08	1.67	2.30	3.01	3.85
this study, experiment	–	1.43	1.67	1.98	2.46	–
this study, calculation	0.87	1.38	1.73	2.05	2.36	2.64

TABLE 2. Comparison of the experimental and calculated values of β_1 for the complex $HoCl^{2+}$

t, °C	25	100	150	200	250	300
this study (experiment)	–	2.14	2.22	2.34	2.66	–
this study (exponential regression)	1.76	2.08	2.25	2.40	2.53	2.63
this study (HKF equation and data by Haas *et al.*, 1995)	0.24	1.03	1.66	2.35	3.27	4.05
average values	1.00	1.59	1.96	2.37	2.90	3.34
uncertainty	±0.76	±0.56	±0.30	±0.03	±0.31	±0.71

through geometric differentiation of the obtained exponential equation of regression. On the base of the equation: $\ln K = \Delta H/RT + \Delta S/R$ the values $\Delta H = 20.80$ kJ/mol and $\Delta S = 86.86$ J/mol grad have been calculated at 150°C, because it is the temperature of maximal closest approach of our experimental and both calculated curves. Moreover, $\log \beta_1 = 0.87$ at 25°C is the most preferable from our point of view, because it is obtained as a result of enough reliable extrapolation from elevated temperatures, where equilibrium is greatly displaced to the right.

The presented in this study new experimental series of the $HoCl^{2+}$ stability constants over 100–250°C interval have been approximated too by the exponential equation of regression with the subsequent geometric differentiation and estimation of enthalpy and entropy of the reaction. These experimental and calculated data are compared below in Table 2 together with another theoretical function, calculated on the base of the revised form of HKF equation and the standard thermodynamic data taken from the paper of Haas *et al.* (1995).

Some conclusions are evident from these data:

(1) satisfactory agreement of the experimental and both calculated values over the interval of 150–250°C, which is close to the situation with the $NdCl^{2+}$ stability constants in Table 1 at the same temperatures;

(2) poor agreement at 100°C, but a particularly great difference between experimental and calculated by HKF equation values at 25°C as well as between both values at 300°C;

(3) the perfect agreement at 200°C.

The main conclusion is the principal discrepancy between unusually slow temperature influence of the experimental curve for $HoCl^{2+}$ form could be emphasized in comparison with both the calculated curve on the base HKF equation and our experimental data for $NdCl^{2+}$ complex. Nevertheless, the crossing of experimental and theoretical curves at 200°C gives a chance to the formal and tentative estimation of enthalpy and entropy of the complex forming reaction at this temperature. The above mentioned procedure offers $\Delta H = 10.8$ kJ/mol and $\Delta S = 68.6$ J/mol grad.

In general, the adequate principal agreement between experimental and theoretical results related with formation of the first chloride complexes of Nd and Ho has been established, at least at intermediate temperatures. In the same time, there is a substantial difference between experimental $NdCl^{2+}$ and $HoCl^{2+}$ stability constants, increasing to both sides from the 150–200°C temperature interval. Finally, an appreciable exceeding difference in both the position and slope of the experimental curves for these complexes in $\log \beta_1$ coordinates versus temperature demonstrates its disagreement with rather small one for similar theoretical dependencies, calculated on the base of the HKF equation and standard thermodynamic data by Haas *et al.*(1995)

Our research was supported by the Russian Foundation of Basic Researches through the grant of N 96-05-65899

References

Gammons, C.H., Wood, S.A. and Williams-Jones, A.E. (1996) *Geochim. Cosmocim. Acta*, **60**, 4615–30.

Haas, J.R., Shock, E.L. and Sassani, D.C. (1995) *Geochim. Cosmocim. Acta*, **59**, 4329–50.

Kolonin, G.R. and Stepanchikova, S.A. (1997) In: *Proccedings Fifth Intern. Symp. Hyrotherm. Reactions*, Gatlinburg, USA, 23–5.

Stepanchikova, S.A. and Kolonin, G.R. (1998) *Russian J. Inorganic Chem.* (in press).

Wood, S.A. and Williams-Jones, A.E. (1994) *Chem. Geol.*, **115**, 47–60.