Hydrolysis of chromium(III) ion and solubility of chromium(III) oxide in high temperature water

D. Hiroishi
C. Matsuura
K. Ishigure

Department of Quantum Engineering and Systems Science, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-0032 Japan

Recently, the chemical behaviour of chromium species in the primary circuit of water-cooled nuclear reactors has gained a great deal of attention because of its important role in accumulation of radioactivity onto the surface of piping systems. To elucidate the behaviour of chromium compounds, the thermodynamic approach plays an important role. However, there is no thermodynamic data set of chromium ion at high temperatures. Thus, the acquisition of experimental data was considered to be essential.

In this work, values of hydrolysis constants and standard free energy of formation of chromium(III) ion at high temperatures were evaluated experimentally.

Experimental

The measurements of the hydrolysis constants of Cr^{3+} were carried out at 25, 50 and 75°C according to the following procedure. Chromium(III) potassium sulphate dodecahydrate was dissolved in diluted $HClO_4$ aqueous solution, the initial chromium(III) concentration was set to be 1×10^{-4} mol/kg, and initial pH of the solution was 3. A closed glass vessel containing 250g of the solution and equipped with a standard pH electrode and a thermometer was set in a thermostated incubator. Bubbling with argon gas continuously to avoid the dissolution of carbon dioxide, NaOH solution was added to the chromium(III) solution gradually (final pH was 11 to 12). At least 2h after every addition, the pH of the solution was measured and a small amount of the solution was collected through a filter of 0.22 micrometer pore size to measure the concentration of dissolved chromium(III) species. Dissolved chromium(III) was analysed spectrophotometrically using diphenylcarbazide. This reagent forms a complex with chromium(VI) ion that has a strong absorption at 540 nm ($\varepsilon = 3.63 \times 10^4$ dm^3/mol cm) in 0.2N H_2SO_4. To analyse chromium(III), it is oxidized to chromium(VI) by permanganate. The detection limit for the chromium(III) ion was 2×10^{-9} mol/kg.

Measurements of hydrolysis constants at 200°C were carried out by a similar procedure using an autoclave system equipped with a Teflon vessel, Teflon-covered pipe lines and a yttria-stabilized zirconia membrane sensor coupled with an Ag/AgCl reference electrode to measure pHs of high temperature solutions directly. HCl was used instead of $HClO_4$ to avoid oxidation of Cr(III) by perchrolate at high temperatures and initial pH was set to be 1.5 because the hydrolysis of Cr(III) ion was expected to start in lower pH region at 200°C than at lower temperatures.

Solubilities of chromium(III) oxide in pure and deoxygenated water were measured at 200°C using a batch-type autoclave equipped with a Teflon vessel and Teflon-covered pipe lines. About 5g of Cr_2O_3 sample was dispersed in 2.6 kg of pure water in the Teflon vessel. After removing dissolved oxygen and carbon dioxide by bubbling with argon, the vessel was pressurized by argon and kept for 600 to 1500 h at 200°C. Test solution was filtered by a Teflon filter

TABLE 1. The experimentally obtained values of hydrolysis constants of Cr^{3+}

Temperature (°C)	K_1	K_2	K_3	K_4
25	2.0×10^{-4}	4.0×10^{-10}	5.0×10^{-17}	6.0×10^{-28}
50	1.5×10^{-3}	1.0×10^{-9}	3.0×10^{-16}	$2. \times 100^{-25}$
75	2.0×10^{-3}	8.0×10^{-9}	1.0×10^{-14}	$2. \times 100^{-23}$
200	1.0×10^{-2}	5.0×10^{-6}	2.5×10^{-9}	5.0×10^{-17}

TABLE 2. The ΔG_f^0 values used for the calculation and evaluated

Chemical species	$-\Delta G_f^0$ (kJ/mol) 200°C
H_2O (Ref.2)	209.98
Cr_2O_3 (Ref.3)	1005.65
Cr^{3+} (this work)	190.05

of 0.1 micrometer pore size inside the autoclave at high temperatures and collected without any contact with metal surface. The chromium(III) concentration and pH at room temperature of the solution were measured.

Results and discussion

Hydrolysis of Chromium(III) ion: As the hydrolysis reactions of chromium(III) ion, the following equations were taken into account:

$$Cr^{3+} + H_2O = CrOH^{2+} + H^+ \quad /K_1 \quad (1)$$
$$Cr^{3+} + 2H_2O = Cr(OH)_2^+ + 2H^+ \quad /K_2 \quad (2)$$
$$Cr^{3+} + 3H_2O = Cr(OH)_3(aq) + 3H^+ \quad /K_3 \quad (3)$$
$$Cr^{3+} + 4H_2O = Cr(OH)_4^- + 4H^+ \quad /K_4 \quad (4)$$

The dissolved chromium(III) concentration observed experimentally is described as CrT by Eq.(5)

$$CrT = [Cr^{3+}] + [CrOH^{2+}] + [Cr(OH)_2^+] + [Cr(OH)_3(aq)] + [Cr(OH)_4^-] \quad (5)$$

The following reaction was considered for precipitation of chromium(III) ion:

$$Cr^{3+} + 3H_2O = Cr(OH)_3(s) + 3H^+ \quad /K_0 \quad (6)$$

If the equilibria of Eqs.(1),(2),(3),(4) and (6) are assumed, Eq.(7) is obtained:

$$CrT = ([H^+]^3 + K_1[H^+]^2 + K_2[H^+] + K_3 + K_4/[H^+]) \quad /K_0 \quad (7)$$

The experimental values of CrT were measured as dissolution curves for each temperature. By fitting to the dissolution curve at each temperature, using measured CrT values and K_1, K_2, K_3, K_4 and K_0 as parameters, the values of these hydrolysis constants were evaluated.

The precipitation of chromium(III) ion is considered as $Cr(OH)_3(s)$ by Eq.(6). The results of X-ray diffraction analyses of the precipitates at 25°C and 75°C showed no diffraction peak and indicated they were amorphous. Because the chemical form of the precipitates was not determined, the values of K_0 obtained from fittings to the dissolution curves are considered to be apparent values.

The values of the hydrolysis constants K_1, K_2, K_3, and K_4 obtained at each temperature through the fittings are listed in Table 1. The values at 25°C are in good agreement with the reported values [1].

To estimate temperature dependence of the hydrolysis constants, the logarithms of the hydrolysis constants were plotted against the reciprocals of temperatures. Those plotts show that the relation between the hydrolysis constants and temperature is described by Eq.(8) as a first approximation:

$$\ln K = a + b/T, \quad (8)$$

where a and b are constants. This indicates that the heat capacity changes of the hydrolysis reactions can be regarded to be negligible in this narrow temperature range.

Solubility of chromium(III) oxide: The equilibrium of Cr_2O_3 dissolution in deoxygenated water is described by Eq.(9).

$$2Cr^{3+} + 3H_2O = Cr_2O_3 + 6H^+ \quad /K_5 \quad (9)$$

The system reached the equilibrium in about 620h at 200°C. At the equilibrium, dissolved chromium(III) concentration was 2.24×10^{-8} mol/kg and pH at room temperature was 4.29. This low pH value was presumed to be mainly due to the remaining HCl used to clean up the Teflon vessel. The equilibrium constant of Cr_2O_3 dissolution, K_5 of Eq.(9) was evaluated as 1.55×10^{-2} mol^4/kg^4 by applying the measured hydrolysis constants of chromium(III) ion to the solubility data.

To evaluate the value of standard free energy of formation of Cr^{3+} from the obtained value of K_5, values of $\Delta G_f^0(H_2O)$ and $\Delta G_f^0(Cr_2O_3)$ for 200°C are required. For the former, the value recommended by Cobble *et al.*[2] was used. The value of $\Delta G_f^0(Cr_2O_3)$ was determined using the values of ΔG_f^0 and ΔS^0 of Cr_2O_3 at 298 K and the data on temperature dependence of ΔCp^0 of Cr_2O_3 [3]. The adopted values of $\Delta G_f^0(H_2O)$ and $\Delta G_f^0(Cr_2O_3)$ for 200°C and evaluated value of $\Delta G_f^0(Cr^{3+})$ for 200°C are listed in Table 2.

References

(1) D. Rai *et al.*, (1987) *Inorg. Chem.*, **26**, p345
(2) J. Cobble *et al.*, "High Temperature Thermodynamic Data for Species in Aqueous Solution", 1982, NP-2400, EPRI
(3) O. Kubaschewski *et al.*, "Materials Thermochemistry", 1993, p272, Pergamon Press.