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Solubility of zinc ferrite in high-temperature oxygenated water

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Abstract

The solubility of zinc ferrite was measured at 423 K, 473 K, and 523 K in an oxygenated water system, which is rather similar to the chemical condition of boiling water reactors. Thermodynamic analysis was performed by a procedure minimizing standard Gibbs free energy of the system at the final state. From both the analysis and the experimental results it was concluded that the dissolution process of $ZnFe_2O_4$ in conditions where no redox reaction occurs is described by combination of $ZnFe_2O_4$ dissolution and Fe_2O_3 precipitation equilibria. By fitting to the experimental results, thermodynamic data of $ZnFe_2O_4$ are re-analyzed at 423 K, 473 K, and 523 K. © 1998 Elsevier Science B.V.

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1. Introduction

The chemical behavior of corrosion products from component materials in the primary circuit of water cooled reactors has been actively investigated in the field of water chemistry for many years, since the activation of these corrosion products by neutron irradiation in the reactor core causes an increase in the radiation dose rates at the plants and increases occupational radiation exposures. The activation reactions are mainly ^{58}Ni(n, p)^{58}Co and ^{59}Co(n, γ)^{60}Co. The species controlling radioactivity transport are not only Ni and Co but also Fe and Cr from component materials, which exist in reactor water in ionic forms or in spinel type oxides, mostly described as (Ni, Fe, Co)(Fe, Cr)$_2$O$_4$. Thermodynamics is a powerful tool to elucidate the dissolution–precipitation behavior of these corrosion products. However, thermodynamic data necessary for the analysis are not available to a large extent especially at high temperatures and the standard analytical procedure for such analysis has not been well established yet.

In recent years there has been a growing interest in zinc injection into reactor water which has significant effects on reduction of radioactivity accumulation on the surfaces of circuit materials. The behavior of zinc species in reactor water, which includes the effects not only on the cobalt uptake but on the oxide deposition upon the fuel surfaces, however, is not well understood, and thermodynamic data of zinc species in aqueous systems at high temperatures, are hardly available.

We have so far measured solubilities of CoO [1], NiO [2], Fe_3O_4 [3] and $NiFe_2O_4$ [4] in pure water systems at high temperatures. The thermodynamic data of Co^{2+}, Ni^{2+} and $NiFe_2O_4$ have been evaluated and some methods of thermodynamic analysis for high temperature aqueous systems have been proposed. Besides, we have determined hydrolysis constants of Zn^{2+} through the direct measurements of pH in the temperature range from 298 K to 498 K, and estimated standard Gibbs free energy of formation for Zn^{2+} by the solubility measurement of ZnO in pure water systems at high temperatures [5]. The experiments in Ref. [5] were carried out in conditions where the pH of the system ranges from neutral to a little acidic and the data obtained from this work were compared also with previously reported thermodynamic data on zinc ion, in Ref. [6], where the experiments were performed in alkaline conditions.

The role of zinc injected into reactor water is not well understood yet but one of the possibilities may be that zinc

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ferrite is formed as a portion of crud or deposits on the surface of the fuel and circuit materials, and it has important effects on the stability of the surface oxide layers, on the dissolution and precipitation mechanism of the corrosion products and on the cobalt uptake in the oxide layers, which is analogous to the role of nickel ferrite in the absence of zinc. Thus, this work deals with zinc ferrite to obtain more information on its thermodynamic stability in aqueous systems. The solubility of $ZnFe_2O_4$ was measured from 423 K to 523 K in an oxygenated and neutral to a little acidic water system, which is similar to the chemical condition of BWR. The dissolution behavior of $ZnFe_2O_4$ in the present experimental condition was elucidated from both experiments and thermodynamic analysis using the data of standard Gibbs free energy of formation for Zn^{2+} obtained in the previous work, and, finally, thermodynamic data of $ZnFe_2O_4$ were evaluated in a form of standard Gibbs free energy of formation.

2. Experimental

Zinc ferrite of guaranteed 99.9% purity produced by High Purity Chemicals, Japan, was used for the experiments. Prior to use, the sample was checked with chemical analysis and X-ray diffraction measurement. The ICP spectroscopy analysis of the sample dissolved in concentrated HCl did not detect any impurity. By X-ray diffraction measurement, however, a small amount of ZnO was detected. After dispersion of the sample in 0.1N HCl and subsequent repeated washing with distilled water, the sample did not indicate any trace of ZnO. The solubilities of the sample measured in this work were much lower than that of ZnO [5] and the pretreatment procedure of the sample described above was considered to be valid for eliminating a small amount of ZnO. The lattice constant of the $ZnFe_2O_4$ sample was measured to be 0.8440 nm before the experiments.

The solubilities of $ZnFe_2O_4$ were measured at 423 K, 473 K and 523 K using a specially designed batch type autoclave containing a Teflon vessel, described in detail previously [1]. About 5 g of $ZnFe_2O_4$ sample was dispersed in 2.6 kg of ultrapure water prepared with a Milli-Q reagent water system (Japan Millipore). After the atmosphere inside the autoclave was replaced with pure argon and the water in the Teflon vessel was bubbled with pure oxygen for at least 2 h, the vessel was pressurized from 4 to 6 MPa argon–oxygen mixture (oxygen content was ~ 2 vol./vol.%) and kept at a certain temperature for 400 to 1000 h. The temperature inside the autoclave was controlled to within ± 1°C. In some cases, a small amount of HCl was added to control acidity of the system. The test solutions were separated from the sample solid with a Teflon filter (0.1 μm pore size) inside the autoclave at high temperatures and collected for chemical analyses. A sampling tube through which the test solutions passed was covered with Teflon, avoiding any direct contact of the solutions with metal surfaces.

The concentrations of dissolved zinc, total iron (Fe(II) + Fe(III)) and F^- ion, which originated from thermal decomposition of Teflon and caused the increase in acidity of the system, were measured spectrophotometrically by the methods reported previously [1,3,5]. The concentration of Cl^- ion from hydrochloric acid added was determined turbidimetrically as described in the previous paper [4]. For other anion species, the test solutions were checked with ion chromatography. The pH of the test solutions at room temperature was measured using a pH meter and oxygen concentration in the gas phase in the autoclave was measured by an oxygen analyzer of zirconia type.

3. Results and discussion

3.1. Solubility of $ZnFe_2O_4$

Fig. 1 shows the time dependence of dissolved Zn ion levels together with that of F^- ion observed in the solubility measurement of zinc ferrite at 523 K, as an example. The concentration of F^- ion increased with the elapse of time, due to the thermal decomposition of the Teflon vessel and it was noted that the F^- ion level almost controlled the acidity of the system unless Cl^- was added. The concentration of dissolved zinc was about 10^{-8} to 10^{-7} mol kg^{-1} and it seemed to increase slightly, mainly accompanying the increase in F^- ion concentration. In the present experimental condition of the oxygenated atmosphere, only dissolved zinc was detected and dissolved iron was generally below the detection limit ($< 4 \times 10^{-9}$ mol kg^{-1}). These phenomena were similar to the case of the dissolution of $NiFe_2O_4$ in oxygenated system, reported previously [4].

X-ray diffraction analyses of the samples of $ZnFe_2O_4$ recovered after the dissolution experiments indicated only diffraction peaks of $ZnFe_2O_4$ and no change in the lattice constant (0.8440 nm) compared with the initial sample was

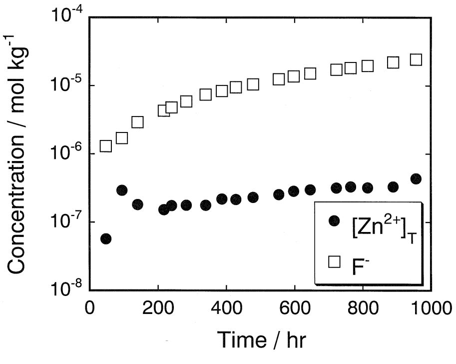

Fig. 1. Time dependence of the concentrations of dissolved Zn ion and F^- ion in the experiment of $ZnFe_2O_4$ dissolution at 523 K.

Table 1

No.	Elapsed time (h)	Zinc concentration (μmol kg^{-1})	[F$^-$]+[Cl$^-$]+[NO$_3^-$] (μmol kg^{-1})
(a) Experimentally observed solubility of zinc from $ZnFe_2O_4$ at 423 K			
1	10.5	0.067	0.3
2	29.5	0.051	0.1
3	244	0.054	0.1
4	320	0.061	0.1
5	362.5	0.105	< 0.1
6	409	0.043	< 0.1
7	432	0.136	< 0.1
8	505.5	0.056	< 0.1
	Restart *		
9	66	0.866	10.2
10	90.5	1.045	9.2
11	116.5	1.275	8.2
12	139.5	1.365	11.5
13	169	1.618	10.5
14	259	2.040	7.5
15	329.5	2.322	10.8
16	403	3.000	9.9
17	498	3.738	9.3
18	811.5	7.537	9.5
19	861.5	5.557	8.4
(b) Experimentally observed solubility of zinc from $ZnFe_2O_4$ at 473 K			
1	79.5	0.075	1.1
2	98.5	0.136	1.1
3	123	0.221	1.4
4	147	0.127	1.2
5	169.5	0.119	1.5
6	243.5	0.134	1.5
7	266.5	0.117	1.4
8	290.5	0.174	1.4
9	339	0.176	1.0
10	414	0.178	1.2
11	458.5	0.106	1.1
12	506	0.119	1.4
13	580	0.370	1.1
14	626.5	0.163	1.6
15	674	0.104	1.3
16	747	0.220	1.3
17	819	0.171	1.3
	Restart *		
18	16	0.416	7.4
19	134	0.577	8.3
20	183.5	0.565	7.4
21	238.5	0.436	10.5
22	349	0.404	9.2
	Restart *		
23	57.5	1.786	21.9
24	106	1.772	27.8
25	170.5	1.831	28.9
26	217.5	1.947	22.8
27	294	1.915	17.1
28	465.5	1.926	28.3
29	507	1.987	23.5
30	552.5	1.879	24.6
(c) Experimentally observed solubility of zinc from $ZnFe_2O_4$ at 523 K			
1	48.5	0.057	1.6
2	95.5	0.293	2.0
3	141	0.181	3.2
4	217.5	0.153	4.6
5	240	0.175	5.1
6	283	0.177	6.2
7	340	0.177	7.7
8	387	0.219	8.7
9	428	0.216	9.8
10	478	0.231	10.8
11	553.5	0.255	12.8
12	597	0.285	14
13	646	0.300	15.4
14	722.5	0.319	17.5
15	764.5	0.331	18.5
16	814.5	0.320	19.9
17	889.5	0.331	22.4
18	957	0.436	24.6

* Hydrochloric acid was added to the system.

noted. In some cases, NO_3^- ion was detected in the test solutions and their concentrations were lower than 3×10^{-7} mol kg^{-1}, which might be a residual reagent during synthesis of the sample of $ZnFe_2O_4$. It was considered that the existence of this level of NO_3^- had no significant influence on chemical reactions in this system except for charge balance of the systems.

The observed solubility data of $ZnFe_2O_4$ are summarized in Table 1 in a form of dissolved zinc concentration together with elapsed time and total concentration of acidic anions in the system, i.e. $[F^-] + [Cl^-] + [NO_3^-]$.

3.2. Thermodynamic analysis

The thermodynamic analysis was applied to the dissolution of $ZnFe_2O_4$ in oxygenated systems according to the same procedure as in the previous papers [3,4]. It is considered that no redox reaction occurs in oxygenated systems because metal ions dissolved from $ZnFe_2O_4$ are not oxidizable. In such a case, on the analogy of $NiFe_2O_4$ [4], the possible mechanism of $ZnFe_2O_4$ dissolution is considered to be either of the following two types:

case I: only the dissolution of $ZnFe_2O_4$ occurs;

case II: in addition to the dissolution of $ZnFe_2O_4$, the precipitation of Fe_2O_3 occurs from Fe(III) ion formed by $ZnFe_2O_4$ dissolution, concurrently.

In both cases, it is necessary that dissolved Zn^{2+} and Fe^{3+} ions together with their hydrolysis products in the aqueous phase are taken into account.

The possibilities of precipitations of other solid phases such as ZnO, $Zn(OH)_2(s)$ and Fe_3O_4 were examined. The solubility of ZnO reported in the previous paper [5] is 10 to 30 times higher than the results of the present experiments. It is known that $Zn(OH)_{2(s)}$ is less stable than ZnO at high temperatures and it converts to ZnO after a while. It is not necessary to consider the formation of Fe_3O_4 in the present experimental conditions because the reduction of Fe(III) into Fe(II) does not occur in this system. Thus, it is reasonable that only the solid phases of $ZnFe_2O_4$ and Fe_2O_3 are taken into account in the analysis of this study.

By the thermodynamic analysis minimizing the Gibbs free energy of the system, as described in the previous papers [3,4], it is found that the establishment of equilibrium of reaction (1)

$$Zn^{2+} + 2Fe^{3+} + 4H_2O = ZnFe_2O_4 + 8H^+ \quad K_{ZF} \tag{1}$$

is required for case I together with the relevant hydrolysis equilibria (3) through (8), and for case II, not only the equilibrium of reaction (1) but also that of reaction (2)

$$2Fe^{3+} + 3H_2O = Fe_2O_3 + 6H^+ \quad K_H \tag{2}$$

are required to hold simultaneously together with the relevant hydrolysis equilibria (3) to (8):

$$Zn^{2+} + H_2O = ZnOH^+ + H^+ \quad K_{21} \tag{3}$$

$$Zn^{2+} + 2H_2O = Zn(OH)_{2(aq)} + 2H^+ \quad K_{22} \tag{4}$$

$$Zn^{2+} + 3H_2O = Zn(OH)_3^- + 3H^+ \quad K_{23} \tag{5}$$

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+ \quad K_{31} \tag{6}$$

$$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+ \quad K_{32} \tag{7}$$

and

$$Fe^{3+} + 3H_2O = Fe(OH)_{3(aq)} + 3H^+ \quad K_{33}. \tag{8}$$

In Eqs. (1)–(8), K represents equilibrium constant of the reaction. The solubilities of zinc and iron were defined as follows:

$$[Zn^{2+}]_T = \sum_{i=0}^{3} \left[Zn(OH)_i^{(2-i)+} \right], \tag{9}$$

$$[Fe^{3+}]_T = \sum_{i=0}^{3} \left[Fe(OH)_i^{(3-i)+} \right]. \tag{10}$$

The calculations of the solubilities were carried out using a charge balance equation described as Eq. (11):

$$3[Fe^{3+}] + 2\{[FeOH^{2+}] + [Zn^{2+}]\} + \left[Fe(OH)_2^+\right] + [ZnOH^+] + [H^+] = \left[Zn(OH)_3^-\right] + [OH^-] + A, \tag{11}$$

where $A = [F^-] + [Cl^-] + [NO_3^-]$.

The molality of each species in Eq. (9) was expressed by $[H^+]$ using equilibrium constants of reactions (1) to (8), mass balance relations and the dissociation constant of water. Equations were solved to obtain expressions for $[Zn^{2+}]_T$ and $[Fe^{3+}]_T$ in terms of $[H^+]$ for cases I and II.

In equilibrium Eqs. (1)–(8), the activities of the related species should be used especially in the case where the acid concentrations were high. The molal ionic activity coefficients, γ_z, were estimated in accordance with the extended Debye–Hückel expression as follows:

$$\log \gamma_z = -(z^2 A I^{1/2})/(1 + 1.5 I^{1/2}), \tag{12}$$

where I is the ionic strength of the system, z is the electric charge of ionic species concerned, A is Debye–Hückel limiting slope (the value of A at each temperature was taken from Ref. [7]). The estimated activity coefficients were close to 1 and it seemed that the use of the activity instead of the concentration has no significant influence on the results of the analyses.

The dissociation constants of water ($K_w = [H^+][OH^-]$) were taken from the recommendation of Marshall and Frank [8].

The equilibrium constants K_{ZF} and K_H for reactions (1) and (2), respectively, were estimated by Eq. (13), which describes a relation between an equilibrium constant and the standard free energy change of a reaction:

$$\Delta G_0(T) = -RT \ln K(T). \tag{13}$$

The standard Gibbs free energy change of a reaction was estimated using the values of standard Gibbs free energy of formation, $\Delta G_f^0(T)$, of related species. The reference state was selected such as standard Gibbs free energies of formation of all elements and H^+(aq) are taken as zero at all temperatures.

For ΔG_f^0 values of Fe^{3+}(aq), H_2O(l) and Fe_2O_3(s) at each temperature, those recommended by Cobble et al. [9] based on their experiments were used for calculations as in previous studies [1–5]. For zinc ion, the $\Delta G_f^0(T)$ values evaluated in the previous paper [5] were used; -1.38×10^5 J mol^{-1} at 423 K, -1.35×10^5 J mol^{-1} at 473 K and -1.29×10^5 J mol^{-1} at 523 K. Values of $\Delta G_f^0(T)$ for $ZnFe_2O_4$[s] were estimated from the extrapolation based on Eq. (14):

$$\Delta G^0(T_1) = \Delta G^0(298) - \Delta S^0(298)(T_1 - 298.15) + \int_{298}^{T_1} \Delta C_p^0 \, dT - T_1 \int_{298}^{T_1} \Delta C_p^0 \, d\ln T, \tag{14}$$

where $\Delta S^0(298)$ is standard entropy change of a reaction at 298 K and ΔC_p^0 is the heat capacity change of a reaction. The estimation using Eq. (14) requires a set of

Table 2
Comparison of $\Delta G_f^0(T)$ values of $ZnFe_2O_4$ among data sources

Reference	$-\Delta G_f^0(T)$ of $ZnFe_2O_4$ (kJ mol^{-1})			
	298 K	423 K	473 K	523 K
[10]	1064	1020	1002	985
[11]	1064	1018	1000	982
[12]	1068	1022	1003	985
[13]	1066	1020	1002	984
[14]	1074	1030	1013	996

Table 3
The values of hydrolysis constants of Zn^{2+} used for calculations

Temp. (K)	K_{21}	K_{22}	K_{23}
423	3.8×10^{-6}	4.1×10^{-13}	7.8×10^{-22}
473	3.2×10^{-5}	1.7×10^{-11}	8.4×10^{-20}
523	1.8×10^{-4}	3.6×10^{-10}	3.7×10^{-18}

literature values of entropy at 298 K, S^0(298 K), and the temperature dependence of heat capacity, C_p^0, for $ZnFe_2O_4$(s), Zn(s), Fe(s) and O_2(g) and the value of ΔG_f^0(298 K) for $ZnFe_2O_4$[s]. For the purpose of the estimation here, five data sets [10–14] were used. Refs. [10–14] show summarized data bases and their data for $ZnFe_2O_4$ are based on the reported experimental measurements of heat capacity [15], specific heat [16] and enthalpy of formation [17,18], not direct determination of ΔG_f^0.

Table 2 shows the calculated values of $\Delta G_f^0(T)$ for $ZnFe_2O_4$ at each temperature using these five different data sets. Among these values, those from Ref. [10] were used for the following calculations. For hydrolysis constants of Zn^{2+}, K_{21}–K_{23}, the values evaluated in the previous paper [5] were used (Table 3). For those of Fe^{3+}, the values recommended by Cobble et al. are available for only K_{31} and K_{32}. On the other hand, it is possible to estimate K_{31}–K_{33} values at 423 K and 523 K from thermodynamic data reported by Zarembo et al. [19]. Therefore, in this study, the following two types of analysis were performed, as in the previous paper [4].

(1) The values of K_{31} and K_{32} by Cobble et al. were used and $Fe(OH)_3$ was neglected.

(2) The values of K_{31}–K_{33} derived from the data by Zarembo et al. were used including $Fe(OH)_3$ for 423 K and 523 K.

The analysis showed that it has no influence on the calculated value of $[Zn^{2+}]_T$ whether $Fe(OH)_3$ is taken into account or not.

In the present experiments, HCl was added to the systems at 423 K and 473 K. It is known that Zn^{2+} forms complexes with Cl^- and equilibrium constants for reactions (15) at high temperatures over 373 K have been reported [20,21]:

$$ZnCl_n^{(2-n)+} + Cl^- = ZnCl_{(n+1)}^{(2-n-1)+} \quad (n = 0\text{–}3). \qquad (15)$$

These reactions of Zn^{2+} may not make significant contribution to the analysis except for the case of $n = 0$ because the values of their equilibrium constants are small and the concentrations of Cl^- were rather low. Then the calculations taking only $ZnCl^+$ into account were performed for the concentrations of Cl^- in the present experiments at 423 K and 473 K. The result shows that the contributions of $[ZnCl^+]$ were limited in a few orders lower than $[Zn^{2+}]_T$. It is noted that F^-, which was present in the experimental systems because of the thermal decomposition of Teflon, also has a possibility to form complexes with Zn^{2+}. The equilibrium constants of complexation reactions of Zn^{2+} with F^-, however, are not available. As a simple approximation, contribution of ZnF^+ complex to the solubility of $ZnFe_2O_4$ was estimated for the conditions of the present experiments at 423 K, 473 K and 523 K, assuming its complexation constant is equal to that of $ZnCl^+$. The estimated contribution of ZnF^+ to the system

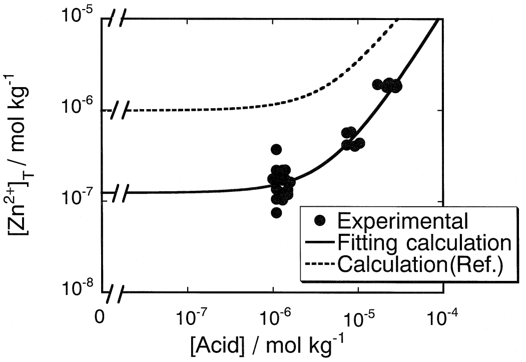

Fig. 3. The dependence of $ZnFe_2O_4$ solubility on acidity at 473 K ([Acid] = [F^-] + [Cl^-] + [NO_3^-]).

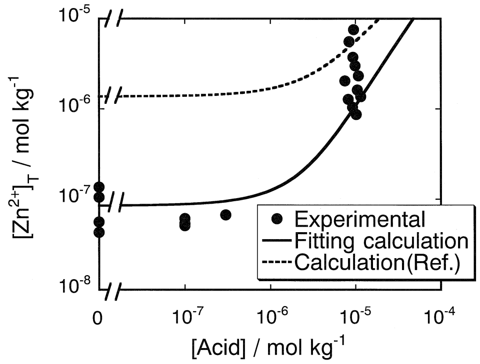

Fig. 2. The dependence of $ZnFe_2O_4$ solubility on acidity at 423 K ([Acid] = [F^-] + [Cl^-] + [NO_3^-]).

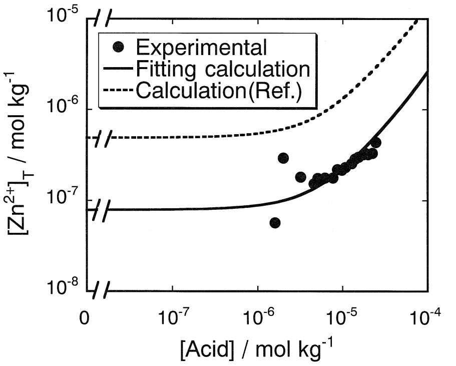

Fig. 4. The dependence of $ZnFe_2O_4$ solubility on acidity at 523 K ([Acid] = [F^-] + [Cl^-] + [NO_3^-]).

Table 4
The estimated values of K_{ZF} and $\Delta G_f^0(T)$ of $ZnFe_2O_4$

Temperature (K)	K_{ZF}	$-\Delta G_f^0(T)$ (kJ mol^{-1})
423	1.5×10^2	1031
473	5.2×10^4	1011
523	1.4×10^7	993

was not significant. Therefore in the following discussion, calculations were performed omitting any complexes of Zn^{2+} with Cl^- and F^-.

The dissolution of $ZnFe_2O_4$ in the oxygenated system was expected to occur through the process of case II, similarly to the case of $NiFe_2O_4$ in the previous paper [4], because the ferric ion concentrations, $[Fe^{3+}]_T$, were under the detection limit as already described and therefore the result is not consistent with the following stoichiometric relation

$$[Fe^{3+}]_T = 2[Zn^{2+}]_T \tag{16}$$

which is required to hold in case I.

The calculated zinc solubilities for case II are plotted against acid concentrations ($[F^-] + [Cl^-] + [NO_3^-]$) in Figs. 2–4 at 423 K, 473 K and 523 K, respectively, compared with the experimental results. The acidity dependence of the calculated solubilities was rather close to those of the experimental results. Thus, the dissolution process of $ZnFe_2O_4$ in conditions where no redox reaction occurs was considered to follow case II.

As seen in Figs. 2–4, however, there were some deviations between the calculated and experimental values. It was supposed that the deviations were due to the unreliability of the thermodynamic data used for the calculation. The data used by the related species except for those of $ZnFe_2O_4$ were the same as those used in the analyses of the previous studies and their validity was confirmed already. On the other hand, the values of $\Delta G_f^0(T)$ for $ZnFe_2O_4$ are somewhat different from source to source, as shown in Table 2. It was considered that the contribution of $\Delta G_f^0(T)$ value of $ZnFe_2O_4$ to the equilibrium constant K_{ZF} is larger than those of the other related species in reaction (1) because the absolute value of $\Delta G_f^0(T)$ for $ZnFe_2O_4$ is relatively large compared with those of the other species at any temperatures. Thus, the main reason for the deviations between the calculated and experimental results was supposed to be the unreliability of the $\Delta G_f^0(T)$ values of $ZnFe_2O_4$ used for the calculation.

The fitting calculations were performed at 423 K, 473 K and 523 K using K_{ZF} as parameters, and the values of $\Delta G_f^0(T)$ for $ZnFe_2O_4$ at these temperatures were evaluated from the K_{ZF} values obtained by these fitting calculations, on the assumption that thermodynamic data for the other related species are valid. The results of the fitting calculations are also shown in Figs. 2–4 and the $\Delta G_f^0(T)$ values of $ZnFe_2O_4$ estimated by the above procedure for 423 K, 473 K and 523 K are listed in Table 4 together with the obtained values of equilibrium constants K_{ZF}. The values in Table 4 are comparatively close to those from Ref. [14] (in Table 2) and they are not extremely deviated even from the values used for the calculations in Ref. [10]. It is evident from Figs. 2–4, however, that a small difference in the ΔG_f^0 value has a significant influence on the solubility values calculated. Hence, it is concluded that solubility measurement is a very good tool to evaluate precise thermodynamic data, if reliable data are already available for the other related species.

The temperature dependence of $\Delta G_f^0(T)$ for $ZnFe_2O_4$ was evaluated for the data in Table 4 following a linear expression introduced in Ref. [22], and Eq. (17) was obtained, where the unit is in J mol^{-1}:

$$\Delta G_f^0(T) = -1.192 \times 10^6 + 380.75T. \tag{17}$$

However, the evaluation of Eq. (17) contains uncertainty to some extent because its fitting points are at only three temperatures, 423 K, 473 K and 523 K, and so it would be valid for the very limited temperature range, for instance, 373 K to 573 K. For reference, the value of $\Delta G_f^0(298\ K)$ for $ZnFe_2O_4$ evaluated using Eq. (17) was -1078 kJ mol^{-1}, which is not widely different from literature values in Table 2.

Using K_{ZF} values in Table 4, the solubilities of Zn and Fe and the Gibbs free energy changes of the systems between the initial state (before the dissolution started) and the final state (at the equilibrium) were calculated for cases I and II. Both calculations were performed including and neglecting $Fe(OH)_{3(aq)}$. The results are shown in Table 5

Table 5
Comparison of the calculated results for standard free energy change of the system[a] and solubility at 423 K between case I and II together with the experimental value

Case	$[Zn^{2+}]_T$ (mol kg^{-1})	$[Fe^{3+}]_T$ (mol kg^{-1})	ΔG^0 (J)
I	$1.0 \times 10^{-10} (1.7 \times 10^{-9})^b$	$2.1 \times 10^{-10} (3.3 \times 10^{-9})^b$	$-0.0001(-0.0031)^b$
II	$8.5 \times 10^{-8} (8.5 \times 10^{-8})^b$	$7.0 \times 10^{-12} (4.5 \times 10^{-10})^b$	$-0.0187(-0.0190)^b$
Experimental[c]	8.5×10^{-8}	$< 4 \times 10^{-9}$(n.d.)	

[a] 5 g of $ZnFe_2O_4$ and 2.5 kg of H_2O at initial state.
[b] Taking $Fe(OH)_3$ into account.
[c] Average value at $A = 0$.

for 423 K together with the experimentally observed solubility values. In case II, the standard free energy evaluated at the final state are lower than in case I. Similar results were obtained at any temperatures, independently of the data sets used, and so case II is more likely to occur than case I. Therefore it is concluded from not only the experimental values of solubilities but also thermodynamic analysis comparing the Gibbs free energy changes of the systems that the dissolution process of $ZnFe_2O_4$ in conditions where no redox reaction occurs is described by the combination of dissolution equilibrium of $ZnFe_2O_4$ and dissolution–precipitation equilibrium of Fe_2O_3 together with hydrolysis equilibria of Zn^{2+} and Fe^{3+}. This conclusion is similar to the cases of Fe_3O_4 and $NiFe_2O_4$ in the previous studies [3,4].

4. Conclusions

(1) The solubility of $ZnFe_2O_4$ was measured in pure and oxygenated water at 423 K, 473 K and 523 K.

(2) The solubility of $ZnFe_2O_4$ in conditions where no redox reaction occurs is determined by simultaneous establishment of dissolution equilibrium of $ZnFe_2O_4$ and precipitation equilibrium of Fe_2O_3 together with hydrolysis equilibria of the relevant metal ions.

(3) From the experimental results, the values of the standard Gibbs free energy of formation for $ZnFe_2O_4$ were reanalyzed at 423 K, 473 K and 523 K.

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