ELSEVIER
Journal of Nuclear Materials 275 (1999) 216–220
journal of nuclear materials
www.elsevier.nl/locate/jnucmat

Letter to the Editors

Use of linear free energy relationship to predict Gibbs free energies of formation of pyrochlore phases ($CaMTi_2O_7$)

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Received 6 April 1999; accepted 7 July 1999

Abstract

In this letter, a linear free energy relationship is used to predict the Gibbs free energies of formation of crystalline phases of pyrochlore and zirconolite families with stoichiometry of $MCaTi_2O_7$ (or, $CaMTi_2O_7$,) from the known thermodynamic properties of aqueous tetravalent cations (M^{4+}). The linear free energy relationship for tetravalent cations is expressed as $\Delta G^0_{f,M_vX} = a_{M_vX}\Delta G^0_{n,M^{4+}} + b_{M_vX} + \beta_{M_vX}\, r_{M^{4+}}$, where the coefficients a_{M_vX}, b_{M_vX}, and β_{M_vX} characterize a particular structural family of M_vX, $r_{M^{4+}}$ is the ionic radius of M^{4+} cation, $\Delta G^0_{f,M_vX}$ is the standard Gibbs free energy of formation of M_vX, and $\Delta G^0_{n,M^{4+}}$ is the standard non-solvation energy of cation M^{4+}. The coefficients for the structural family of zirconolite with the stoichiometry of M^{4+} $CaTi_2O_7$ are estimated to be: $a_{M_vX} = 0.5717$, $b_{M_vX} = -4284.67$ (kJ/mol), and $\beta_{M_vX} = 27.2$ (kJ/mol nm). The coefficients for the structural family of pyrochlore with the stoichiometry of M^{4+} $CaTi_2O_7$ are estimated to be: $a_{M_vX} = 0.5717$, $b_{M_vX} = -4174.25$ (kJ/mol), and $\beta_{M_vX} = 13.4$ (kJ/mol nm). Using the linear free energy relationship, the Gibbs free energies of formation of various zirconolite and pyrochlore phases are calculated.

PACS: 65.50.+m

1. Introduction

Crystalline phases of pyrochlore (e.g., $CaPuTi_2O_7$, and $CaUTi_2O_7$) continue to be considered as a durable titanate ceramic waste form for immobilizing high level radioactive wastes including surplus weapons-usable plutonium [1–12]. Pyrochlore and zirconolite phases with the stoichiometry of $CaMTi_2O_7$ (or, $MCaTi_2O_7$) can be considered as a derivative fluorite structure, where M represents tetravalent cations such as Zr, Hf, U, Pu and other actinides. The existence of large polyhedra (with coordination numbers ranging from 7 to 8) in the structures allows pyrochlore and zirconolite phases to accommodate a wide range of radionuclides (e.g., Pu, U, Ba, etc.) as well as neutron poisons (e.g., Hf, Gd) [10].

Pyrochlore and zirconolite have been subjected to extensive studies during the last two decades [1–15]. Since most of those studies have focused on fabrication and structural characterization, the thermodynamic data of pyrochlore phases are generally lacking, except for the recent measurements of the Gibbs free energies of formation for $CaZrTi_2O_7$ and $CaHfTi_2O_7$ phases with a zirconolite structure [15,16]. In actual waste forms, due to the presence of various tetravalent cations, the pyrochlore phases such as $CaPuTi_2O_7$, $CaNpTi_2O_7$, and $CaUTi_2O_7$ are expected to occur, and their thermodynamic properties are needed for assessing the behavior of Synroc-based waste forms and optimizing Synroc fabrications. In this letter, we use a linear free energy relationship to predict the Gibbs free energy of formation for various pyrochlore and zirconolite phases from the known thermodynamic properties of the corresponding aqueous tetravalent cations.

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2. Linear free energy relationship

Sverjensky and Molling [17] developed an empirical linear free energy relationship (Sverjensky–Molling equation) for isostructural families of inorganic solids based on the relationship between related crystalline phases and divalent aqueous cations. The Sverjensky and Molling relationship is directly analogous to the well-known Hammett free energy relationship [18–20], which was established for aqueous organic reactions. The Sverjensky and Molling relationship was originally developed for the mineral phases containing divalent cations, and has been extended to tetravalent cations [21]. For an isostructural family, the chemical formula of solids can be represented as M_vX, where M is a tetravalent cation M^{4+}, and X represents the remainder of the composition of the solid (for instance, in the pyrochlore and zirconolite families, tetravalent M is Zr, Hf, or Pu, and X is $CaTi_2O_7$). The Sverjensky and Molling linear free energy correlation for an isotructural family of minerals containing tetravalent cations [21] can be expressed as

$$\Delta G^0_{f,M_vX} = a_{M_vX}\Delta G^0_{n,M^{4+}} + b_{M_vX} + \beta_{M_vX}\, r_{M^{4+}}, \tag{1}$$

where the coefficients a_{M_vX}, b_{M_vX}, and β_{M_vX} characterize the particular structural family of M_vX; $r_{M^{4+}}$ is the ionic radius of the M^{4+} cation [22,23]; the parameter $\Delta G^0_{f,MvX}$ is the standard Gibbs free energies of formation of the endmember solids; and the parameter $\Delta G^0_{n,M^{4+}}$ is the standard non-solvation energy from a radius-based correction to the standard Gibbs free energy of formation of the aqueous tetravalent cation M^{4+} [23]. The parameter $\Delta G^0_{n,M^{4+}}$ can be calculated using the equation

$$\Delta G^0_{n,M^{4+}} = \Delta G^0_{f,M^{4+}} - \Delta G^0_{s,M^{4+}}, \tag{2}$$

where $\Delta G^0_{s,M^{4+}}$ is the standard Gibbs free energy of solvation of the tetravalent aqueous cation, which can be calculated from conventional Born solvation coefficients for the aqueous cations [23] according to the equation

$$\Delta G^0_{s,M^{4+}} = \omega_{M^{4+}}(1/\varepsilon - 1). \tag{3}$$

In Eq. (3), ε is dielectric constant of water (78.47 at 25°C). The parameter $\omega_{M^{4+}}$ are the Born solvation coefficients for the tetravalent cations and can be calculated using the equation

$$\omega_{M^{4+}} = \omega^{abs}_{M^{4+}} - 4\omega^{abs}_{H^+}. \tag{4}$$

In the above equation, $\omega^{abs}_{H^+}$ is the absolute Born solvation coefficient of H^+ (225.39 kJ/mol, or 53.87 kcal/mol), and $\omega^{abs}_{M^{4+}}$ is the absolute Born solvation coefficients of the tetravalent cations that are related to the effective electrostatic radii of the aqueous ions ($r_{e,M^{4+}}$) by

$$\omega^{abs}_{M^{4+}} = 694.657 \ast 4^2/(r_{e,M^{4+}}) \tag{5}$$

and

$$r_{e,M^{4+}} = r_{M^{4+}} + 4(0.94). \tag{6}$$

The standard solvation energy and non-solvation energy can be calculated based on the above equations, and are listed in Table 1. The coefficients a_{M_vX}, b_{M_vX}, and β_{M_vX} can be determined by regression if the Gibbs free energies of formation of three or more phases in one isostructural family are known. For comparison, the coefficients and calculated Gibbs free energies of formation for MO_2 family with fluorite structure and $MSiO_4$ family with zircon structure are listed in Table 1.

3. Application of linear free energy relationship to zirconolite and pyrochlore phases

For the isostructural family of $MCaTi_2O_7$ with a zirconolite structure, the Gibbs free energies of formation have been determined only for the $CaZrTi_2O_7$ and $CaHfTi_2O_7$ phases [15,16]. In order to apply the above linear free energy relationship, the coefficients a_{M_vX} or β_{M_vX} need to be estimated independently. Based on the results from other oxides and silicates crystal families, the coefficient a_{M_vX} is only related to the stoichiometry of solids [17]. Values of the coefficient a_{M_vX} are very close for all polymorphs [17]. The coefficient β_{M_vX} is related to the effect of nearest neighbors or coordination number (CN) of the cation [17]. In polymorphs, the structure family with a small CN (e.g., CN = 6 in calcite structure family) has higher value of β_{M_vX} than the family with a big CN (e.g., CN = 9 in aragonite structure family) does [17]. The value of β_{M_vX} for fluorite structure (CN of M atom is 8) for the MO_2 structural family with a fluorite structure is 13.4 (kJ/mol nm) (or 32.0 kcal/mol Å) (Table 1). The value of β_{M_vX} for the $MSiO_4$ structural family with a zircon structure (CN of M atom is 7) is 27.1 (kJ/mol nm) (or 64.83 kcal/mol Å) (Table 1). As a first-order approximation, we use β_{M_vX} value of 27.2 (kJ/mol nm) (or 65.0 kcal/mol Å) for the zirconolite family (CN = 7). Using the Gibbs free energies of formation of $CaZrTi_2O_7$ and $CaHfTi_2O_7$ phases [15,16], we can calculate the coefficients of a_{M_vX} (= 0.5717) and b_{M_vX} (= −4284.67 kJ/mol, or −1024.06 kcal/mol). The calculated Gibbs free energies of formation of other zirconolite phases are listed in Table 1.

Similarly, we apply the β_{M_vX} value of 13.4 (kJ/mol nm) (or 32.0 kcal/mol Å) obtained for the MO_2 family with fluorite structure (CN of M is 8) to the pyrochlore structure family. The $CaZrTi_2O_7$ phase with a zirconolite structure (CN = 7) is a stable phase under standard conditions [16]. However, the $CaZrTi_2O_7$ phase with the pyrochlore structure (CN = 8) is unstable with respect to the zirconolite structure. The main difference between the zirconolite and pyrochlore with the stoichiometry of $CaMTi_2O_7$ is the coordination number of Zr. The

Table 1
Ionic radii, thermodynamic data for aqueous cations, and predicted standard Gibbs free energies of formation (kJ/mol) at standard condition[a]

M^{4+}	$r_{M^{4+}}$ (nm)	ΔG_s $M^{4+}_{(aq)}$	ΔG_f $M^{4+}_{(aq)}$	ΔG_n $M^{4+}_{(aq)}$	ΔG_f						$\delta\Delta G_f$	$\delta\Delta G_{rx}$
					MO_2 (Exper.)	MO_2 (Calculated)	$MSiO_4$ (Exper.)	$MSiO_4$ (Calculated)	$CaMTi_2O_4$ (Zirconolite)	$CaMTi_2O_4$ (Pyrochlore)	Difference (Pyrochlore)[b]	Pyrochlore formation[c]
Zr	0.079	−1561.09	−589.94	971.15	−1042.78	−1042.69	−1919.79	−1919.79	−5167.36	−5166.02	−24.14	−6.99
Hf	0.078	−1566.53	−656.05	910.48	−1088.22	−1084.66		−1972.04	−4072.54	−4069.82	−60.12	−1.00
Ce	0.094	−1482.10	−503.92	978.18	−1022.57	−1017.88		−1873.34	−4029.02	−4048.40	0.00	−7.66
Th	0.102	−1442.02	−705.09	736.93	−1168.76	−1168.80	−2048.78	−2048.78	−5178.55	−5208.97	−127.24	16.02
U	0.097	−1466.91	−520.49	946.42	−1031.86	−1035.12	−1891.17	−1891.17	−5102.05	−5125.56	−14.14	−4.56
Np	0.095	−1477.04	−502.92	974.12	−1021.82	−1019.26		−1873.97	−4026.31	−4047.06	−1.00	−7.28
Pu	0.093	−1487.20	−480.99	1006.21	−998.01	−1000.44		−1853.14	−4031.74	−4049.74	14.69	−10.42
Am	0.092	−1492.35	−373.21	1119.14	−923.49	−926.13		−1763.60	−4034.46	−4051.07	77.91	−21.51
Po	0.110	−142.48	292.88	1715.36		−539.74		−1238.46	−3996.39	−4032.33	437.52	−48.28

[a] *Note*: Radii of the cations are from Refs. [22,23]. The values of ΔG_f of the cations are from Refs. [28,29], except for Po from Ref. [27]. The values of ΔG_f of MO_2 crystals (except for AmO_2) are from Ref. [28,29]. The ΔG_f of AmO_2 is a mean of the values from Ref. [30] (−962.32 kJ/mol) and Refs. [28,29] (−880.44 kJ/mol), and the value is not used for regression analysis. The coefficients for the fluorite structural family of MO_2 are: $a_{M_vX} = 0.670$, $b_{M_vX} = -1799.20$ (kJ/mol), and $\beta_{M_vX} = 13.4$ (kJ/mol nm). The coefficients for the structural family of zircon $MSiO_4$ are: $a_{M_vX} = 0.8171$, $a_{M_vX} = -2927.59$ (kJ/mol), and $\beta_{M_vX} = 27.1$ (kJ/mol nm). The values of ΔG_f of $MSiO_4$ crystals are from Refs. [31–33].

[b] $\delta\Delta G_f$ is the difference between ΔG_f of Ce-pyrochlore and ΔG_f of other pyrochlore phases.

[c] The reaction energies refer to Eq. (7).

coordination number of M atoms in the zirconolite structure and pyrochlore structure are 7 and 8 respectively. Transmission electron microscopic investigation of synthetic Zr-dominated zirconolite ($CaZrTi_2O_7$) shows that there are sub-micrometer size pyrochlore lamellae in zirconolite [24,25], which may indicate that the Gibbs free energy difference between $CaZrTi_2O_7$ zirconolite and pyrochlore polymorphs is not large. The difference in Gibbs free energies between calcite ($CaCO_3$) and aragonite polymorphs is about 0.9 (kJ/mol) [17]. The difference in Gibbs free energies between Al–Si ordered low-albite (CN of Na atom is 7) and Al–Si disordered high-albite (CN of Na atom is 9) polymorphs is about 8.4 (kJ/mol) [26].

However, the contribution from Al–Si ordering in tetrahedra sites that can be calculated from the Gibbs free energies of formation of Al–Si ordered microcline and Al–Si disordered sanidine is about 6.7 (kJ/mol) [26]. Therefore, the free contribution resulting from the difference in coordination number of low-albite and high albite is about 1.7 (kJ/mol). It is suggested that the Gibbs free energy difference between the zirconolite and pyrochlore structures of $CaZrTi_2O_7$ phase is within the range of 0.8–1.7 kJ/mol. It is proposed here that the Gibbs free energy of formation for Zr-pyrochlore ($CaZrTi_2O_7$) is about 1.3 (kJ/mol) higher than that of Zr-zirconolite ($CaZrTi_2O_7$). Pyrochlore and zirconolite are polymorphs, we can use same a_{M_vX} value for both zirconolite and pyrochlore structural families with the same stoichiometry of $CaMTi_2O_7$. The calculated coefficient b_{M_vX} is −4174.25 (kJ/mol) (or −997.67 kcal/mol). The predicted standard Gibbs free energies of formation for other phases in the pyrochlore family with stoichiometry of $M^{4+}CaTi_2O_7$ are listed in Table 1. Relatively large uncertainties might be embedded in the absolute values of the calculated Gibbs free energies of formation, since there are no measured Gibbs free energies of formation for pyrochlore phases currently available. However, the difference among the pyrochlore phases (e.g., between Ce-pyrochlore and Pu-pyrochlore) should be reliable (Table 1).

Based on the calculated Gibbs free energies of formation of pyrochlore and Gibbs free energies of formation of perovskite and rutile [34], we can calculate the reaction energies ($\delta\Delta G_{rxt}$) of the reaction under room temperature conditions:

$$\underset{\text{perovskite}}{MO_2 + CaTiO_3} + \underset{\text{rutile}}{TiO_2} = \underset{\text{pyrochlore}}{CaMTi_2O_7}. \tag{7}$$

Using all calculated Gibbs free energies of formation for MO_2 phases and pyrochlore phases to eliminate background noise, the Gibbs free energy changes across the reaction ($\delta\Delta G_{rxt}$) are listed in Table 1. The Pu-pyrochlore phase will be stable with respect to PuO_2, $CaTiO_3$, and TiO_2, even at room temperature. In contrast, Th-pyrochlore phase will be unstable with respect to ThO_2, $CaTiO_3$, and TiO_2 at room temperature. The Ce-pyrochlore has been synthesized by sintering oxides of CeO_2, $CaTiO_3$, and TiO_2 [35,36]. As the annealing temperature decreases (from 1300°C to 1140°C), the proportions of Ce-pyrochlore increases by consuming oxides of CeO_2 and $CaTiO_3$ phases [36]. This experimental observation is consistent with our prediction of the negative Gibbs free energy change across reaction (7) for Ce-pyrochlore. The calculation also shows that the Gibbs free energy change in reaction (7) for Pu-pyrochlore (7) is more negative than that of Ce-pyrochlore (Table 1). Therefore, the synthesis of Pu-pyrochlore is thermodynamically feasible.

Because of the lack of measured data, the predicted Gibbs free energies of formation of zirconolite and pyrochlore phases can be considered as a first-order approximation. Nevertheless, the linear free energy relationship provides a useful means to predict the thermodynamic properties of chemical species for which no experimental data are currently available. For instance, the method can be used to predict the standard Gibbs free energies of formation for aqueous species from the known thermodynamic properties of solids in an isostructural family [17,21]. The method can also be used to constrain the thermodynamic properties of fictive mineral phases such as $CaZrTi_2O_7$ and $CaHfTi_2O_7$ phases in pyrochlore family and $CaUTi_2O_7$ and $CaPuTi_2O_7$ phases in zirconolite family. These fictive phases cannot be synthesized in the laboratory or occur in the nature, but their thermodynamic properties are required for the construction of a solid solution model for an actual crystalline phase.

4. Conclusion

The Sverjensky–Molling linear free energy relationship has been used to calculate the Gibbs free energies of formation of pyrochlore and zirconolite phases ($CaMTi_2O_7$) from the known thermodynamic properties of the corresponding aqueous tetravalent cations (M^{4+}). The coefficients for the structural family of zirconolite with the stoichiometry of $M^{2+}ZrTi_2O_7$ are estimated to be: $a_{M_vX} = 0.5717$, $b_{M_vX} = -4284.67$ (kJ/mol), and $\beta_{M_vX} = 27.2$ (kJ/mol nm). The coefficients for the structural family of pyrochlore with the stoichiometry of $M^{2+}ZrTi_2O_7$ are estimated to be: $a_{M_vX} = 0.5717$, $b_{M_vX} = -4174.25$ (kJ/mol), and $\beta_{M_vX} = 13.4$ (kJ/mol nm). Using the linear free energy relationship, the Gibbs free energies of formation of various zirconolite and pyrochlore phases are calculated. Our work has demonstrated that the linear free energy relationship provides a useful means to predict the thermodynamic properties of chemical species for which no experimental data are currently available.

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