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Letter to the Editors

Use of linear free energy relationship to predict Gibbs free energies of formation of zirconolite phases ($MZrTi_2O_7$ and $MHfTi_2O_7$)

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Abstract

In this letter, the Sverjensky–Molling equation derived from a linear free energy relationship is used to calculate the Gibbs free energies of formation of zirconolite crystalline phases ($MZrTi_2O_7$ and $MHfTi_2O_7$) from the known thermodynamic properties of the corresponding aqueous divalent cations (M^{2+}). Sverjensky–Molling equation is expressed as $\Delta G^0_{f,M_vX} = a_{M_vX}\Delta G^0_{n,M^{2+}} + b_{M_vX} + \beta_{M_vX} r_{M^{2+}}$, where the coefficients a_{M_vX}, b_{M_vX}, and β_{M_vX} characterize a particular structural family of M_vX, $r_{M^{2+}}$ is the ionic radius of M^{2+} cation, $\Delta G^0_{f,M_vX}$ is the standard Gibbs free energy of formation of M_vX, and $\Delta G^0_{n,M^{2+}}$ is the standard non-solvation energy of cation M^{2+}. This relationship can be used to predict the Gibbs free energies of formation of various fictive phases (such as $BaZrTi_2O_7$, $SrZrTi_2O_7$, $PbZrTi_2O_7$, etc.) that may form solid solution with $CaZrTi_2O_7$ in actual Synroc-based nuclear waste forms. Based on obtained linear free energy relationships, it is predicted that large cations (e.g., Ba and Ra) prefer to be in perovskite structure, and small cations (e.g., Ca, Zn, and Cd) prefer to be in zirconolite structure. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zirconolite ($CaZrTi_2O_7$, $CaHfTi_2O_7$)-dominated Synroc has been considered as a durable titanate ceramic waste forms for immobilizing high level radioactive wastes including surplus weapons-usable plutonium [1–12]. Zirconolite phases with the stoichiometry of $MZrTi_2O_7$ can be considered as an anion deficient derivative of fluorite type structure, where M represents divalent cations such as Ca coordinated by eight oxygen atoms [13–16]. The existence of large polyhedra (with coordination numbers ranging from 7 to 8) in the structures allows zirconolite to accommodate a wide range of radionuclides (e.g., Pu, U, Ba, Sr, etc.) as well as neutron poisons (e.g., Hf, Gd) [10].

Zirconolite has been subjected to extensive studies during the last two decades [1–18]. However, since most of those studies have been focused on fabrication and structural characterization, the thermodynamic data of zirconolite mineral phases are generally lacking, except for the recent measurement of the Gibbs free energy of formation for $CaZrTi_2O_7$ phase [19,20]. In actual waste forms, due to the presence of various divalent cations, divalent cations such as Ba, Sr, Pb, etc. will substitute for Ca and occur in the form of solid solution in zirconolite. It is reported that small amount of Mn substitutes for Ca in zirconolite, although this substitution is not obvious in natural zirconolite [21,22]. Therefore, thermodynamic properties of these (fictive) phases (such as $BaZrTi_2O_7$, $SrZrTi_2O_7$, $PbZrTi_2O_7$, etc.) are also needed for assessing the behavior of Synroc-based waste forms, optimizing Synroc fabrications, and modeling the interactions between water and waste-loaded zirconolite. The fictive phases cannot be synthesized in the laboratory or occur in the nature, but their thermodynamic

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properties are required for the construction of a solid solution model for an actual crystalline phase. In this letter, we use a linear free energy relationship developed by Sverjensky and Molling to predict the Gibbs free energy of formation for various zirconolite phases from the known thermodynamic properties of the corresponding aqueous divalent cations.

2. Linear free energy relationship

The Hammett linear free energy relationship was established for substituted aqueous organic species and reactions [23–25]. Directly analogoue to the Hammett linear free energy relationship, Sverjensky and Molling developed a linear free energy relationship that can correlate the standard Gibbs free energies of formation of one isostructural family of crystalline phases to those of aqueous cations of a given charge [26,27]. For an isostructural family, the chemical formula of solids may be represented as M_vX, where M is a divalent cation M^{2+}, and X represents the remainder of the composition of solid (for instance, in olivine family, the divalent cation M is Mg, Fe, or Ni, and X is SiO_4; in zirconolite family, divalent M is Ca, Ba, or Sr, and X is $ZrTi_2O_7$). The linear free energy correlation for divalent cations (Sverjensky–Molling equation) derived from Born solvation theory is

$$\Delta G^0_{f,M_vX} = a_{M_vX}\Delta G^0_{n,M^{2+}} + b_{M_vX} + \beta_{M_vX} r_{M^{2+}}. \qquad (1)$$

In this equation, the coefficients a_{M_vX}, b_{M_vX}, and β_{M_vX} characterize a particular crystal family of M_vX, and $r_{M^{2+}}$ is the ionic (Shannon–Prewitt) radius of M^{2+} cation [26,29]. The parameter $\Delta G^0_{f,M_vX}$ is the standard Gibbs free energies of formation of a solid phase, and the parameter $\Delta G^0_{n,M^{2+}}$ is the standard non-solvation energy that is a radius-based correction to the standard Gibbs free energy of formation of the aqueous cation M^{2+} [26]. The parameter $\Delta G^0_{n,M^{2+}}$ can be calculated using

$$\Delta G^0_{n,M^{2+}} = \Delta G^0_{f,M_vX} - \Delta G^0_{s,M^{2+}}, \qquad (2)$$

where $\Delta G^0_{n,M^{2+}}$ represents the standard Gibbs free energy of solvation of aqueous cation that can be calculated from conventional Born solvation coefficients for the aqueous cations [28]. Eq. (1) can be re-arranged as

$$\Delta G^0_{f,M_vX} - \beta_{M_vX} r_{M^{2+}} = a_{M_vX}\Delta G^0_{n,M^{2+}} + b_{M_vX}. \qquad (3)$$

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. The discrepancy between the calculated and measured data is generally within 6 kJ/mol [26,27]. Fig. 1 illustrates the linear free energy relationship of perovskite ($MTiO_3$) family.

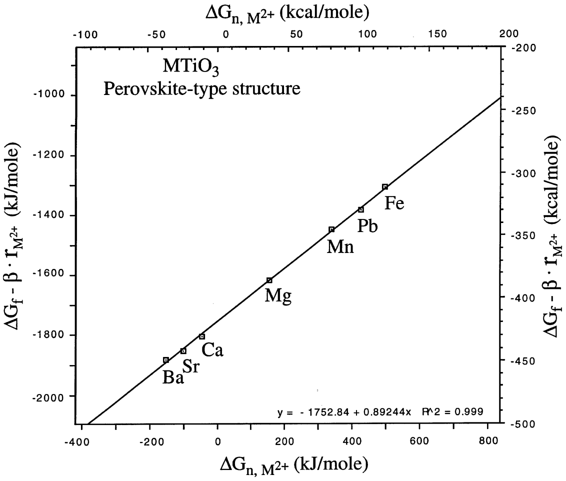

Fig. 1. Linear free energy relationship of Eq. (3) for the isostructural family of $MTiO_3$ perovskite.

3. Application of linear free energy relationship to zirconolite phases

For the isostructural family of $MZrTi_2O_7$, the Gibbs free energy of formation has been determined only for $CaZrTi_2O_7$ phase [19,20]. In order to apply the above linear free energy relationship, the coefficients a_{M_vX}, and β_{M_vX} need to be estimated independently. Based on the results from other oxides and silicates

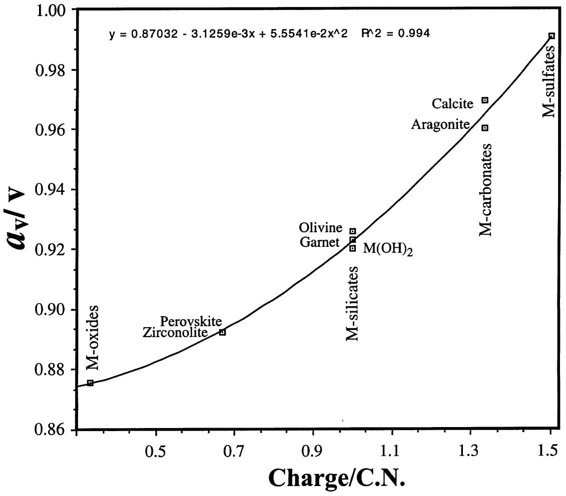

Fig. 2. A relationship for coefficient a_{M_vX} and the ratio between charge and coordination number (CN) of the oxy-anions in sulfate, carbonate, and silicate structural families. The data are from Refs. [26,27] except for the perovskite family from Table 1. The charge/CN ratios for oxy-anions in sulfate, carbonate, silicate, hydroxide, and titanate families are 6/4, 4/3, 4/4, 1/1, and 4/6 respectively. The ratio for divalent cation oxides is 2/6.

crystal families, the coefficient a_{M_vX}, or the slope of Eq. (3) is only related to the stoichiometry of solids. The slopes for all polymorphs of composition M_vX are same within experimental error [26,27]. Based on the known values of a_{M_vX} for carbonate, sulfate, hydroxide, and silicate families, the coefficient a_{M_vX} is related to the ratio between the charge of S, C, or Si and their coordination numbers (CN) or the nearest neighbor of the oxy-anions of SO_4^2 (sulfate), CO_3^2 (carbonate), titanates (TiO_6^{2-}), OH^- (hydroxide) and SiO_4^4 (silicate) (Fig. 2). High ratio of charge/CN may hint strong interaction between the divalent cation and oxy-anions. The value of a_{M_vX} for zirconolite calculated from this relation is 0.89 (Fig. 2). It is estimated that the error of a_{M_vX} is about 0.01. The error of predicted Gibbs free energy of formation resulting from the error of a_{M_vX} is within 4 kJ/mol.

The coefficient β_{M_vX} is related to structure or nearest neighbor environment of the cation. The cation with higher coordination numbers (CN) will have lower value of β_{M_vX} [26]. The β_{M_vX} value for calcite family (CN = 6), aragonite family (CN = 9), and perovskite family (CN = 12) are 33.68 kJ/mol nm (or, 80.5 kcal/mol Å), 27.87 kJ/mol nm (or, 66.6 kcal/mol Å) [26], and 22.59 kJ/mol nm (or, 54 kcal/mol Å) (Table 1), respectively. The β_{M_vX} value for zirconolite family (CN = 8) should be higher than that for perovskite and aragonite families, and lower than that for calcite family. It is estimated that the β_{M_vX} value for zirconolite is 29.29 kJ/mol nm (or, 70 kcal/mol Å). The error resulting from estimated β_{M_vX} coefficient is 8 kJ/mol. The total error resulting from the estimated coefficients is within 12 kJ/mol. Using the Gibbs free energy of formation for zirconolite ($CaZrTi_2O_7$) [19,20], we can calculate the coefficient (i.e., intercept) b_{M_vX} of the Eq. (3) for M $ZrTi_2O_7$ family. The calculated b_{M_vX} value is −3767.11 kJ/mol (or, −900.36 kcal/mol). The predicted standard Gibbs free energies of formation for other phases in the zirconolite ($M^{2+}ZrTi_2O_7$) family are listed in Table 1.

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

M^{2+}	$r_{M^{2+}}$ (nm)	$M^{2+}_{(aq)}$			ΔG_f			
		ΔG_s	ΔG_f	ΔG_n	Perovskite (exper.)	Perovskite (calc.)	$MZrTi_2O_7$ (zirconolinte)	$MHfTi_2O_7$ (zirconolite)
Be	0.045	−732.28	−375.72	356.56		−1333.00	−3318.00	−3355.00
Mg	0.072	−610.03	−455.34	154.68	−1451.07	−1452.00	−3419.00	−3456.00
Ca	0.100	−507.44	−552.79	−45.35	−1575.25	−1567.00	−3515.00	−3552.00
Mn	0.082	−570.95	−230.96	339.99	−1258.46	−1264.00	−3224.00	−3262.00
Fe	0.077	−590.11	−91.50	498.61	−1130.85	−1134.00	−3098.00	−3135.00
Co	0.0735	−603.96	−54.39	549.57		−1096.00	−3063.00	−3100.00
Ni	0.070	−618.19	−45.61	572.58		−1084.00	−3052.00	−3090.00
Cu	0.073	−605.97	65.06	671.03		−989.00	−2956.00	−2993.00
Zn	0.0745	−599.57	−147.15	452.42		−1181.00	−3146.00	−3184.00
Sr	0.116	−457.31	−559.48	−102.17	−1587.31	−1582.00	−3518.00	−3556.00
Cd	0.095	−524.30	−77.70	446.60		−1140.00	−3091.00	−3129.00
Sn	0.111	−472.42	−27.74	444.68		−1105.00	−3046.00	−3084.00
Ba	0.136	−401.62	−555.34	−153.72	−1572.44	−1583.00	−3506.00	−3543.00
Eu	0.117	−454.34	−540.15	−85.81		−1565.00	−3501.00	−3538.00
Hg	0.102	−500.87	164.68	665.55		−928.00	−2876.00	−2913.00
Pb	0.118	−451.41	−24.23	427.19	−1111.85	−1105.00	−3041.00	−3079.00
Ra	0.139	−393.88	−561.49	−167.61		−1588.00	−3509.00	−3547.00
UO_2	0.0754	−596.39	−952.70	−356.31		−1900.00	−3863.00	−3901.00
NpO_2	0.073	−621.74	−795.80	−174.05		−1743.00	−3708.00	−3746.00
PuO_2	0.071	−630.07	−767.76	−137.70		−1715.00	−3682.00	−3719.00
AmO_2	0.070	−634.29	−655.63	−21.34		−1614.00	−3581.00	−3618.00
Pd	0.080	−593.58	177.78	771.36		−884.00	−2846.00	−2884.00
Pt	0.080	−593.58	229.28	822.87		−838.00	−2800.00	−2838.00

[a] *Note*: Radii of the cations are from references of [26] and [29]. Radii of NpO_2^{2+}, PuO_2^{2+}, and AmO_2^{2+} are calculated from the radius difference between U^{6+} and Np^{6+} (or Pu^{6+}, Am^{6+}). The values of ΔG_f of the cations are from Refs. [28,30] except for NpO_2^{2+} from Refs. [31,32], and PuO_2^{2+} and AmO_2^{2+} from Ref. [33]. The coefficients for the perovskite family are calculated using Eq. (3) and the values of ΔG_f are from Refs. [34,35]. The coefficients for the structural family of perovskite $M^{2+}TiO_3$ are: $a_{M_vX} = 0.8924$, $b_{M_vX} = -1752.84$ kJ/mol, and $\beta_{M_vX} = 22.59$ kJ/mol nm.

Similarly, we can calculate the value of coefficient b_{M_vX} for the zirconolite $M^{2+}HfTi_2O_7$ family by using same a_{M_vX} and β_{M_vX}, and measured Gibbs free energy of formation for $CaHfTi_2O_7$ phase. The calculated b_{M_vX} value for the zirconolite is −3804.51 kJ/mol (or, −909.30 kcal/mol). The predicted Gibbs free energies for other phases in the zirconolite $M^{2+}HfTi_2O_7$ family are also listed in Table 1. In addition, because the structure of zirconolite is considered as a modified structure of pyrochlore, we have also applied the linear free energy relationship to the pyrochlore family (e.g., $Gd_2Ti_2O_7$,and $CaCeTi_2O_7$), and the result will be reported elsewhere.

Using the obtained linear free energy relationships for $MTiO_3$ perovskite and $MZrTi_2O_7$ zirconolite, we can illustrate the effect of cations on the reaction energy (ΔG_{rxt}) of the reaction

$$\underset{\text{Perovskite}}{M^{2+}TiO_3} + \underset{\text{Rutile}}{TiO_2} + \underset{\text{Zirconia}}{ZrO_2} = \underset{\text{Zirconolite}}{MZrTi_2O_7}. \tag{4}$$

According to the illustrated relationship (Fig. 3) for reaction (4), large cations (e.g., Ba, and Ra) prefer to be in perovskite structure, and small cations (e.g., Ca, Zn, and Cd) prefer to be in zirconolite structure. Divalent oxycation UO_2^{2+} prefers to be in zirconolite structure. Although the reaction energy calculation of reaction (4) is based on room temperature condition, the above prediction is basically consistent with experimental observation at high temperature.

Because of the lack of sufficient experimental data, the predicted Gibbs free energies of formation of zirconolite phases and fictive phases with zirconolite structure can be considered as a first-order approximation. Nevertheless, we want to emphasize 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. 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 [26].

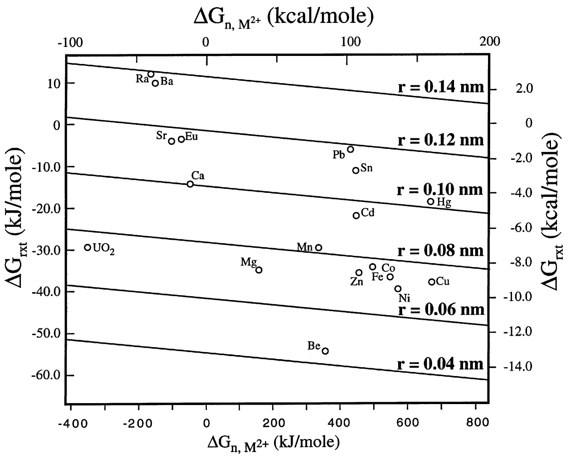

Fig. 3. Effect of cations on the reaction energies of reaction (4). Both non-solvation energy and ionic radii of cations affect the reaction energies.

4. Conclusion

Sverjensky–Molling equation derived from a linear free energy relationship has been used to calculate the Gibbs free energies of formation of zirconolite mineral phases ($MZrTi_2O_7$ and $MHfTi_2O_7$) from the known thermodynamic properties of the corresponding aqueous divalent cations (M^{2+}). The coefficients for the structural family of zirconolite with the stoichiometry of $M^{2+}ZrTi_2O_7$ are estimated to be: $a_{M_vX} = 0.89$, $b_{M_vX} = -3767.11$ kJ/mol, and $\beta_{M_vX} = 29.29$ kJ/mol nm. Using the linear free energy relationship, the Gibbs free energies of formation of various zirconolite phases are calculated. In the letter, we also emphasize 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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