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Letter to the Editors

Application of a linear free energy relationship to crystalline solids of MO_2 and $M(OH)_4$

Huifang Xu [a,*], Yifeng Wang [b], Larry L. Barton [c]

[a] *Department of Earth and Planetary Sciences, The University of New Mexico, Albuquerque, NM 87131, USA*
[b] *Sandia National Laboratories, 115 North Main Street, Carlsbad, NM 88220, USA*
[c] *Department of Biology, The University of New Mexico, Albuquerque, NM 87131, USA*

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Abstract

In this letter, a linear free energy relationship developed by Sverjensky and Molling is used to predict the Gibbs free energies of formation of crystalline phases of $M^{4+}O_2$ and $M^{4+}(OH)_4$ from the known thermodynamic properties of aqueous tetravalent cations (M^{4+}). The modified Sverjensky and Molling equation 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+}. By fitting the equation to the existing thermodynamic data, the coefficients in the equation for the MO_2 family minerals are estimated to be: $a_{M_vX} = 0.670$, $\beta_{M_vX} = 32$ (kcal/mol Å), and $b = -430.02$ (kcal/mol). The constrained relationship can be used to predict the standard Gibbs free energies of formation of crystalline phases and fictive phases (i.e., phases which are thermodynamically unstable and do not occur at standard conditions) within the isostructural families of $M^{4+}O_2$ and $M^{4+}(OH)_4$ if the standard Gibbs free energies of formation of the tetravalent cations are known. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The mineral phases (Zr, U, Pu, Np, Am)O_2 with a fluorite structure have been considered as a ceramic waste form to incorporate excess weapons Pu and other radionuclides [1], due to their resistance to radiation damage [2–5]. The solid solution phases of (Th, U)O_2 and (Th, Pu)O_2 have also been proposed as nuclear fuels [6]. Natural minerals such as thorianite, cerianite, and zirconia may contain other tetravalent cations including Sn and Pb. The pure phases of TiO_2, SnO_2 and PbO_2 with a fluorite structure may not occur in nature, and their standard Gibbs free energies of formation are thus is difficult to obtain experimentally. However, as end-members of solid solutions, the thermodynamic properties of these phases are still needed for geochemical modeling of the metal partitioning between solids, or between solids and aqueous solutions. In this letter, we use a linear free energy relationship developed by Sverjensky and Molling to predict the Gibbs free energies of formation for the whole suite of MO_2 and $M(OH)_4$ crystalline phases from the known thermodynamic properties of aqueous tetravalent cations (M^{4+}).

2. Linear free energy relationship and its application

Directly analogous to the well-known Hammett free energy relationship [7,8] which was established for aqueous organic reactions, Sverjensky and Molling [9] developed an empirical linear free energy relationship (Sverjensky–Molling equation) for isostructural families

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[*] Corresponding author.: Tel.: +1 505 277 7536; fax: +1 505 277 8843; e-mail: hfxu@unm.edu

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of inorganic solids based on the relationship between crystalline phases and aqueous cations. The Sverjensky–Molling equation for divalent cations is written as [9]

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

In this equation, the coefficients $a_{\mathrm{M_vX}}$, $b_{\mathrm{M_vX}}$, and $\beta_{\mathrm{M_vX}}$ characterize the particular crystal structure of $\mathrm{M_vX}$, and $r_{\mathrm{M}^{2+}}$ is the ionic (Shannon–Prewitt) radius of the M^{2+} cation [9,10]. The parameter $\Delta G^0_{\mathrm{f},\mathrm{M_vX}}$ is the standard Gibbs free energies of formation of the endmember solids, and the parameter $\Delta G^0_{\mathrm{n},\mathrm{M}^{2+}}$ is standard non-solvation energy from a radius-based correction to the standard Gibbs free energy of formation of the aqueous cation M^{2+} [9,11]. One major contribution of Sverjensky and Molling is to split the solvation energy ($\Delta G_{\mathrm{s},\mathrm{M}^{2+}}$) and non-solvation energy ($\Delta G^0_{\mathrm{n},\mathrm{M}^{2+}}$) from standard Gibbs free energy of formation of cations ($\Delta G_{\mathrm{f},\mathrm{M}^{2+}}$). The coefficient $a_{\mathrm{M_vX}}$ characterizes the interaction between divalent cation and the remainder anion and complex anion. The non-solvation (not Gibbs free energies of formation) energies of cations directly contribute to Gibbs free energy of the crystalline phases containing the cations. Values of the coefficient $a_{\mathrm{M_vX}}$ are very close for all polymorphs of the composition $\mathrm{M_vX}$ [9], The coefficient $\beta_{\mathrm{M_vX}}$ is related to the effect of nearest neighbors (or coordination number: CN) of the cation [9]. In polymorphs, the structure family with small CN (e.g., CN = 6 in calcite structure family) has higher value of $\beta_{\mathrm{M_vX}}$ than the family with big CN (e.g., CN = 9 in aragonite structure family) does [9]. In this communication, we present a parallel application of Sverjensky–Molling equation to tetravalent cations. Following the procedures of Sverjensky and Molling [9], an isostructural family with tetravalent cations (M^{4+}), the chemical formula of solids may be represented as $\mathrm{M_vX}$, where M is a tetravalent cation M^{4+}, and X represents the remainder of the composition of solid (for instance, in $\mathrm{MO_2}$ solids with fluorite structure, the tetravalent cation M is Hf, Th, Ce, U, and X is $\mathrm{O_2}$; in $\mathrm{M(OH)_4}$ solids, X is $\mathrm{(OH)_4}$). The linear free energy correlation can be expressed as

$$\Delta G^0_{\mathrm{f},\mathrm{M_vX}} = a_{\mathrm{M_vX}} \Delta G^0_{\mathrm{n},\mathrm{M}^{4+}} + b_{\mathrm{M_vX}} + \beta_{\mathrm{M_vX}} r_{\mathrm{M}^{4+}}. \tag{2}$$

In this equation, the coefficients $a_{\mathrm{M_vX}}$, $b_{\mathrm{M_vX}}$, and $\beta_{\mathrm{M_vX}}$ characterize the particular crystal of $\mathrm{M_vX}$, and $r_{\mathrm{M}^{4+}}$ is the ionic (Shannon–Prewitt) radius of the M^{4+} cation [9,11]. The parameter $\Delta G^0_{\mathrm{f},\mathrm{M_vX}}$ is the standard Gibbs free energies of formation of the endmember solids, and the parameter $\Delta G^0_{\mathrm{n},\mathrm{M}^{4+}}$ is standard non-solvation energy from a radius-based correction to the standard Gibbs free energy of formation of the aqueous tetravalent cation M^{4+} [11]. The parameter $\Delta G^0_{\mathrm{n},\mathrm{M}^{4+}}$ can be calculated using the equation

$$\Delta G^0_{\mathrm{f},\mathrm{M_vX}} = \Delta G^0_{\mathrm{n},\mathrm{M}^{4+}} + \Delta G^0_{\mathrm{s},\mathrm{M}^{4+}}, \tag{3}$$

where $\Delta G^0_{\mathrm{s},\mathrm{M}^{4+}}$ is the standard Gibbs free energy of solvation of tetravalent aqueous cation that can be calculated from conventional Born solvation coefficients for the aqueous cations [11] according to the equation

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

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

$$\omega_{\mathrm{M}^{4+}} = \omega^{\mathrm{abs}}_{\mathrm{M}^{4+}} - 4\omega^{\mathrm{abs}}_{\mathrm{H}^{+}}. \tag{5}$$

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

$$\omega^{\mathrm{abs}}_{\mathrm{M}^{4+}} = 166.027 * 4^2/(r_{\mathrm{e},\mathrm{M}^{4+}}), \tag{6}$$

Table 1

Ionic radii, thermodynamic data for aqueous cations, and predicted standard Gibbs free energies of formation

M^{4+}	$r_{\mathrm{M}^{4+}}$ (Å)	ΔG_s $\mathrm{M}^{4+}_{\mathrm{(aq)}}$	ΔG_f $\mathrm{M}^{4+}_{\mathrm{(aq)}}$	ΔG_n $\mathrm{M}^{4+}_{\mathrm{(aq)}}$	ΔG_f			
					$\mathrm{MO_2}$ (Experimental)	$\mathrm{MO_2}$ (Calculated)	$\mathrm{M(OH)_4}$ (Experimental)	$\mathrm{M(OH)_4}$ (Calculated)
Zr	0.79	−373.11	−141.00	232.11	−249.23	−249.21	−370.00	−370.14
Hf	0.78	−374.41	−156.80	217.61	−260.09	−259.24		−382.93
Ce	0.94	−354.23	−120.44	233.79	−244.40	−243.28		−346.62
Th	1.02	−344.65	−168.52	176.13	−279.34	−279.35	−379.00	−379.76
U	0.97	−350.60	−124.40	226.20	−246.62	−247.40	−351.00	−348.10
Np	0.95	−353.02	−120.20	232.82	−244.22	−243.61	−346.60	−345.90
Pu	0.93	−355.45	−114.96	240.49	−238.53	−239.11	−340.0	−342.88
Am	0.92	−356.68	−89.20	267.48	−220.72 [a]	−221.39		−323.31
Po	1.06	−339.98	70.00	409.98		−121.39		−191.44

[a] Radii of the cations are from Refs. [10,11]. The values of ΔG_f of the cations are from Refs. [12,13], except for Pb from Ref. [14], and Po from reference [15]. The values of ΔG_f of $\mathrm{MO_2}$ crystals (except for $\mathrm{AmO_2}$) are from Refs. [12,13]. The ΔG_f of $\mathrm{AmO_2}$ is a mean of the values from Ref. [14] (−230.00 kcal/mol) and Refs. [12,13] (−210.43 kcal/mol), and the value is not used for regression analysis. The values of ΔG_f of $\mathrm{M(OH)_4}$ crystals (except for $\mathrm{Zr(OH)_4}$) are from Ref. [14]. The ΔG_f of $\mathrm{Zr(OH)_4}$ is from Ref. [16].

$$r_{e,M^{4+}} = r_{M^{4+}} + 4(0.94). \quad (7)$$

The standard solvation energy and non-solvation energy can be calculated based on above equations, and are listed in Table 1. Based on experimental Gibbs free energies of formation for the fluorite phases of ZrO_2, HfO_2, CeO_2, ThO_2, UO_2, NpO_2, and PuO_2, the regression coefficients for the Eq. (1) are: $a_{M_vX} = 0.670$, $\beta_{M_vX} = 32$ (kcal/mol Å), and $b = -430.02$ (kcal/mol). The calculated Gibbs free energies of formation are also listed in Table 1. The discrepancy between calculated and experimental free energies is less than 1.1 kcal/mol (Fig. 1). Only the data for AmO_2 was not used for the regression analysis, because the value from Refs. [12,14] are −210.43 kcal/mol and −233.00 kcal/mol. Table 1 lists the mean of these two values. This mean value (−220.72 kcal/mol) is very close to the calculated value (−221.39 kcal/mol). The standard Gibbs free energies of formation for PoO_2 phase with fluorite structure are also calculated (Table 1).

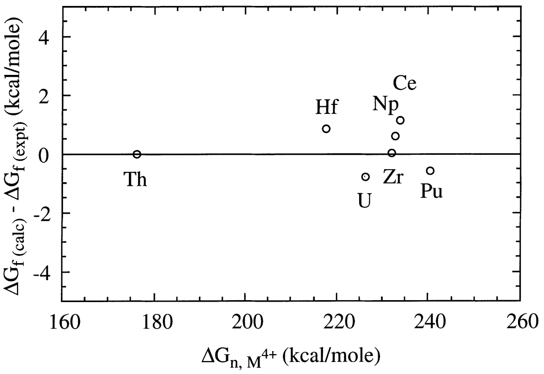

Fig. 1. The difference between calculated and experimental values of the standard Gibbs free energies of formation of the crystalline solids of MO_2 with fluorite structure.

The Eq. (2) can be re-arranged as

$$\Delta G^0_{f,M_vX} - \beta_{M_vX} r_{M^{4+}} = a_{M_vX} \Delta G_{n,M^{4+}} + b_{M_vX}. \quad (8)$$

The linear free energy correlation can be expressed as Eq. (8), and this linear relationship is illustrated in Fig. 2. Because values of the coefficient a_{M_vX} are very close for all polymorphs of the composition M_vX [9], we predict a_{M_vX} value for rutile isostructural family is similar to that for the fluorite structural family (i.e., ~0.67). It is suggested that the value of β_{M_vX} for the rutile phases should be larger than that for the fluorite phases, because the cation coordination number in rutile phases is smaller than that in the fluorite phase [9].

Similarly, we can calculate the coefficients of the Eq. (1) for the $M(OH)_4$ phases. The coefficients from the regression analysis are: $a_{M_vX} = 0.780$, $\beta_{M_vX} = 148$ (kcal/mol Å), and $b = -668.10$ (kcal/mol). The calculated standard Gibbs free energies for other $M(OH)_4$ phases are also listed in Table 1.

The above predictions of thermodynamic properties can be considered as first-order approximations and yet need to be confirmed by experiments. Nevertheless, we believe that Sverjensky–Molling linear free energy relationship provides a useful tool for predicting unknown thermodynamic properties from a limited number of currently available thermodynamic data, such as ceramic waste forms of Pu- and Np-bearing zircon ($M^{4+}SiO_4$) phases and zirconolite ($CaM^{4+}Ti_2O_7$) phases.

3. Conclusion

Sverjensky–Molling linear free energy relationship has been used to calculate the Gibbs free energies of formation of MO_2 and $M(OH)_4$ phases from the known thermodynamic properties of the corresponding aqueous cations (M^{4+}). The coefficients for the structural family of MO_2 with fluorite structure are: $a_{M_vX} = 0.670$,

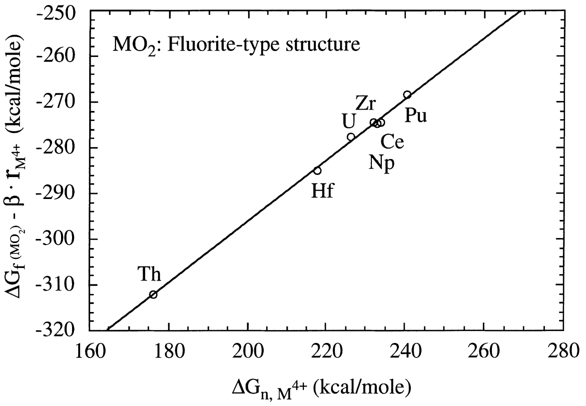

Fig. 2. The diagram showing the linear relationship of the Eq. (8) for the crystalline phases of MO_2 with fluorite structure.

$\beta_{\mathrm{M_vX}} = 32$ (kcal/mol Å), and $b_{\mathrm{M_vX}} = -430.02$ (kcal/mol). The coefficients for the $\mathrm{M(OH)_4}$ family phases are: $a_{\mathrm{M_vX}} = 0.780$, $\beta_{\mathrm{M_vX}} = 148$ (kcal/mol Å), and $b_{\mathrm{M_vX}} = -668.10$ (kcal/mol). Using the linear free energy relationship, the Gibbs free energies of formation of various $\mathrm{MO_2}$ and $\mathrm{M(OH)_4}$ phases are calculated. Sverjensky–Molling linear free energy relationship provides a useful tool for predicting unknown thermodynamic properties from a limited number of currently available thermodynamic data.

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