

Linear free energy relationship applied to trivalent cations with lanthanum and actinium oxide and hydroxide structure

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Abstract

Linear free energy relationships for trivalent cations with crystalline M_2O_3 and, $M(OH)_3$ phases of lanthanides and actinides were developed from known thermodynamic properties of the aqueous trivalent cations, modifying the Sverjensky and Molling equation. The linear free energy relationship for trivalent cations is as $\Delta G_{f,MvX}^0 = a_{MvX} \Delta G_{n,M^{3+}}^0 + b_{MvX} + \beta_{MvX} r_{M^{3+}}$, where the coefficients a_{MvX} , b_{MvX} , and β_{MvX} characterize a particular structural family of MvX , $r_{M^{3+}}$ is the ionic radius of M^{3+} cation, $\Delta G_{f,MvX}^0$ is the standard Gibbs free energy of formation of MvX and $\Delta G_{n,M^{3+}}^0$ is the standard non-solvation free energy of the cation. The coefficients for the oxide family are: $a_{MvX} = 0.2705$, $b_{MvX} = -1984.75$ (kJ/mol), and $\beta_{MvX} = 197.24$ (kJ/mol nm). The coefficients for the hydroxide family are: $a_{MvX} = 0.1587$, $b_{MvX} = -1474.09$ (kJ/mol), and $\beta_{MvX} = 791.70$ (kJ/mol nm).

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1. Introduction

The crystalline oxide, and hydroxide phases of lanthanides (lanthanum (La) to lutetium (Lu)), are useful and increasingly being considered for trace element removal in water and waste-water treatment systems. The lanthanides are chemically very similar to each other, show similar crystal-chemical and solution-chemical properties, and most often form ionic compounds with other trivalent cations. Roughly one fourth of the production of lanthanides is used as metal alloys. The pure metals have

little use in their own right, but alloys (known as mischmetals) have sufficiently strong reducing power for metallurgical applications. Mischmetal is an excellent scavenger for oxyanions (nitrate, sulfate, carbonate, arsenate, selenate) in aqueous solution. They form bidentate surface complexes with oxyanions with high coordination numbers that reduce their toxicity. Mischmetal adds high-temperature strength to aluminum, have high strength and creep resistance at 450–600 °F to be useful in jet engine parts. Recently LA: a mixture of 10% lanthanum oxide and 90% activated alumina has been proved to be a better adsorbent than activated alumina alone for selenium removal from synthetic solutions and waste-water. The University of Nevada Reno has been granted a patent protection on using LA as an adsorbent for waste-water

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remediation. LA will compete with SORBPLUS, a mixed metal oxide developed by ALCOA as an adsorbent for several metals from aqueous streams.

Standard Gibbs free energies of formation of the oxide and hydroxide phases of lanthanides are often required as end-members of solid solutions (co-precipitation of the sorbate metal hydroxide phase with the original metal oxide surface phase), for geochemical modeling of the trace element partitioning between solids, or between solids and aqueous solutions. As a solid surface is loaded with sorbed ions, for example, trivalent metal ion M^{3+} onto hydrous lanthanum oxide surfaces (HLO, with a nominal formula of $La(OH)_3$; a surface precipitate is formed as a solid solution of $La(OH)_3-M(OH)_3$. Surface precipitation starts at low sorbate/sorbent ratios and becomes the dominant sorption mechanism at high sorbate/sorbent ratios. In solid solution models activity of the co-precipitating solid metal hydroxide ($M(OH)_3$) phase increases from near zero to unity as the amount of surface precipitate increases (an ideal solid solution formation). At lower coverage the lower activities of the metal hydroxide phases allow solubility product for onset of precipitation of the metal hydroxide to remain lower than the precipitation of the pure solid [2]. Because the solubility of the solid solution component $M(OH)_3(s)$ is far lower than the bulk $M(OH)_3(s)$ [1] surface precipitation starts at an aqueous concentration of M^{3+} much lower than that for pure $M(OH)_3(s)$. With increasing aqueous M^{3+} concentrations saturation with respect to bulk $M(OH)_3$ is approached. Precipitation constants of the ‘fictitious’ pure $M(OH)_3(s)$ solid solution phases are difficult to obtain experimentally. Other studies have found the surface precipitation constants to parallel the precipitation constants of the pure $M(OH)_3(s)$ with the structure of the surface phase [3]. Linear free energy relationship has been successfully applied to obtain standard state Gibbs free energy of formation (ΔG_f^0) of surface precipitates of divalent cations on HFO, calcite and other solids [3,4].

Intensive chemical studies have shown that the elements, with atomic numbers 89–103 (actinium (Ac) through lawrencium (Lw)) or the actinides resemble the lanthanides in all characteristics that the similarities become increasingly striking with increase in atomic number. Many of the actinides are almost indistinguishable from lanthanides in their reactions. Only the lightest of these elements exist in nature and the others must be obtained synthetically, and such processes may yield only a few

atoms of product. The heavy elements do resemble the lanthanides very closely and the known chemistry of the lanthanides proves invaluable in predicting the chemistry of the actinides. As the atomic number increases, the stability of the tri-positive state of actinides increases and parallels with the lanthanides, that the known properties of the latter can be used to predict quite exactly the properties of the comparable actinides including their free energy of formation. No reliable free energy of formation data is presently available for actinides.

In this letter, a linear correlation relationship for the Gibbs free energies of formation of thirteen trivalent cations with crystalline oxide (M_2O_3) and hydroxide ($M(OH)_3$) structure of lanthanum and actinium were developed using the known thermodynamic properties such as the ionic radii [5,6] and the standard state Gibbs free energy of formation [7,8] of the aqueous trivalent cations (M^{3+}) modifying the linear free energy relationship developed for divalent cations by Sverjensky and Molling [4]. The results are applicable to all trivalent cations with lanthanum and actinium oxide and hydroxide structure. The currently available experimentally derived formation energies are less useful since the formation energies of metal alloys and solid solutions of these ions are often required.

2. The linear free energy relationship

Sverjensky and Molling [4] developed an empirical free energy relationship (Sverjensky–Molling equation) for isostructural families of inorganic solids using the relationship between crystalline phases and the respective aqueous cations, directly analogous to the well-known Hammett free energy relationship [9,10], applied to aqueous organic reactions. The procedures of Sverjensky and Molling were followed for the iso-structural family of trivalent cations with lanthanum and actinium oxide and hydroxide structure in this application. The chemical formula of solids was represented as MvX , where M is a trivalent cation M^{3+} , and X is the remainder of the composition of solids (for instance, in M_2O_3 , the trivalent cation M is La, Ce, Pu, etc. and X is O_3 ; in $M(OH)_3$ solids, X is $(OH)_3$). The original Sverjensky–Molling linear free energy correlation was modified for trivalent cations as

$$\Delta G_{f,MvX}^0 = a_{MvX} \Delta G_{n,M^{3+}}^0 + b_{MvX} + \beta_{MvX} r_{M^{3+}}, \quad (1)$$

where the coefficients a_{MvX} , b_{MvX} , and, β_{MvX} are characteristic of the particular crystal structure represented by MvX , and, $r_{M^{3+}}$ is the Shannon–Prewitt radius of the M^{3+} cation in a given coordination state [4]. β_{MvX} is a coefficient related to the coordination number (CN) of the cation. In polymorphs, the structure family with smaller CN has higher value of β_{MvX} than the family with higher CN [4]. The parameter $\Delta G_{f,MvX}^0$ is the standard Gibbs free energies of formation of the end member solids, and the parameter, $\Delta G_{n,M^{3+}}^0$ is the standard Gibbs free energy of non-solvation based on a radius-based correction to the standard Gibbs free energy of formation of the aqueous cation M^{3+} . The standard Gibbs free energy of non-solvation directly contributes to the standard Gibbs free energy of the crystalline phases containing the cation not the standard Gibbs free energy of solvation ($\Delta G_{S,M^{3+}}^0$) of the trivalent cation or the Gibbs free energy of formation ($\Delta G_{f,M^{3+}}^0$) of the cation. The $\Delta G_{n,M^{3+}}^0$ and $\Delta G_{S,M^{3+}}^0$ were separated from $\Delta G_{f,M^{3+}}^0$ as [4]

$$\Delta G_{f,M^{3+}}^0 = \Delta G_{n,M^{3+}}^0 + \Delta G_{S,M^{3+}}^0, \quad (2)$$

where $\Delta G_{S,M^{3+}}^0$ were calculated using the conventional Born solvation Eq. (4) for the aqueous cation M^{3+} as

$$\Delta G_{S,M^{3+}}^0 = \omega_{M^{3+}} * ((1/\varepsilon) - 1), \quad (3)$$

where ε is the dielectric constant of water (78.47 at 25 °C) and parameter $\omega_{M^{3+}}$ are conventional Born solvation coefficients for the trivalent cations. $\omega_{M^{3+}}$ were calculated using the equation

$$\omega_{M^{3+}} = \omega_{M^{3+}}^{\text{abs}} + \omega_{H^+}^{\text{abs}}, \quad (4)$$

where $\omega_{M^{3+}}^{\text{abs}}$ and $\omega_{H^+}^{\text{abs}}$ are the absolute Born solvation coefficient of trivalent cation and the absolute Born solvation coefficient of H^+ ion (225.39 kJ/mol), respectively. The $\omega_{M^{3+}}^{\text{abs}}$ are related to the effective electrostatic radii ($r_{e,M^{3+}}$) of the aqueous cations by

$$\omega_{M^{3+}}^{\text{abs}} = 694.657 * 3^2 / (r_{e,M^{3+}}), \quad (5)$$

where the effective electrostatic radii ($r_{e,M^{3+}}$) of the aqueous cation can be calculated from its crystallographic radii ($r_{M^{3+}}$) as

$$r_{e,M^{3+}} = r_{M^{3+}} + (3 * 0.94). \quad (6)$$

3. Application of the linear free energy relationship

The standard non-solvation and solvation energies were calculated using the above equations for eighteen trivalent cations ($Z = 3$), and are shown in Table 1. Eq. (1) was used to regress the free

Table 1

Ionic radii, thermodynamic data for aqueous cations and, calculated standard Gibbs free energies of formation at standard conditions (298.15 K and 1 atm)

M^{3+}	$a_{r_{M^{3+}}}$ (nm)	$\Delta G_{S,M^{3+}}^0$ (kJ/mol)	$b_{G_{f,M^{3+}}^0}$ (kJ/mol)	$\Delta G_{n,M^{3+}}^0$ (kJ/mol)	${}^c \Delta G_{f,M_2O_3}^0$ (kJ/mol) (Experiment)	${}^d \Delta G_{f,M_2O_3}^0$ (kJ/mol) (Calculated)	${}^c \Delta G_{f,M(OH)_3}^0$ (kJ/mol) (Experiment)	${}^d \Delta G_{f,M(OH)_3}^0$ (kJ/mol) (Calculated)
Dy ³⁺	0.0908	-1452.91	-665.70	787.21	-1772.69	-1753.90	-1286.18	-1279.79
Er ³⁺	0.0881	-1454.88	-669.47	785.41	-1809.95	-1754.92	-1275.81	-1279.41
Tm ³⁺	0.0870	-1455.68	-662.35	793.33	-1795.72	-1752.99	-1288.70	-1279.96
Lu ³⁺	0.0850	-1457.14	-628.02	829.12	-1790.28	-1743.71	-1257.30	-1283.03
Ho ³⁺	0.0894	-1453.93	-674.07	779.85	-1792.37	-1756.17	-1298.33	-1271.73
La ³⁺	0.1061	-1441.82	-684.12	757.70	-1706.96	-1758.87	-1280.32	-1267.16
Nd ³⁺	0.0995	-1446.59	-671.98	774.61	-1722.03	-1755.59	-1277.81	-1273.79
Ce ³⁺	0.1034	-1443.77	-672.40	771.37	-1707.38	-1755.70	-1271.11	-1268.14
Pr ³⁺	0.1013	-1445.29	-679.52	765.77	-1720.77	-1757.63	-1285.77	-1267.01
Gd ³⁺	0.0938	-1450.73	-661.51	789.21	-1754.27	-1752.77	-1284.93	-1273.93
Sm ³⁺	0.0964	-1448.84	-666.96	781.88	-1735.85	-1754.24	-1284.93	-1269.71
Tb ³⁺	0.0923	-1451.82	-652.30	799.51	-1779.39	-1750.28	-1270.28	-1248.95
Yb ³⁺	0.0930	-1451.31	-644.35	806.96	-1727.89	-1748.12	-1272.37	-1254.21
Eu ³⁺	0.0950	-1449.85	-574.43	875.42	-	-1729.21	-	-1274.23
Am ³⁺	0.1070	-1437.94	-599.51	841.66	-	-1735.97	-	-1269.13
Np ³⁺	0.1100	-1435.42	-517.45	921.57	-	-1713.77	-	-1248.07
U ³⁺	0.1165	-1434.71	-476.50	957.85	-	-1702.67	-	-1245.05
Pu ³⁺	0.1080	-1436.14	-578.41	862.05	-	-1730.26	-	-1255.01

^a Cationic radii are from Refs. [5,6].

^b Values of ΔG_f of the cations are from Refs. [7,8].

^c The values of the experimental ΔG_f of the M_2O_3 and $M(OH)_3$ crystals are from Refs. [7,8].

^d The calculated ΔG_f values are from Eq. (1).

energies of the solids belonging to the isostructural families of oxides, and, hydroxides along with the values of ionic radii of cations and the experimental free energies of formation of the cations. Eq. (1) closely fitted ($R^2 = 1$) the calculated with the experimental standard Gibbs free energies of formation of the isostructural families of oxide and hydroxide solids. Based on experimental Gibbs free energies of formation of oxide phases of thirteen trivalent cations, the regression coefficients for Eq. (1) are: $a_{MvX} = 0.2705$, $b_{MvX} = -1984.75 \text{ kJ mol}^{-1}$, and $\beta_{MvX} = 197.24 \text{ kJ mol}^{-1} \text{ nm}$. The calculated Gibbs free energies of formation are also listed in Table 1. The regression coefficients for the hydroxide phases using Eq. (1) based on thirteen cations are: $a_{MvX} = 0.1587$, $b_{MvX} = -1474.09 \text{ kJ mol}^{-1}$, and $\beta_{MvX} = 791.70 \text{ kJ mol}^{-1} \text{ nm}$. The standard Gibbs free energies of formation for the hydroxide phases were also calculated and shown in Table 1. Eq. (1) was rearranged for plotting reasons as follows:

$$\Delta G_{f,MvX}^0 - \beta_{MvX} r_{M^{3+}} = a_{MvX} \Delta G_{n,M^{3+}}^0 + b_{MvX}. \quad (7)$$

The linear free energy correlation expressed as a rearranged Eq. (1) is shown for oxides in Fig. 1. The lanthanide ion Eu^{3+} was excluded from the analysis. Since Eu^{2+} is the weakest reducing agent of the elemental lanthanides does not readily oxidize to the tri positive state (Eu^{3+}) in aqueous solutions. The currently available free energy of formation data Eu^{3+} ion is not reliable.

The discrepancy between experimental and calculated free energies for oxides was within $\pm 3.0\%$ of the experimental free energies (Fig. 2). The discrepancy between experimental and calculated free energies for hydroxides, was within $\pm 2.0\%$ of the

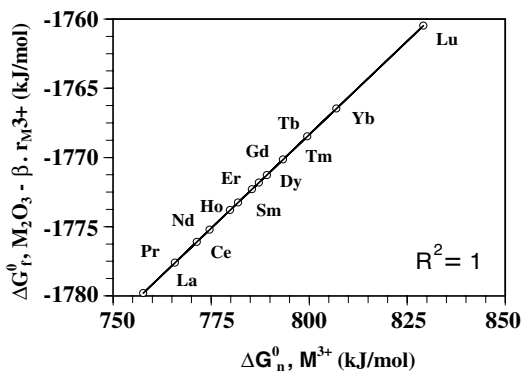


Fig. 1. Linear free energy relationship based on Eq. (1) for the crystalline phases of M_2O_3 with lanthanum oxide structure.

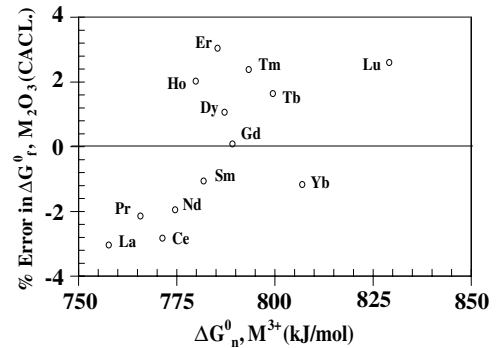


Fig. 2. The difference between calculated and experimental values of the standard Gibbs free energies of formation of the crystalline solids of M_2O_3 with Lanthanum oxide structure.

experimental free energies. The Sverjensky–Molling equation is a useful tool to calculate linear free energy of formation of solids of pure and solid-solution phases of trivalent cations with lanthanum and actinium oxide and hydroxide structure whenever the formation energies of the cations forming the solids are known. The standard Gibbs free energies of formation of solids thus calculated are first-order approximations and need confirmation by experiments [11].

4. Conclusion

The Gibbs free energies of formation of trivalent cations with lanthanum and actinium oxide and hydroxide structure were computed from the known thermodynamic properties of thirteen trivalent aqueous cations (M^{3+}) using the Sverjensky–Molling equation. The calculated free energies of formation of the oxides are within 3.0% of the experimental free energies and that of the hydroxides are within 2.0% of the experimental free energies. The equation fits the experimental data very closely with $R^2 = 1$. Sverjensky–Molling relationship is useful in predicting unknown thermodynamic properties for metal partitioning for which no experimental data are available.

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