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REVIEW OF THE SYNTHESIS OF LAYERED DOUBLE HYDROXIDES: A THERMODYNAMIC APPROACH

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The synthesis of layered double hydroxides (LDHs) by hydrothermal-LDH reconstruction and coprecipitation methods is reviewed using a thermodynamic approach. A mixture model was used for the estimation of the thermodynamics of formation of LDHs. The synthesis and solubility of LDHs are discussed in terms of standard molar Gibbs free energy change of reaction. Data for numerous divalent and trivalent metals as well as for some monovalent and tetravalent metals that may be part of the LDH structure have been compiled. Good agreement is found between theoretical and experimental data. Diagrams and tables for the prediction of possible new LDH materials are provided.

Keywords: layered double hydroxides; synthesis; thermodynamics.

INTRODUCTION

Layered double hydroxides (LDHs) are a broad class of inorganic lamellar compounds of basic character with high capacity for anion intercalation. The LDHs are also widely known as hydrotalcite-like compounds due to their structural similarities to hydrotalcite, a mineral with the formula $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$. The hydrotalcite structure results from the stacking of brucite-like layers $[Mg(OH)_2]$ containing a positive residual charge arising from the partial isomorphous substitution of Mg^{2+} cations by Al^{3+} cations. This positive excess charge is balanced by the carbonate anions, which reside in the interlamellar spaces[1-2]. Natural hydrotalcite was first reported by Hochstetter[3] in 1842 and synthesized 100 years later by Feitknecht[4]. In the last 20 years there have been numerous publications related with the synthesis and applications of LDH compounds[5-14]. They are represented by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}\ (A^{n-}_{x/n})\cdot mH_2O$ [2], where M^{2+} and M^{3+} can be any divalent and trivalent metal ions (whose ionic radius is not too different from that of Mg^{2+}), which can be accommodated in the octahedral holes in the brucite-like layers and x is the metal ratio $M^{3+}/(M^{2+}+M^{3+})$. The species A^{n-} in the interlamellar region can be any charge compensating anion (organic or inorganic) and m is the amount of water present in the same region[6, 9]. A special case occurs when A^{n-} is the hydroxide ion, OH^-. This class of compounds are called Meixnerite-like compounds (MLCs) because of their similarities to $Mg^{2+}_6Al^{3+}_2(OH)_{16}(OH)_2\cdot 4H_2O$, a compound named after Meixner[15].

LDH compounds have been synthesized by direct methods, which include coprecipitation[4, 6, 9], sol-gel synthesis[16], chimie douce[17], salt-oxide reaction[10], hydrothermal growth[18-21] and electrochemical synthesis[22]. Indirect methods include all syntheses that use an LDH as a precursor. Examples of these are all anion exchange based methods such as direct anion exchange[10,23], anion exchange by acid attack with elimination of the guest species in the interlayer region[24,25] and anion exchange by surfactant salt formation[26]. The non-anion exchange methods include the delamination-restacking method[27] and LDH reconstruction method[28-34]. Metals that have been reported as constituents of LDH layers as well as some claimed in patents[9, 35-52] are shown in Figure 1.

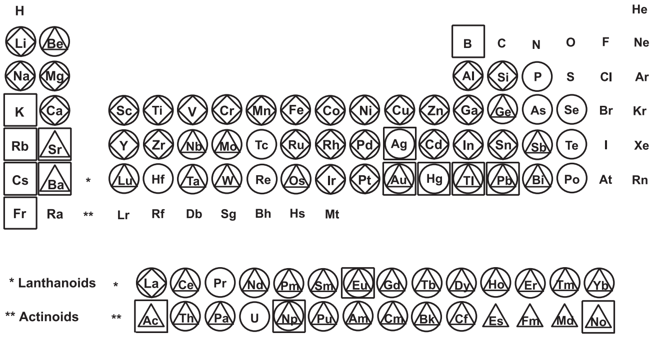

Figure 1. *Metals in LDH layers[9, 35-52]. ◇ Reported in journals, △ Claimed in patents, □ Deviation from Shannon ionic radius[53] of Mg^{2+} > 50%, ○ Deviation from Shannon ionic radius of Mg^{2+} < 50%. Some elements have ionic radius deviations from Mg^{2+} > and < 50% because they may exist in different oxidation states*

There is currently an increasing interest in LDHs, due to their properties as catalysts and catalyst supports[9,12,54], antacids[9,55-56], trapping agents for anionic contaminants[57-60], flame retardants[9,61], polymer stabilizers[9,62], molecular sieves[5], ion exchangers and adsorbents[63,64]. New areas have been investigated for applications in the field of medicine[65,66], thin films[67], conducting materials[68,69], electrodes[70-72] and corrosion protection[73-75]. LDHs have also been recently related to the origin of life[76,77].

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One of the advantages of LDHs among layered materials is the great number of possible compositions and metal-anion combinations that can be synthesized. In spite of this uniqueness, there has not been a practical guide to assist in synthesizing LDH materials with specific properties.

For this reason a thermodynamic study of the reactions involved in the synthesis of LDHs is desirable. However, this is no easy task, due to the great amount of thermodynamic data required including standard free energies, enthalpies and entropies of formation for all the wide range of compositional variations of LDHs. Moreover, very few articles are found in the literature[78-80] dealing with all the necessary data to make this work feasible. We have recently proposed[81] and evaluated five different models for the estimation of thermodynamic properties of LDH compounds. The main idea in these models was to treat the LDH as a mixture of structurally simple compounds. In the present work, for the sake of usefulness, we use the most simple and practical model for the estimation of standard molar Gibbs free energies of formation for $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-}_{x/n})$ compounds. These free energies of formation are used for the calculation of the standard free energy changes of reaction, the basis of comparison among the different reactions under consideration. We particularly concentrate our analysis on the synthesis of LDHs by hydrothermal-LDH reconstruction and coprecipitation methods. Similarly, the solubility of LDHs is also studied. An understanding of this property is important for LDH applications in aqueous media such as in the controlled release of interlayer anionic compounds by LDH layer dissolution[65,66,82,83] and geochemistry.

SOURCES OF THERMODYNAMIC DATA

Thermodynamic data for a great number of compounds (oxides, hydroxides, salts and ions) are readily available in several existing compilations of thermochemical data[84-89]. In the cases where standard molar entropies of formation of compounds are not available, they are estimated by the method of Latimer[90] as described by Naumov *et al.*[84]. Reference states used in the thermodynamic databases are 298.15 K and 101325 Pa for compounds and a hypothetical ideal 1 mol kg^{-1} solution at 298.15 K and 101325 Pa for dissolved species.

The models we proposed for the estimation of the thermodynamic properties of formation of LDH materials based on the combinations of simple compounds in the LDH structure are:

Model 0: a combination of the compounds $M^{2+}(OH)_2$, $M^{3+}(OH)_3$ and the ion (A^{n-})
Model 1: a combination of the compounds $M^{2+}(OH)_2$, $M^{3+}(OH)_3$ and $H_n(A^{n-})$
Model 2: a combination of the compounds $M^{2+}(OH)_2$, $M^{3+}(OH)_3$ and $M^{2+}(A^{n-})_{2/n}$
Model 3: a combination of the compounds $M^{2+}(OH)_2$, $M^{3+}(OH)_3$ and $M^{3+}_n(A^{n-})_3$
General Model: a combination of all the single models.

All the mixture models require thermodynamic data of the single species involved. Among all of the models, model 2 and the general model gave the best results for the estimation of the thermodynamic properties of formation. Although the general model has the attractiveness of being less arbitrary and averaging more information when available, model 2 has the advantage of simplicity, requiring less thermodynamic information than the general model. Model 2 requires thermodynamic data of metal hydroxides and salts of the divalent metal and is based on the following reaction:

$$(1 - 3x/2)M^{2+}(OH)_2 + (x)M^{3+}(OH)_3 + (x/2)M^{2+}(A^{n-})_{2/n} = [M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A^{n-}_{x/n} \qquad (1)$$

For n = 1 or 2

The standard molar Gibbs free energy of formation at any temperature, T, of the LDHs is given by the sum of the standard molar Gibbs free energies of formation of the components:

$$\Delta_f G^o_m\{T, LDH\} = (1 - 3x/2)\Delta_f G^o_m\{T, M^{2+}(OH)_2\} + (x)\Delta_f G^o_m\{T, M^{3+}(OH)_3\} + (x/2)\Delta_f G^o_m\{T, M^{2+}(A^{n-})_{2/n}\} \qquad (2)$$

SYNTHESIS OF LDHs BY HYDROTHERMAL-LDH RECONSTRUCTION (H-R) METHODS

Hydrothermal and LDH reconstruction methods are similar since both methods involve reactions of metal oxides, customarily in aqueous solution, with the anion of interest. A general reaction is given by:

$$(1 - x)M^{2+}O + (x/2)M^{3+}_2O_3 + (x/n)A^{n-} + (1 + x/2)H_2O = [M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A^{n-}_{x/n} + (x)OH^- \qquad (3)$$

The standard molar Gibbs free energy change of the hydrothermal-reconstruction reaction $(\Delta_{HR}G^o_m)$ is given by:

$$\Delta_{HR}G^o_m\{T\} = [\Delta_f G^o_m\{T, LDH\} + (x)\Delta_f G^o_m\{T, OH^-\}] - [(1 - x)\Delta_f G^o_m\{T, M^{2+}O\} + (x/2)\Delta_f G^o_m\{T, M_2{}^{3+}O_3\} + (x/2)\Delta_f G^o_m\{T, A^{n-}\} + (1 + x/2)\Delta_f G^o_m\{T, H_2O\}] \qquad (4)$$

Two cases can be distinguished: 1) Hydroxyl anion $(A^{n-} = OH^-)$ and 2) Non-hydroxyl anions $(A^{n-} \neq OH^-)$.

Synthesis of hydroxyl anion based LDHs by H-R methods: meixnerite-like compounds (MLCs)

MLC refers to layered double hydroxides in which the interlamellar anion is OH$^-$. Replacing OH$^-$ in reactions 1 and 3:

$$(1 - x)M^{2+}(OH)_2 + (x)M^{3+}(OH)_3 = [M^{2+}_{1-x}M^{3+}_{x}(OH)_2]OH_x \qquad (5)$$

$$(1 - x)M^{2+}O + (x/2)M^{3+}_2O_3 + (1 + x/2)H_2O = [M^{2+}_{1-x}M^{3+}_{x}(OH)_2]OH_x \qquad (6)$$

For the thermodynamic calculations, reactions 5 and 6 are combined:

$$(1 - x)M^{2+}O + (x/2)M^{3+}_2O_3 + (1 + x/2)H_2O = (1 - x)M^{2+}(OH)_2 + (x)M^{3+}(OH)_3 \qquad (7)$$

Terms in the lhs of Equation 7 are rearranged in the following way:

$$(1 - x)[M^{2+}O + H_2O] + (x)[(1/2)M^{3+}_2O_3 + (3/2)H_2O] = (1 - x)M^{2+}(OH)_2 + (x)M^{3+}(OH)_3 \qquad (8)$$

Using $\Delta_R G^o_m\{T\} = \sum_i^p \Delta_f G^o_m\{T, \text{Products } i\} - \sum_j^r \Delta_f G^o_m\{T, \text{Reac tan ts } j\}$, then

$$\Delta_{HR}G^o_m\{T, MLC\} = (1 - x)\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}O\} - \Delta_f G^o_m\{T, H_2O\}] + (x)[\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - (1/2)\Delta_f G^o_m\{T, M^{3+}_2O_3\} - (3/2)\Delta_f G^o_m\{T, H_2O\}] \qquad (9)$$

Equation 9 is a linear combination of the hydration reactions of the divalent and trivalent oxides:

$$M^{2+}O + H_2O = M^{2+}(OH)_2 \qquad (10)$$

$$\Delta_H G^o_m\{T, M^{2+}O\} = \Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}O\} - \Delta_f G^o_m\{T, H_2O\} \quad (11)$$

$$(1/2)M^{3+}_2O_3 + (3/2)H_2O = M^{2+}(OH)_2 \quad (12)$$

$$\Delta_H G^o_m\{T, M^{3+}_2O_3\} = \Delta_f G^o_m\{T, M^{3+}(OH)_3\} - (1/2)\Delta_f G^o_m\{T, M^{3+}_2O_3\} - (3/2)\Delta_f G^o_m\{T, H_2O\} \quad (13)$$

Equation 9 is rewritten in terms of Gibbs free energies of hydration of oxides:

$$\Delta_{HR} G^o_m\{T, MLC\} = (1 - x)\Delta_H G^o_m\{T, M^{2+}O\} + (x)\Delta_H G^o_m\{T, M^{3+}_2O_3\} \quad (14)$$

This result is not surprising if we account for the assumptions in the mixture model, as seen in Equations 5 and 7 and stated by Allada *et al.*[78]: "*Metal and anion coordination environments in the hydrotalcite are structurally similar, and therefore probably energetically similar, to those in the simple minerals used as components*".

Gibbs free energies of hydration for metal oxides at different temperatures

Data for the standard molar Gibbs free energy change of hydration at different temperatures are given in Figures 2 and 3. Results for the hydration reactions of some M^+ and M^{2+} oxides can be seen in Figure 2. Some hydration reactions of M^{3+} and M^{4+} oxides are also shown in Figure 3. All the calculations are based on the following well-known thermodynamic relationships[84-85]:

$$\Delta_f G^o_m\{T\} = \Delta_f H^o_m\{T\} - T \cdot S^o_m\{T\} \quad (15)$$

$$\Delta_f H^o_m\{T\} = \Delta_f H^o_m\{298.15\ K\} + \int_{298.15\ K}^{T} C^o_{p,m}\, dT \quad (16)$$

$$S^o_m\{T\} = S^o_m\{298.15\ K\} + \int_{298.15\ K}^{T} C^o_{p,m}\, dT/T \quad (17)$$

Where $C^o_{p,m}$ is a function of temperature of the following form:

$$C^o_{p,m} = a + b \cdot 10^{-3}T + c \cdot 10^{6}T^{-2} + d \cdot 10^{-6}T^{2} \quad (18)$$

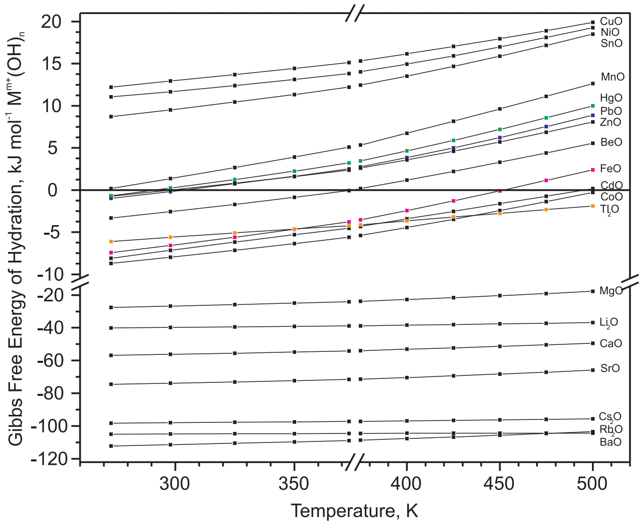

Figure 2. *Standard molar Gibbs free energy change of hydration for some M^+ and M^{2+} oxides at different temperatures*

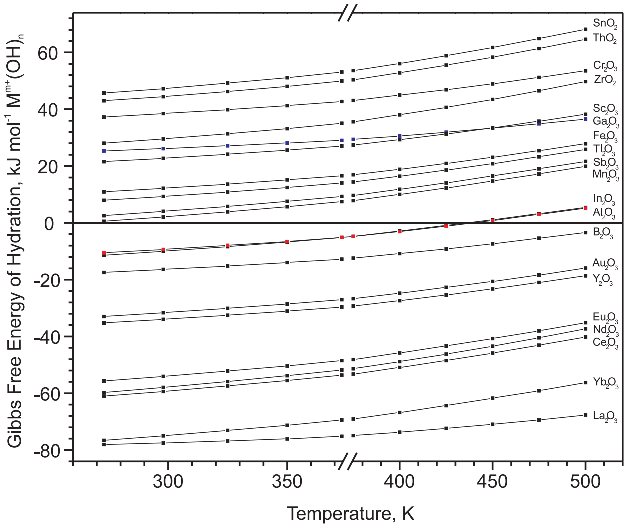

Figure 3. *Standard molar Gibbs free energy change of hydration for some M^{3+} and M^{4+} oxides at different temperatures*

Combining Equation 18 with Equations 16 and 17 and substituting the obtained results in Equation 15, the following expressions are obtained:

$$\begin{aligned}\Delta_f G^o_m\{T\} = {} & a[\{T - 298.15\} - T \cdot \ln(T/298.15)] + \\ & b[0.5 \cdot 10^{-3}(T^2 - 298.15^2) - T \cdot 10^{-3}(T - 298.15)] + \\ & c[10^6(298.15^{-1} - T^{-1}) + T \cdot 10^6(T^{-2} - 298.15^{-2})/2] + \\ & d[10^{-6}(T^3 - 298.15^3)/3 - T \cdot 10^{-6}(T^2 - 298.15^2)/2] + \\ & \Delta_f H^o_m\{298.15\} - T \cdot \Delta_f S^o_m\{298.15\ K\} \end{aligned} \quad (19)$$

$$\begin{aligned}\Delta_f G^o_m\{T\} = {} & a[(T - 298.15) - T \cdot \ln(T/298.15)] + \\ & b[0.5 \cdot 10^{-3}(T^2 - 298.15^2) - T \cdot 10^{-3}(T - 298.15)] + \\ & c[10^6(298.15^{-1} - T^{-1}) + T \cdot 10^6(T^{-2} - 298.15^{-2})/2] + \\ & d[10^{-6}(T^3 - 298.15^3)/3 - T \cdot 10^{-6}(T^2 - 298.15^2)/2] + \\ & \Delta_f G^o_m\{298.15\ K\} - (T - 298.15) \cdot S^o_m\{298.15\ K\} \end{aligned} \quad (20)$$

The selection of Equations 19 or 20 for $\Delta_f G^o_m\{T\}$ calculations is mainly based on the availability of the thermodynamic properties of the compounds. Equations 19 or 20 are applied to each compound in Equations 10 and 12. At a specific temperature the standard molar Gibbs free energy of hydration is calculated by the expression:

$$\Delta_H G^o_m\{T\} = \sum_i^p \Delta_f G^o_m\{T, \text{Products } i\} - \sum_j^r \Delta_f G^o_m\{T, \text{Reac tan ts } j\} \quad (21)$$

For temperatures over 373 K, a constant pressure of 5 MPa is used. In general, for solids and liquids there is little noticeable change of $\Delta_f G^o_m\{T\}$ with pressure due to the relatively small changes in molar volumes[91,92]. Data of $C^o_{p,m}$ as a function of temperature for compressed water at a pressure of 5 MPa were taken from Perry *et al*[89].

The standard molar Gibbs free energy change of hydration for many M^+, M^{2+}, M^{3+} and M^{4+} oxides are given in Tables 1 and 2. Information about the reactions, equations used, calculated $\Delta_H G^o_m\{T\}$'s and references for each of the entries are also provided in Tables 1 and 2. When Equations 19 and 20 are listed for one of the reactions, it indicates that either equation can be applied since there are enough published thermodynamic data.

Data in Tables 1 and 2 together with Equation 14 are used to estimate the standard molar Gibbs free energy change of reaction for the synthesis of MLCs by H-R methods. These results are summarized schematically in Figure 4 as a nomogram, and some typical examples

Table 1. Standard molar Gibbs free energy change of the hydration reaction for some M^+ and M^{2+} oxides at 298.15 K

Hydration Reaction	Equations	$\Delta_H G^o_m\{298.15\ K, M^{m+}(OH)_n\}$, kJ mol^{-1}	References
1/2Ag$_2$O (s) + 1/2H$_2$O (l) = AgOH (s)	20	-1.6	87, 89
1/2Tl$_2$O (s) + 1/2H$_2$O (l) = TlOH (s)	19	-5.6	86, 88, 89, 92
1/2Li$_2$O (s) + 1/2H$_2$O (l) = LiOH (s)	19	-39.8	86, 88, 89
1/2Cs$_2$O (s) + 1/2H$_2$O (l) = CsOH (s)	19	-97.9	86, 88, 89
1/2Na$_2$O (s) + 1/2H$_2$O (l) = NaOH (s)	19-20	-74.1	86,87, 89
1/2Rb$_2$O (s) + 1/2H$_2$O (l) = RbOH (s)	19	-104.8	86, 88, 89
PdO (s) + H$_2$O (l) = Pd(OH)$_2$ (s)	19	144.8	86-87, 89
TiO (s) + H$_2$O (l) = Ti(OH)$_2$ (s)	19	33.5	86, 87, 89, 90
CuO (s) + H$_2$O (l) = Cu(OH)$_2$ (s)	20	12.9	85, 86, 89, 90
NiO (s) + H$_2$O (l) = Ni(OH)$_2$ (s)	20	11.7	86, 89, 90, 92
SnO (s) + H$_2$O (l) = Sn(OH)$_2$ (s)	19-20	9.5	86, 89, 90, 92
MnO (s) + H$_2$O (l) = Mn(OH)$_2$ (s)	19-20	1.3	86, 89, 90, 92
HgO (s) + H$_2$O (l) = Hg(OH)$_2$ (s)	19-20	0.2	86, 89, 90, 92
ZnO (s) + H$_2$O (l) = Zn(OH)$_2$ (s)	19-20	-0.1	86, 89, 90, 92
PbO (s) + H$_2$O (l) = Pb(OH)$_2$ (s)	19-20	-0.2	86, 89, 90, 92
PtO (s) + H$_2$O (l) = Pt(OH)$_2$ (s)	20	-0.9	87, 89
BeO (s) + H$_2$O (l) = Be(OH)$_2$ (s)	19-20	-2.6	86, 88, 89
FeO (s) + H$_2$O (l) = Fe(OH)$_2$ (s)	19-20	-6.6	86, 88, 89
CdO (s) + H$_2$O (l) = Cd(OH)$_2$ (s)	19-20	-7.2	85, 86, 89
CoO (s) + H$_2$O (l) = Co(OH)$_2$ (s)	19-20	-8.0	86, 88, 89
MgO (s) + H$_2$O (l) = Mg(OH)$_2$ (s)	19-20	-26.8	86, 89
CaO (s) + H$_2$O (l) = Ca(OH)$_2$ (s)	19-20	-56.2	86, 89
SrO (s) + H$_2$O (l) = Sr(OH)$_2$ (s)	19-20	-73.9	85, 86, 89
RaO (s) + H$_2$O (l) = Ra(OH)$_2$ (s)	19	-110.1	86, 87, 89, 90
BaO (s) + H$_2$O (l) = Ba(OH)$_2$ (s)	19-20	-111.4	86, 88, 89

Table 2. Standard molar Gibbs free energy change of the hydration reaction for some M^{3+} and M^{4+} oxides at 298.15 K

Hydration Reaction	Equations	$\Delta_H G^o_m\{298.15\ K, M^{m+}(OH)_n\}$, kJ mol^{-1}	References
1/2Pu$_2$O$_3$ (s) + 3/2H$_2$O (l) = Pu(OH)$_3$ (s)	20	105.9	87, 89
1/2Tm$_2$O$_3$ (s) + 3/2H$_2$O (l) = Tm(OH)$_3$ (s)	20	55.7	86, 87, 89
1/2Cr$_2$O$_3$ (s) + 3/2H$_2$O (l) = Cr(OH)$_3$ (s)	20	38.5	86, 89, 92
1/2Bi$_2$O$_3$ (s) + 3/2H$_2$O (l) = Bi(OH)$_3$ (s)	19-20	27.6	86, 87, 89
1/2Ga$_2$O$_3$ (s) + 3/2H$_2$O (l) = Ga(OH)$_3$ (s)	19-20	26.2	86, 89, 92
1/2Sc$_2$O$_3$ (s) + 3/2H$_2$O (l) = Sc(OH)$_3$ (s)	19-20	22.7	86, 87, 89, 92
1/2-Ti$_2$O$_3$ (s) + 3/2H$_2$O (l) = Ti(OH)$_3$ (s)	19	15.9	86, 87, 89, 90
1/2Fe$_2$O$_3$ (s) + 3/2H$_2$O (l) = Fe(OH)$_3$ (s)	19-20	12.1	86, 89, 92
1/2Tl$_2$O$_3$ (s) + 3/2H$_2$O (l) = Tl(OH)$_3$ (s)	19-20	9.8	86, 89, 92
1/2V$_2$O$_3$ (s) + 3/2H$_2$O (l) = V(OH)$_3$ (s)	19	7.0	86, 87, 89, 90
1/2Sb$_2$O$_3$ (s) + 3/2H$_2$O (l) = Sb(OH)$_3$ (s)	19-20	4.0	86, 89, 92
1/2Mn$_2$O$_3$ (s) + 3/2H$_2$O (l) = Mn(OH)$_3$ (s)	19-20	2.1	86, 89, 90, 92
1/2Lu$_2$O$_3$ (s) + 3/2H$_2$O (l) = Lu(OH)$_3$ (s)	19-20	-8.6	86, 87, 89, 90
1/2In$_2$O$_3$ (s) + 3/2H$_2$O (l) = In(OH)$_3$ (s)	19-20	-9.4	86, 89, 92
1/2Al$_2$O$_3$ (s) + 3/2H$_2$O (l) = Al(OH)$_3$ (s)	19-20	-10.0	86, 89
1/2B$_2$O$_3$ (s) + 3/2H$_2$O (l) = B(OH)$_3$ (s)	19-20	-16.4	86, 89, 92
1/2Er$_2$O$_3$ (s) + 3/2H$_2$O (l) = Er(OH)$_3$ (s)	20	-30.0	87, 89
1/2Au$_2$O$_3$ (s) + 3/2H$_2$O (l) = Au(OH)$_3$ (s)	19-20	-31.7	85, 86, 88, 89
1/2Y$_2$O$_3$ (s) + 3/2H$_2$O (l) = Y(OH)$_3$ (s)	19-20	-34.0	86, 89, 92
1/2Dy$_2$O$_3$ (s) + 3/2H$_2$O (l) = Dy(OH)$_3$ (s)	20	-51.5	86, 87, 89
1/2Eu$_2$O$_3$ (s) + 3/2H$_2$O (l) = Eu(OH)$_3$ (s)	19-20	-54.1	86, 89, 92
1/2Pr$_2$O$_3$ (s) + 3/2H$_2$O (l) = Pr(OH)$_3$ (s)	20	-54.9	87, 89
1/2Nd$_2$O$_3$ (s) + 3/2H$_2$O (l) = Nd(OH)$_3$ (s)	19-20	-57.9	86, 89, 92
1/2Ce$_2$O$_3$ (s) + 3/2H$_2$O (l) = Ce(OH)$_3$ (s)	19-20	-59.4	86, 89, 92
1/2Tb$_2$O$_3$ (s) + 3/2H$_2$O (l) = Tb(OH)$_3$ (s)	20	-71.2	86, 87, 89
1/2Yb$_2$O$_3$ (s) + 3/2H$_2$O (l) = Yb(OH)$_3$ (s)	20	-75.0	86, 89, 92
1/2La$_2$O$_3$ (s) + 3/2H$_2$O (l) = La(OH)$_3$ (s)	19-20	-77.5	86, 89, 92
1/2Gd$_2$O$_3$ (s) + 3/2H$_2$O (l) = Gd(OH)$_3$ (s)	20	-93.4	87, 89
1/2Sm$_2$O$_3$ (s) + 3/2H$_2$O (l) = Sm(OH)$_3$ (s)	20	-94.4	86, 87, 89
PoO$_2$ (s) + 2H$_2$O (l) = Po(OH)$_4$ (s)	20	125.4	87, 89
SnO$_2$ (s) + 2H$_2$O (l) = Sn(OH)$_4$ (s)	19-20	47.3	86, 89, 92
ThO$_2$ (s) + 2H$_2$O (l) = Th(OH)$_4$ (s)	19-20	44.4	86, 89, 92
UO$_2$ (s) + 2H$_2$O (l) = U(OH)$_4$ (s)	20	36.3	87, 89
ZrO$_2$ (s) + 2H$_2$O (l) = Zr(OH)$_4$ (s)	19-20	29.5	86, 89, 92
AmO$_2$ (s) + 2H$_2$O (l) = Am(OH)$_4$ (s)	20	-25.6	87, 89

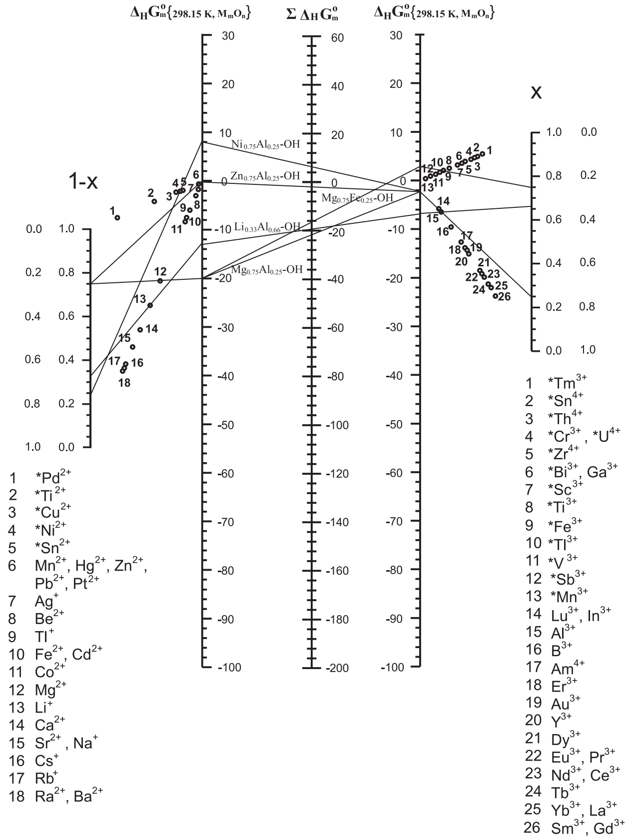

Figure 4. *Estimated standard molar Gibbs free energy change of reaction for the synthesis of MLCs by H-R methods at 298.15 K, in kJ mol^{-1}*

of MLCs are shown. To estimate the standard free energy change of reaction at a temperature different from 298.15 K, data from Figures 2 and 3 can be used.

The $\Delta_{HR}G^o_m\{T\}$ for a MLC is easily estimated taking into account its formula. For a MLC with the general formula: $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}(OH)_x$, the $\Delta_{HR}G^o_m\{T\}$ is the result of hydration contributions from M^{2+} and M^{3+} oxides. Given a metal ratio, x, the contribution from the hydration of M^{3+} oxides is obtained by drawing a straight line from the x scale, going through the selected M^{3+} mark and finally intersecting the $\Delta_HG^o_m\{298.15\ K\}$ right axis. Similarly, the contribution from the hydration of M^{2+} oxides is obtained, but now using the 1-x values and the scale on the left of Figure 4. Finally, the intersect formed from the straight line, joining the resulting contributions from the M^{2+} and M^{3+} oxides, and the central axis gives the estimated standard molar Gibbs free energy change of reaction for the synthesis of MLCs by H-R methods. When an asterisk precedes one of the M^{3+} and M^{2+} metals, then x and 1-x inverted scales should be used, respectively. Although the previous procedure is intended for M^{2+}-M^{3+} metal mixed oxides, it is not restricted to that specific case. For instance, M^{+}-M^{3+} metal mixed oxides among others can also be easily analyzed by using a proper general formula.

Synthesis of non-hydroxyl anion based LDH by H-R methods

For thermodynamic calculations, Equations 1 and 3 are combined and rearranged to give:

$$(1-x)[M^{2+}O + H_2O] + [(x/2)M^{3+}_2O_3 + (3x/2)H_2O] + (x/n)A^{n-} + (x/2)M^{2+}(OH)_2 = (1-x)[M^{2+}(OH)_2] + (x)[M^{3+}(OH)_3] + (x/2)M^{2+}(A^{n-})_{2/n} + (x)OH^- \tag{22}$$

Similarly to Equation 9, the standard Gibbs free energy change of the reaction is:

$$\Delta_{HR}G^o_m\{T, LDH-A\} = (1-x)\Delta_HG^o_m\{T, M^{2+}O\} + (x)\Delta_HG^o_m\{T, M^{3+}_2O_3\} + (x)[(1/2)\Delta_fG^o_m\{T, M^{2+}(A^{n-})_{2/n}\} - (1/2)\Delta_fG^o_m\{T, M^{2+}(OH)_2\} + \Delta_fG^o_m\{T, OH^-\} - (1/n)\Delta_fG^o_m\{T, A^{n-}\}] \tag{23}$$

The term in brackets may be regarded as a contribution due to anion difference in the MLCs ($\Delta_CG^o_m\{T, M^{2+}A\}$).

$$\Delta_CG^o_m\{T, M^{2+}A\} = (1/2)\Delta_fG^o_m\{T, M^{2+}(A^{n-})_{2/n}\} - (1/2)\Delta_fG^o_m\{T, M^{2+}(OH)_2\} + \Delta_fG^o_m\{T, OH^-\} - (1/n)\Delta_fG^o_m\{T, A^{n-}\} \tag{24}$$

Finally,

$$\Delta_{HR}G^o_m\{T, LDH-A\} = (1-x)\Delta_HG^o_m\{T, M^{2+}O\} + (x)\Delta_HG^o_m\{T, M^{3+}_2O_3\} + (x)\Delta_CG^o_m\{T, M^{2+}A\} \tag{25}$$

Equation 24 is used for the calculation of $\Delta_CG^o_m\{T, M^{2+}A\}$. For example, the standard Gibbs free energy for the anion contribution term in the $[Mg^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]Cl_x$ LDH is calculated by:

$$\Delta_CG^o_m\{298.15\ K, Mg^{2+}A\} = (1/2)\Delta_fG^o_m\{298.15\ K, Mg(Cl)_2\} - (1/2)\Delta_fG^o_m\{298.15\ K, Mg(OH)_2\} + \Delta_fG^o_m\{298.15\ K, OH^-\} - \Delta_fG^o_m\{298.15\ K, Cl^-\}$$

$$\Delta_CG^o_m\{298.15\ K, Mg^{2+}A\} = (1/2)(-591.8) - (1/2)(-833.6) + (-157.3) - (-131.3) = 94.9\ kJ\ mol^{-1}$$

Other results shown in Table 3 are calculated in a similar manner. The thermodynamic data of the compounds were taken from Naumov *et al.*[86], Karapet'yants *et al.*[87] and Perry *et al.*[89]. The results of Figure 4 combined with values in Table 3 can be substituted into Equation 25 to estimate standard Gibbs free energies of the synthesis of LDHs by H-R methods. For instance, the standard Gibbs free energy for the synthesis of a $[Mg^{2+}{}_{0.75}Al^{3+}{}_{0.25}(OH)_2]F_{0.25}$ LDH by H-R methods is obtained from:

$$\Delta_{HR}G^o_m\{298.15\ K, MgAl-F\} = 0.75\Delta_HG^o_m\{298.15\ K, MgO\} + 0.25\Delta_HG^o_m\{298.15\ K, Al_2O_3\} + 0.25\Delta_CG^o_m\{298.15\ K, MgF\}$$

Table 3. Standard molar Gibbs free energy anion contribution term, $\Delta_CG^o_m\{298.15\ K, M^{2+}A\}$

	$\Delta_CG^o_m\{298.15\ K, M^{2+}A\}$, kJ mol^{-1}							
M^{2+}	I^-	Br^-	Cl^-	NO_3^-	SO_4^{2-}	CO_3^{2-}	F^-	OH^-
Ba^{2+}	22.3	9.5	2.7	-15.8	-31.5	-33.7	-20.8	0
Be^{2+}	197.3	179.0	160.4	0.0	76.8	41.8	48.7	0
Ca^{2+}	75.9	34.6	46.3	31.6	15.0	-9.2	-16.8	0
Cd^{2+}	29.6	36.3	39.1	59.4	40.6	9.4	34.4	0
Co^{2+}	73.4	69.5	64.8	66.7	50.6	10.4	44.0	0
Cu^{2+}	61.2	73.6	66.9	71.9	62.3	26.5	58.9	0
Fe^{2+}	71.7	71.6	64.1	43.2	47.7	11.7	50.9	0
Hg^{2+}	-8.2	13.5	32.3	69.1	67.3	20.0	89.5	0
Mg^{2+}	131.2	114.1	94.9	76.7	49.4	17.8	3.9	0
Mn^{2+}	61.6	63.3	53.1	5.4	36.1	-2.3	46.8	0
Ni^{2+}	70.7	61.6	65.3	57.1	44.0	21.5	36.7	0
Pb^{2+}	21.3	30.9	30.8	41.8	22.8	6.7	26.7	0
Pd^{2+}	-5.1	45.9	44.3	-68.0	-34.3	-45.4	20.9	0
Sn^{2+}	68.1	68.1	89.9	-51.8	-18.1	-12.4	33.4	0
Sr^{2+}	48.3	27.8	13.5	-5.9	-18.6	-27.3	-22.5	0
Zn^{2+}	67.1	67.9	65.4	81.9	57.6	16.9	43.2	0

From Figure 4:

$0.75\Delta_H G^o_m\{298.15\ K, MgO\} + 0.25\Delta_H G^o_m\{298.15\ K, Al_2O_3\} \approx -22.5\ kJ\ mol^{-1}$

And from Table 3:

$0.25\Delta_C G^o_m\{298.15\ K, MgF\} \approx 1.0\ kJ\ mol^{-1}$

Thus

$\Delta_{HR} G^o_m\{298.15\ K, MgAl - F\} \approx -21.5\ kJ\ mol^{-1}$

SYNTHESIS OF LDHs BY THE COPRECIPITATION METHOD

In the coprecipitacion method, LDHs are generally precipitated from a mixture of metal salts and the interlamellar anion of interest under basic conditions. As previously stated, the different combinations of these metal salts and anions are numerous. In this work, a number of these combinations are studied.

Case 1: divalent and trivalent metal with the same univalent anion

$$(1 - x)M^{2+}(B^-)_2 + (x)M^{3+}(B^-)_3 + 2OH^- + (x/n)A^{n-} = [M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} + (2 + x)B^- \quad (26)$$

Replacing Equation 1 in Equation 26, the standard Gibbs free energy change of reaction for coprecipitation (CP), ($\Delta_{CP}G^o_m\{T, LDH\}$), can be expressed by:

$$\Delta_{CP}G^o_m\{T, LDH\} = (1 - x)[\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}(B^-)_2\}] + (x)[\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - \Delta_f G^o_m\{T, M^{3+}(B^-)_3\}] + (x)[(1/2)\Delta_f G^o_m\{T, M^{2+}(A^{n-})_{2/n}\} - (1/2)\Delta_f G^o_m\{T, M^{2+}(OH)_2\} + \Delta_f G^o_m\{T, OH^-\} - (1/n)\Delta_f G^o_m\{T, A^{n-}\}] + (2 + x)[\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, OH^-\}] \quad (27)$$

The third term in Equation 27 is the free energy anion contribution term as given by Equation 24. Finally, the standard molar Gibbs free energy change of reaction is:

$$\Delta_{CP}G^o_m\{T, LDH\} = (1 - x)[\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}(B^-)_2\}] + (x)[\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - \Delta_f G^o_m\{T, M^{3+}(B^-)_3\}] + (x)[\Delta_C G^o_m\{T, M^{2+}A\}] + (2)[\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, OH^-\}] + (x)[\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, OH^-\}] \quad (28)$$

From Equation 28, five different contributions (terms in brackets) to the Gibbs free energy of the synthesis of LDHs by coprecipitation are considered:

1) Contribution due to the difference in the anion of the starting divalent metal from the divalent metal hydroxide.
2) Contribution due to the difference in the anion of the starting trivalent metal from the trivalent metal hydroxide.
3) Contribution due to the anion in the final LDH.
4) Contribution due to the free anions remaining in solution from divalent metal.
5) Contribution due to the free anions remaining in solution from trivalent metal.

Calculated values for the first, second and third contribution terms of Equation 28 are given in Tables 4, 5 and 3, respectively. Results for the fourth and fifth contribution terms are given in the last row of Table 4. Several examples of the calculations are:

$Zn(Cl)_2$ first contribution term to the standard Gibbs free energy of the CP reaction:

$$\Delta_f G^o_m\{298.15\ K, Zn(OH)_2\} - \Delta_f G^o_m\{298.15\ K, Zn(Cl)_2\} = -554.4 - (-371.5) = -182.9\ kJ\ mol^{-1}$$

$Al(Cl)_3$ second contribution term to the standard Gibbs free energy of the CP reaction:

$$\Delta_f G^o_m\{298.15\ K, Al(OH)_3\} - \Delta_f G^o_m\{298.15\ K, Al(Cl)_3\} = -1156.9 - (-737.7) = -419.2\ kJ\ mol^{-1}$$

Cl^- fourth contribution term to the standard Gibbs free energy of the CP reaction:

$$\Delta_f G^o_m\{298.15\ K, Cl^-\} - \Delta_f G^o_m\{298.15\ K, OH^-\} = -131.3 - (-157.3) = 26.0\ kJ\ mol^{-1}$$

The thermodynamic data of the compounds for the first and second contribution term were taken from Naumov *et al.*[86], Karapet'yants *et al.*[87] and Perry *et al.*[89]. For the fourth contribution term data for the ionic species comes from Naumov *et al.*[86].

Table 4. Standard molar Gibbs free energy contribution term of starting divalent metal cation for Equation 28 at 298.15 K[a]

	Contribution Term, kJ mol^{-1}, B$^-$							D^{2-}, Equation 34	
M^{2+}	I$^-$	Br$^-$	Cl$^-$	F$^-$	NO$_3^-$	OH$^-$		SO$_4^{2-}$	CO$_3^{2-}$
Ba^{2+}	-256.1	-125.1	-57.4	287.0	-60.1	0		492.2	280.7
Be^{2+}	-605.9	-464.1	-372.8	148.0	-91.7	0		275.6	129.6
Ca^{2+}	-363.3	-175.3	-144.7	279.0	-154.8	0		399.2	231.6
Cd^{2+}	-270.7	-178.7	-130.2	176.6	-210.5	0		348.0	194.6
Co^{2+}	-358.2	-245.2	-181.6	157.3	-225.1	0		328.1	192.5
Cu^{2+}	-333.9	-253.3	-185.9	127.6	-235.6	0		304.6	160.3
Fe^{2+}	-354.8	-249.4	-180.3	143.5	-178.2	0		333.9	190.0
Hg^{2+}	-195.0	-133.1	-116.7	66.4	-229.9	0		294.6	173.2
Mg^{2+}	-473.8	-334.4	-241.8	237.5	-245.1	0		330.4	177.7
Mn^{2+}	-334.5	-232.8	-158.2	151.9	-102.5	0		357.1	218.0
Ni^{2+}	-352.7	-229.3	-182.6	172.0	-205.9	0		341.2	170.3
Pb^{2+}	-254.1	-167.9	-113.6	192.0	-175.3	0		383.7	200.0
Pd^{2+}	-201.3	-198.0	-140.7	203.6	-74.6	0		497.8	304.1
Sn^{2+}	-347.7	-242.3	-231.9	178.7	-138.2	0		465.4	238.1
Sr^{2+}	-307.9	-161.8	-79.1	290.4	-79.9	0		466.4	267.9
Zn^{2+}	-345.6	-241.9	-182.9	158.9	-255.6	0		314.1	179.4
(B$^-$-OH$^-$)	105.7	53.1	26.0	-122.7	45.9	0	(D^{2-}/2-OH$^-$)	-214.6	-106.7

[a] Results for the contribution term of free anions in solution are given in last row.

Table 5. Standard molar Gibbs free energy contribution term of starting trivalent metal cation for Equation 28 at 298.15 K

	Contribution Term, kJ mol^{-1}, B$^-$						D^{2-}, Equation 32
M^{3+}	I$^-$	Br$^-$	Cl$^-$	F$^-$	NO$_3^-$	OH$^-$	SO$_4^{2-}$
Al^{3+}	-845.6	-668.4	-419.2	261.7	-377.9	0	390.2
Au^{3+}	-397.6	-324.3	-300.4	-51.5	x	0	x
Bi^{3+}	-407.5	-283.3	-267.8	338.2	x	0	x
Ce^{3+}	-586.2	-319.9	-250.6	481.2	x	0	558.9
Cr^{3+}	-644.3	-333.5	-257.9	196.2	x	0	704.0
Dy^{3+}	-678.6	-398.2	-357.7	x	x	0	753.2
Er^{3+}	-710.0	-436.1	-406.3	x	x	0	656.7
Eu^{3+}	-474.0	-264.3	-218.0	x	x	0	1158.5
Fe^{3+}	-593.7	-468.2	-378.2	296.2	x	0	626.1
Ga^{3+}	-618.4	-482.4	-343.1	105.4	x	0	691.0
Gd^{3+}	-676.6	-384.1	-357.7	x	x	0	517.7
In^{3+}	-638.5	-410.0	-317.1	182.0	x	0	502.9
La^{3+}	-591.2	-386.6	-254.8	482.0	x	0	x
Lu^{3+}	-711.3	-472.8	-380.3	x	x	0	1023.4
Nd^{3+}	-613.8	-348.7	-284.6	x	x	0	538.2
Pr^{3+}	-623.4	-329.1	-288.7	382.0	x	0	488.7
Pu^{3+}	-613.4	-409.2	-277.0	321.3	x	0	x
Sb^{3+}	-578.2	-433.0	-348.7	163.6	x	0	570.9
Sc^{3+}	-645.6	-525.1	-382.0	332.1	x	0	x
Sm^{3+}	-673.6	-367.6	-314.2	x	x	0	479.1
Tb^{3+}	-596.8	-387.0	-343.1	x	x	0	1043.5
Tl^{3+}	-325.1	-277.8	-215.9	6.3	x	0	x
Tm^{3+}	-693.7	-414.7	-379.5	x	x	0	x
Y^{3+}	-766.5	-723.0	-397.9	348.5	x	0	x
Yb^{3+}	-762.7	-430.9	-415.9	x	x	0	x

x = not enough data available

Case 2: divalent and trivalent metal with different univalent anion

$$(1-x)M^{2+}(B^-)_2 + (x)M^{3+}(C^-)_3 + 2OH^- + (x/n)A^{n-} = [M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} + 2(1-x)B^- + 3(x)C^- \qquad (29)$$

A similar analysis as in Case 1 gives the Gibbs free energy change of reaction:

$$\begin{aligned}\Delta_{CP}G^o_m\{T, \text{LDH}\} = {} & (1-x)[\Delta_fG^o_m\{T, M^{2+}(OH)_2\} - \Delta_fG^o_m\{T, M^{2+}(B^-)_2\}] \\ & + (x)[\Delta_fG^o_m\{T, M^{3+}(OH)_3\} - \Delta_fG^o_m\{T, M^{3+}(C^-)_3\}] + \\ & (x)[\Delta_CG^o_m\{T, M^{2+}A\}] + (2)[\Delta_fG^o_m\{T, B^-\} - \Delta_fG^o_m\{T, OH^-\}] + \\ & (x)[3\Delta_fG^o_m\{T, C^-\} - 2\Delta_fG^o_m\{T, B^-\} - \Delta_fG^o_m\{T, OH^-\}] \qquad (30)\end{aligned}$$

Equation 30 is similar to Equation 28. Results for the fifth contribution term are shown in Table 6. For example, the Cl$^-$-NO$_3^-$ (B$^-$-C$^-$) fifth contribution term to the standard Gibbs free energy is given by:

$$3\Delta_fG^o_m\{298.15\text{ K}, NO_3^-\} - 2\Delta_fG^o_m\{298.15\text{ K}, Cl^-\} - \Delta_fG^o_m\{298.15\text{ K}, OH^-\} = 3(-111.4) - 2(-131.3) - (-157.3) = 85.6\text{ kJ mol}^{-1}$$

Case 3: divalent metal-univalent anion and trivalent metal-divalent anion

$$(1-x)M^{2+}(B^-)_2 + (x/2)M^{3+}_2(D^{2-})_3 + 2OH^- + (x/n)A^{n-} = [M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} + 2(1-x)B^- + (3x/2)D^{2-} \qquad (31)$$

The standard Gibbs free energy change of reaction is:

$$\begin{aligned}\Delta_{CP}G^o_m\{T, \text{LDH}\} = {} & (1-x)[\Delta_fG^o_m\{T, M^{2+}(OH)_2\} - \Delta_fG^o_m\{T, M^{2+}(B^-)_2\}] \\ & + (x)[\Delta_fG^o_m\{T, M^{3+}(OH)_3\} - (1/2)\Delta_fG^o_m\{T, M^{3+}_2(D^{2-})_3\}] + \\ & (x)[\Delta_CG^o_m\{T, M^{2+}A\}] + (2)[\Delta_fG^o_m\{T, B^-\} - \Delta_fG^o_m\{T, OH^-\}] + \\ & (x)[(3/2)\Delta_fG^o_m\{T, D^{2-}\} - 2\Delta_fG^o_m\{T, B^-\} - \Delta_fG^o_m\{T, OH^-\}] \qquad (32)\end{aligned}$$

Contribution terms are defined as in Case 1. The contribution due to the difference in the anion of the trivalent metal from the

Table 6. Standard molar Gibbs free energy contribution term of trivalent metal anions in solution for Equation 30 at 298.15 K

	Contribution Term, kJ mol^{-1}, C$^-$						D^{2-}, Equation 32
B$^-$	I$^-$	Br$^-$	Cl$^-$	NO$_3^-$	F$^-$	OH$^-$	SO$_4^{2-}$
I$^-$	105.7	-52.2	-133.3	-73.8	-579.5	-211.4	-855.3
Br$^-$	211.0	53.1	-28.0	31.5	-474.2	-106.1	-750.0
Cl$^-$	265.0	107.1	26.0	85.6	-420.2	-52.1	-695.9
NO$_3^-$	225.4	67.5	-13.6	45.9	-459.8	-91.7	-735.6
F$^-$	562.5	404.6	323.5	383.0	-122.7	245.4	-398.5
OH$^-$	317.1	159.2	78.1	137.6	-368.1	0.0	-643.9

trivalent metal hydroxide (second term) is given in the last column of Table 5. Results of the free energy contribution of the trivalent metal anion in solution, for Equation 32, are shown in the last column of Table 6. Calculations are straightforward. For instance, the NO_3^--SO_4^{2-} (B^--D^{2-}) fifth contribution term to the standard Gibbs free energy is obtained by:

$$(3/2)\Delta_f G^o_m\{298.15\text{ K}, SO_4^{2-}\} - 2\Delta_f G^o_m\{298.15\text{ K}, NO_3^-\} - \Delta_f G^o_m\{298.15\text{ K}, OH^-\} = (3/2)(-743.8) - 2(-111.4) - (-157.3) = -735.6\text{ kJ mol}^{-1}$$

Case 4: divalent metal-divalent anion and trivalent metal-univalent anion

$$(1-x)M^{2+}(D^{2-}) + (x)M^{3+}(B^-)_3 + 2OH^- + (x/n)A^{n-} = [M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} + (1-x)D^{2-} + 3(x)B^- \quad (33)$$

and

$$\Delta_{CP}G^o_m\{T, LDH\} = (1-x)[\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}(D^{2-})\}] + (x)[\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - \Delta_f G^o_m\{T, M^{3+}(B^-)_3\}] + (x)[\Delta_C G^o_m\{T, M^{2+}A\}] + (2)[(1/2)\Delta_f G^o_m\{T, D^{2-}\} - \Delta_f G^o_m\{T, OH^-\}] + (x)[3\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, D^{2-}\} - \Delta_f G^o_m\{T, OH^-\}] \quad (34)$$

The first and fourth contribution term of Equation 34 are shown in the last two columns and last row of Table 4, respectively. Some results for the Gibbs free energy contribution of the trivalent metal anion in solution, fifth contribution term of Equation 34, are given in Table 7. Calculations are similar to the ones used in case 3 for the (B^--D^{2-}) fifth contribution term.

Case 5: divalent and trivalent metal with the same divalent anion

$$(1-x)M^{2+}(D^{2-}) + (x/2)M^{3+}_2(D^{2-})_3 + 2OH^- + (x/n)A^{n-} = [M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} + (1 + x/2)D^{2-} \quad (35)$$

and

$$\Delta_{CP}G^o_m\{T, LDH\} = (1-x)[\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}(D^{2-})\}] + (x)[\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - (1/2)\Delta_f G^o_m\{T, M^{3+}_2(D^{2-})_3\}] + (x)[\Delta_C G^o_m\{T, M^{2+}A\} + (2)[(1/2)\Delta_f G^o_m\{T, D^{2-}\} - \Delta_f G^o_m\{T, OH^-\}] + (x)[(1/2)\Delta_f G^o_m\{T, D^{2-}\} - \Delta_f G^o_m\{T, OH^-\}] (36)$$

Values of the first, second and third contribution terms are shown in the last column of Table 4, last column of Tables 5 and 3, respectively. Results for the fourth and fifth contribution terms are given in the last row of Table 4. A summary of all studied cases is given in Table 8, and some examples of standard Gibbs free energy calculations for the synthesis of LDHs by coprecipitation are given in Table 9.

Table 7. Standard molar Gibbs free energy contribution term of trivalent metal anion in solution for Equation 34 at 298.15 K

	Contribution Term, kJ mol^{-1}, B^-					
D^{2-}	I^-	Br^-	Cl^-	NO_3^-	F^-	OH^-
SO_4^{2-}	746.4	588.5	507.3	566.9	61.1	429.2
CO_3^{2-}	530.4	372.5	291.4	350.9	-154.8	213.3

Table 8. Summary of Gibbs free energy calculations for the synthesis of LDHs: $[M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n}$ by coprecipitation $\Delta_{CP}G^o_m\{T, LDH\} = (1-x)CT1 + (x)CT2 + (x)CT3 + (2)CT4 + (x)CT5$

Case	M^{2+} Anion	M^{3+} Anion	CT1: M^{2+} salt Table 4	CT2: M^{3+} salt Table 5	CT3: LDH-A Table 3	CT4: anions in solution from M^{2+} salt	CT5: anions in solution from M^{3+} salt
1 Equation 28	B^-	B^-	$\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}(B^-)_2\}$	$\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - \Delta_f G^o_m\{T, M^{3+}(B^-)_3\}$	$\Delta_C G^o_T M^{2+}A$	$\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, OH^-\}$ Table 4	$\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, OH^-\}$ Table 4
2 Equation 30	B^-	C^-	$\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}(B^-)_2\}$	$\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - \Delta_f G^o_m\{T, M^{3+}(C^-)_3\}$	$\Delta_C G^o_T M^{2+}A$	$\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, OH^-\}$ Table 4	$3\Delta_f G^o_m\{T, C^-\} - 2\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, OH^-\}$ Table 6
3 Equation 32	B^-	D^{2-}	$\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}(B^-)_2\}$	$\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - (1/2)\Delta_f G^o_m\{T, M^{3+}_2(D^{2-})_3\}$	$\Delta_C G^o_T M^{2+}A$	$\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, OH^-\}$ Table 4	$(3/2)\Delta_f G^o_m\{T, D^{2-}\} - 2\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, OH^-\}$ Table 6
4 Equation 34	D^{2-}	B^-	$\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}(D^{2-})\}$	$\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - \Delta_f G^o_m\{T, M^{3+}(B^-)_3\}$	$\Delta_C G^o_T M^{2+}A$	$(1/2)\Delta_f G^o_m\{T, D^{2-}\} - \Delta_f G^o_m\{T, OH^-\}$ Table 4	$3\Delta_f G^o_m\{T, B^-\} - \Delta_f G^o_m\{T, D^{2-}\} - \Delta_f G^o_m\{T, OH^-\}$ Table 7
5 Equation 36	D^{2-}	D^{2-}	$\Delta_f G^o_m\{T, M^{2+}(OH)_2\} - \Delta_f G^o_m\{T, M^{2+}(D^{2-})\}$	$\Delta_f G^o_m\{T, M^{3+}(OH)_3\} - (1/2)\Delta_f G^o_m\{T, M^{3+}_2(D^{2-})_3\}$	$\Delta_C G^o_T M^{2+}A$	$(1/2)\Delta_f G^o_m\{T, D^{2-}\} - \Delta_f G^o_m\{T, OH^-\}$ Table 4	$(1/2)\Delta_f G^o_m\{T, D^{2-}\} - \Delta_f G^o_m\{T, OH^-\}$ Table 4

Table 9. Estimated standard molar Gibbs free energies of reaction for some LDHs synthesized by coprecipitation at 298.15 K

Case	M^{2+} Anion	M^{3+} Anion	LDH-A x	CT1: M^{2+} salt (1-x)CT1	CT2: M^{3+} salt (x)CT2	CT3: LDH-A (x)CT3	CT4: Anion M^{2+} (2)CT4	CT5: Anion M^{3+} (x)CT5	$\Delta_{CP}G^o_m$ kJ mol^{-1}
1	Mg Cl	Al Cl	Cl 0.25	-181.4	-104.8	23.7	52.0	6.5	-204.0
1	Zn Cl	Al Cl	Cl 0.25	-137.2	-104.8	16.4	52.0	6.5	-167.1
1	Ni Cl	Al Cl	Cl 0.25	-136.9	-104.8	16.3	52.0	6.5	-166.9
1	Mg NO_3	Al NO_3	NO_3 0.25	-183.8	-94.5	19.2	91.8	11.5	-155.8
1	Zn NO_3	Al NO_3	NO_3 0.25	-191.7	-94.5	20.5	91.8	11.5	-162.4
1	Ni NO_3	Al NO_3	NO_3 0.25	-154.4	-94.5	14.3	91.8	11.5	-131.3
1	Mg NO_3	Al NO_3	CO_3 0.25	-183.8	-94.5	4.5	91.8	11.5	-170.6
1	Zn NO_3	Al NO_3	CO_3 0.25	-191.7	-94.5	4.2	91.8	11.5	-178.7
1	Ni NO_3	Al NO_3	CO_3 0.25	-154.4	-94.5	5.4	91.8	11.5	-140.2

SOLUBILITY OF LAYERED DOUBLE HYDROXIDES

A general expression of the dissolution of LDHs in acidic media is given by:

$$[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} + 2H^+ (aq) = (1-x)M^{2+} (aq) + (x)M^{3+} (aq) + (x/n)A^{n-} + 2H_2O \quad (37)$$

The standard molar Gibbs free energy change of the dissolution is:

$$\Delta_D G^o_m\{T, LDH\} = (1-x)\Delta_f G^o_m\{T, M^{2+}\} + (x)\Delta_f G^o_m\{T, M^{3+}] + (x/n)\Delta_f G^o_m\{T, A^{n-}\} + 2\Delta_f G^o_m\{T, H_2O\} - \Delta_f G^o_m\{T, LDH\} - 2\Delta_f G^o_m\{T, H^+\} \quad (38)$$

Similarly to the synthesis of LDHs by H-R methods, depending on the LDH interlamellar anion, two cases are distinguished: 1) Hydroxyl anion ($A^{n-} = OH^-$) and 2) Non-hydroxyl anions ($A^{n-} \neq OH^-$).

Dissolution of meixnerite-like compounds

Substituting OH^- and Equation 6 into Equation 37 and taking into account that: $(x)OH^- + (x)H^+ = (x)H_2O$, then

$$(1-x)[M^{2+}(OH)_2 + 2H^+ (aq)] + (x)[M^{3+}(OH)_3 + 3H^+ (aq)] = (1-x)[M^{2+} (aq) + 2H_2O] + (x)[M^{3+} (aq) + 3H_2O] \quad (39)$$

and

$$\Delta_D G^o_m\{T, MLC\} = (1-x)[2\Delta_f G^o_m\{T, H_2O\} + \Delta_f G^o_m\{T, M^{2+}] - \Delta_f G^o_m\{T, M^{2+}(OH)_2\}] + (x)[3\Delta_f G^o_m\{T, H_2O\} + \Delta_f G^o_m\{T, M^{3+}\} - \Delta_f G^o_m\{T, M^{3+}(OH)_3\}] \quad (40)$$

Equation 40 is a linear combination of the dissolution reactions of the divalent and trivalent hydroxides:

$$M^{2+}(OH)_2 + 2H^+ = M^{2+} + 2H_2O \quad (41)$$

$$\Delta_D G^o_m\{T, M^{2+}(OH)_2\} = 2\Delta_f G^o_m\{T, H_2O\} + \Delta_f G^o_m\{T, M^{2+}\} - \Delta_f G^o_m\{T, M^{2+}(OH)_2\} \quad (42)$$

$$M^{3+}(OH)_3 + 3H^+ = M^{3+} + 3H_2O \quad (43)$$

$$\Delta_D G^o_m\{T, M^{3+}(OH)_3\} = 3\Delta_f G^o_m\{T, H_2O\} + \Delta_f G^o_m\{T, M^{3+}\} - \Delta_f G^o_m\{T, M^{3+}(OH)_3\} \quad (44)$$

Finally, Equation 40 is rewritten in terms of the standard Gibbs free energies of dissolution of metal hydroxides:

$$\Delta_D G^o_m\{T, MLC\} = (1-x)\Delta_D G^o_m\{T, M^{2+}(OH)_2\} + (x)\Delta_D G^o_m\{T, M^{3+}(OH)_3\} \quad (45)$$

Standard molar Gibbs free energies of dissolution of metal hydroxides at different temperatures

Data for the standard molar Gibbs free energy change of dissolution at different temperatures are given in Figures 5 and 6. Results for the dissolution reactions of some M^+ and M^{2+} hydroxides can be seen in Figure 5. Some dissolution reactions of M^{3+} and M^{4+} hydroxides are also shown in Figure 6. All the calculations are based on Equations 41 and 43. A procedure similar to the one described for the Gibbs free energy of hydration for metal oxides at different temperatures is followed. Standard Gibbs free energy change of dissolution for many M^+, M^{2+}, M^{3+} and M^{4+} hydroxides are given in Tables 10 and 11. Again, information about the reactions, equations used, calculated $\Delta_D G^o_m\{T\}$'s and references for each of the entries are provided.

Data in Tables 10 and 11 together with Equation 45 are used to estimate the standard molar Gibbs free energy change of dissolution of MLCs in acidic media. These results are summarized schematically in Figure 7 as a nomogram, and some examples of MLCs are shown. Data from Figures 5 and 6 can be used for the estimation of the standard free energy change of dissolution at temperatures different from 298.15 K. The procedure described before to use Figure 4 can be applied for Figure 7.

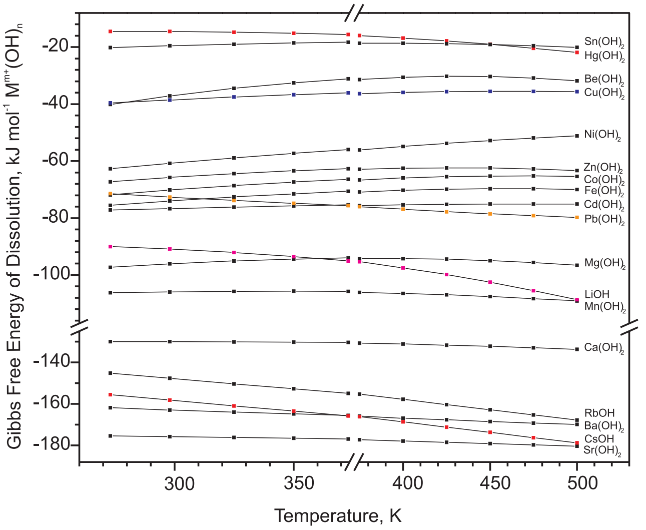

Figure 5. *Standard molar Gibbs free energy change of dissolution for some M^+ and M^{2+} hydroxides at different temperatures*

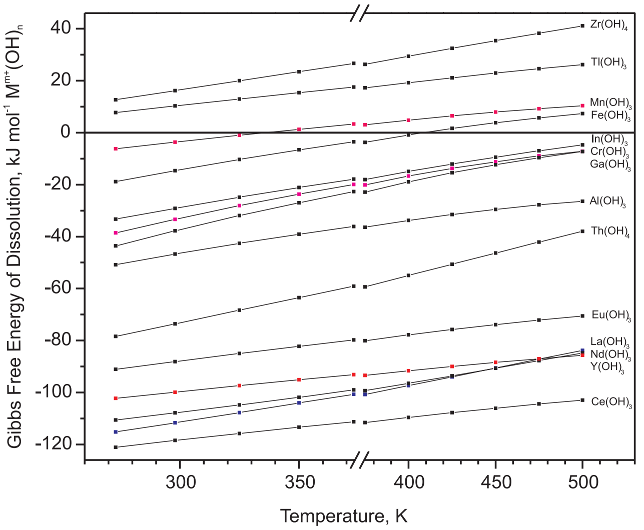

Figure 6. *Standard molar Gibbs free energy change of dissolution for some $M^{3+}$and M^{4+} hydroxides at different temperatures*

Table 10. Standard molar Gibbs free energy change of the dissolution reaction for some M^+ and M^{2+} hydroxides at 298.15 K

Dissolution Reaction	Equations	$\Delta_D G^o_m\{298.15\ K, M^{m+}(OH)_n\}$, kJ mol^{-1}	Ref.
$AgOH\ (s) + H^+\ (aq) = Ag^+\ (aq) + H_2O$	20	-35.3	86, 89
$TlOH\ (s) + H^+\ (aq) = Tl^+\ (aq) + H_2O$	19-20	-73.6	86, 89, 92
$LiOH\ (s) + H^+\ (aq) = Li^+\ (aq) + H_2O$	19-20	-90.8	86, 88-89
$NaOH\ (s) + H^+\ (aq) = Na^+\ (aq) + H_2O$	19-20	-120.0	86, 89
$RbOH\ (s) + H^+\ (aq) = Rb^+\ (aq) + H_2O$	20	-147.7	86, 88, 89
$CsOH\ (s) + H^+\ (aq) = Cs^+\ (aq) + H_2O$	19	-158.2	86, 88, 89
$Pt(OH)_2\ (s) + 2H^+\ (aq) = Pt^{2+}\ (aq) + 2H_2O$	20	39.0	87, 89
$Pd(OH)_2\ (s) + 2H^+\ (aq) = Pd^{2+}\ (aq) + 2H_2O$	20	7.3	87, 89
$Hg(OH)_2\ (s) + 2H^+\ (aq) = Hg^{2+}\ (aq) + 2H_2O$	19-20	-14.6	86, 89
$Sn(OH)_2\ (s) + 2H^+\ (aq) = Sn^{2+}\ (aq) + 2H_2O$	19-20	-16.4	86, 89, 90, 92
$Be(OH)_2\ (s) + 2H^+\ (aq) = Be^{2+}\ (aq) + 2H_2O$	19-20	-36.9	86, 88, 89
$Cu(OH)_2\ (s) + 2H^+\ (aq) = Cu^{2+}\ (aq) + 2H_2O$	20	-51.4	85, 86, 89, 90
$Ni(OH)_2\ (s) + 2H^+\ (aq) = Ni^{2+}\ (aq) + 2H_2O$	19-20	-60.4	86, 89, 90, 92
$Zn(OH)_2\ (s) + 2H^+\ (aq) = Zn^{2+}\ (aq) + 2H_2O$	19-20	-65.8	86, 89, 90, 92
$Co(OH)_2\ (s) + 2H^+\ (aq) = Co^{2+}\ (aq) + 2H_2O$	19-20	-70.8	86, 88, 89
$Pb(OH)_2\ (s) + 2H^+\ (aq) = Pb^{2+}\ (aq) + 2H_2O$	19-20	-71.2	86, 89-90, 92
$Fe(OH)_2\ (s) + 2H^+\ (aq) = Fe^{2+}\ (aq) + 2H_2O$	19-20	-73.6	86, 88, 89
$Cd(OH)_2\ (s) + 2H^+\ (aq) = Cd^{2+}\ (aq) + 2H_2O$	19-20	-76.5	85, 86, 89
$Mg(OH)_2\ (s) + 2H^+\ (aq) = Mg^{2+}\ (aq) + 2H_2O$	19-20	-96.1	86, 89
$Mn(OH)_2\ (s) + 2H^+\ (aq) = Mn^{2+}\ (aq) + 2H_2O$	19-20	-105.6	86, 89, 92
$Ca(OH)_2\ (s) + 2H^+\ (aq) = Ca^{2+}\ (aq) + 2H_2O$	19-20	-130.1	86, 89
$Ba(OH)_2\ (s) + 2H^+\ (aq) = Ba^{2+}\ (aq) + 2H_2O$	19-20	-147.4	86, 88, 89
$Sr(OH)_2\ (s) + 2H^+\ (aq) = Sr^{2+}\ (aq) + 2H_2O$	19-20	-174.4	85, 86, 89

Dissolution of LDHs with anions different from OH$^-$

Combining Equation 1 and Equation 37 and rearranging terms, the following expression is obtained:

$$(1 - x)[M^{2+}(OH)_2 + 2H^+\ (aq)] + (x)[M^{3+}(OH)_3 + 3H^+\ (aq)] + (x/2)M^{2+}(A^{n-})_{2/n} + (x)H_2O = (1 - x)[M^{2+}\ (aq) + 2H_2O] + (x)[M^{3+}\ (aq) + 3H_2O] + (x/n)A^{n-} + (x/2)M^{2+}(OH)_2 + (x)H^+ \quad (46)$$

and

$$\Delta_D G^o_m\{T, LDH\} = (1 - x)\Delta_D G^o_m\{T, M^{2+}(OH)_2\} + (x)\Delta_D G^o_m\{T, M^{3+}(OH)_3\} - (x)[(1/2)\Delta_f G^o_m\{T, M^{2+}(A^{n-})_{2/n}\} - (1/2)\Delta_f G^o_m\{T, M^{2+}(OH)_2\} + \Delta_f G^o_m\{T, OH^-\} - (1/n)\Delta_f G^o_m\{T, A^{n-}\}] \quad (47)$$

Again, the term in brackets is the contribution term due to anion difference in the MLCs as defined by Equation 24 and shown in Table 3.

Finally,

$$\Delta_D G^o_m\{T, LDH\} = (1 - x)\Delta_D G^o_m\{T, M^{2+}(OH)_2\} + (x)\Delta_D G^o_m\{T, M^{3+}(OH)_3\} - (x)\Delta_C G^o_m\{T, M^{2+}A\} \quad (48)$$

LIMITATIONS OF THE THERMODYNAMIC STUDY

The validity of the results given in the present work depends greatly on the accuracy of the Gibbs free energy of formation data for the species under consideration. Most of the thermodynamic quantities have been gathered from different sources. All of the standard state properties were determined or estimated by a large diversity of methods and techniques. Therefore, it is expected that some random errors will

Table 11. Standard molar Gibbs free energy change of the dissolution reaction for some M^{3+} and M^{4+} hydroxides at 298.15 K

Dissolution Reaction	Equations	$\Delta_D G^o_m\{298.15\ K, M^{m+}(OH)_n\}$, kJ mol^{-1}	References
$Au(OH)_3$ (s) + $3H^+$ (aq) = Au^{3+} (aq) + $3H_2O$	20	70.8	86, 87, 89
$Tl(OH)_3$ (s) + $3H^+$ (aq) = Tl^{3+} (aq) + $3H_2O$	19-20	9.7	86, 89, 92
$Mn(OH)_3$ (s) + $3H^+$ (aq) = Mn^{3+} (aq) + $3H_2O$	19-20	-2.0	86, 89, 90, 92
$Er(OH)_3$ (s) + $3H^+$ (aq) = Er^{3+} (aq) + $3H_2O$	20	-9.9	86, 87, 89
$Fe(OH)_3$ (s) + $3H^+$ (aq) = Fe^{3+} (aq) + $3H_2O$	19-20	-14.8	86, 89, 92
$In(OH)_3$ (s) + $3H^+$ (aq) = In^{3+} (aq) + $3H_2O$	19-20	-29.2	86, 89
$Cr(OH)_3$ (s) + $3H^+$ (aq) = Cr^{3+} (aq) + $3H_2O$	20	-33.3	86, 89, 92
$Ga(OH)_3$ (s) + $3H^+$ (aq) = Ga^{3+} (aq) + $3H_2O$	19-20	-37.7	86, 89, 92
$Bi(OH)_3$ (s) + $3H^+$ (aq) = Bi^{3+} (aq) + $3H_2O$	19-20	-46.5	86, 87, 89
$Al(OH)_3$ (s) + $3H^+$ (aq) = Al^{3+} (aq) + $3H_2O$	19-20	-46.7	86, 89
$Gd(OH)_3$ (s) + $3H^+$ (aq) = Gd^{3+} (aq) + $3H_2O$	20	-60.2	86, 87, 89
$Sm(OH)_3$ (s) + $3H^+$ (aq) = Sm^{3+} (aq) + $3H_2O$	20	-63.1	86, 87, 89
$Yb(OH)_3$ (s) + $3H^+$ (aq) = Yb^{3+} (aq) + $3H_2O$	20	-69.3	86, 87, 89
$Sc(OH)_3$ (s) + $3H^+$ (aq) = Sc^{3+} (aq) + $3H_2O$	20	-84.8	86, 89
$Eu(OH)_3$ (s) + $3H^+$ (aq) = Eu^{3+} (aq) + $3H_2O$	19-20	-88.2	86, 89, 92
$Tb(OH)_3$ (s) + $3H^+$ (aq) = Tb^{3+} (aq) + $3H_2O$	20	-89.7	87, 89
$Dy(OH)_3$ (s) + $3H^+$ (aq) = Dy^{3+} (aq) + $3H_2O$	20	-98.6	87, 89
$Y(OH)_3$ (s) + $3H^+$ (aq) = Y^{3+} (aq) + $3H_2O$	19-20	-99.9	86, 89, 92
$Lu(OH)_3$ (s) + $3H^+$ (aq) = Lu^{3+} (aq) + $3H_2O$	20	-104.9	87, 89
$Tm(OH)_3$ (s) + $3H^+$ (aq) = Tm^{3+} (aq) + $3H_2O$	20	-105.7	87, 89
$Nd(OH)_3$ (s) + $3H^+$ (aq) = Nd^{3+} (aq) + $3H_2O$	19-20	-107.8	86, 89, 92
$La(OH)_3$ (s) + $3H^+$ (aq) = La^{3+} (aq) + $3H_2O$	19-20	-111.6	86, 89, 92
$Ce(OH)_3$ (s) + $3H^+$ (aq) = Ce^{3+} (aq) + $3H_2O$	19-20	-118.7	86, 89, 92
$Pu(OH)_3$ (s) + $3H^+$ (aq) = Pu^{3+} (aq) + $3H_2O$	20	-127.1	87, 89
$Pr(OH)_3$ (s) + $3H^+$ (aq) = Pr^{3+} (aq) + $3H_2O$	20	-128.3	87, 89
$Am(OH)_4$ (s) + $4H^+$ (aq) = Am^{4+} (aq) + $4H_2O$	20	42.0	87, 89
$Zr(OH)_4$ (s) + $4H^+$ (aq) = Zr^{4+} (aq) + $4H_2O$	20	16.2	87, 89
$Sn(OH)_4$ (s) + $4H^+$ (aq) = Sn^{4+} (aq) + $4H_2O$	20	-0.5	87, 89
$U(OH)_4$ (s) + $4H^+$ (aq) = U^{4+} (aq) + $4H_2O$	20	-27.9	86, 87, 89
$Th(OH)_4$ (s) + $4H^+$ (aq) = Th^{4+} (aq) + $4H_2O$	19-20	-73.6	86, 89, 92
$Po(OH)_4$ (s) + $4H^+$ (aq) = Po^{4+} (aq) + $4H_2O$	20	-112.0	87, 89

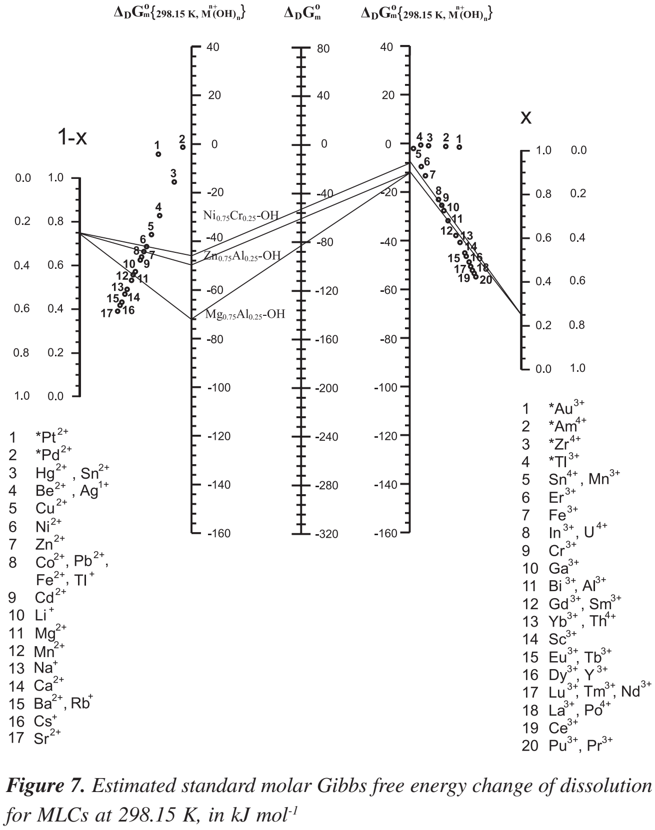

Figure 7. *Estimated standard molar Gibbs free energy change of dissolution for MLCs at 298.15 K, in kJ mol^{-1}*

be present due to the variability of the published data. Also, restrictions imposed by the mixture model involving the calculations of standard state properties of formation of LDHs should be taken into account. Although, efforts were made to check for self-consistency of results, this was not always possible due to the lack of data. Although the majority of the thermodynamic quantities (free energies, entropies, enthalpies and heat capacities) were collected from well-known and recognized compilations of thermochemical data, care must be taken when interpreting predicted results.

Moreover, while interpreting results of free energies of reaction, it should not be forgotten that calculations are based on only the species involved in the general reactions. Accordingly, calculations apply only when no other species are present or when these other species do not have a large effect on the overall thermochemical results.

In the present study, information regarding the kinetics of reactions (i.e. reaction rate, activation energy, reaction pathways, etc.) is not provided. For such work, experimental methods are commonly employed.

DISCUSSION

Synthesis of LDHs by hydrothermal reconstruction methods

Several studies of LDH synthesis have been carried out, but it was Sato *et al.*[31] who first noted a correlation between the hydration reaction of the divalent hydroxide and the easy of reconstitution of the hydrotalcite-like structure for various mixed metal oxides. They proposed the following decreasing order for the easy of reconstruction: Mg-Al > Mg-Fe > Co-Al > Ni-Al > Ni-Fe. In light of the data shown in Figure 4, this trend is not surprising because the metal ratio $M^{3+}/(M^{2+}+M^{3+})$ of all the starting LDHs was the same, and the standard Gibbs free energies of the hydration of the divalent oxides are quite different. This order is the same as the order predicted by Figure 4 which gives the corresponding free energies, $\Delta_{HR}G^o_m\{298.15$ K, MLC$\}$, of -21.8 kJ mol^{-1} < -15.1 kJ mol^{-1} < -8.6 kJ mol^{-1} < 5.2 kJ mol^{-1} < 11.8 kJ mol^{-1}, where the larger the negative value of the free energy of the H-R reaction the easier the MLC is formed.

Some other examples[28-33, 93-94] found in the literature, whose synthesis methods are described in detail, are shown in Figure 4. The estimated Gibbs free energy change of reaction agrees qualitatively quite well with the reported observations on the simple preparation of these MLCs. For instance, $[Ni_{1-x}Al_x(OH)_2]OH_x$ (for x = 0.25, $\Delta_{HR}G^o_m\{298.15$ K, MLC$\}$ = 6.3 kJ mol^{-1}) is difficult to prepare, and even with high temperature and pressure conditions and prolonged times of reaction, a rather small conversion of the MLC was achieved[33].

$[Mg_{1-x}Al_x(OH)_2]OH_x$, known as meixnerite[15], is so far the most studied MLC, given its relatively smooth formation by reconstruction methods[30]. It should have a fairly negative Gibbs free energy of reaction and Figure 4 supports this result (for x = 0.25, $\Delta_{HR}G^o_m\{298.15$ K, MLC$\}$ = –22.6 kJ mol^{-1}). It is noteworthy to mention that although the hydration of Fe^{3+} oxide is not favorable thermodynamically, $[Mg_{1-x}Fe_x(OH)_2]OH_x$ can be prepared successfully thanks to the contribution of the Mg^{2+} free energy of hydration to the total free energy of the LDH reconstruction[93].

Data of hydration of some M^+ and M^{4+} oxides have also been included in Figure 4 since they have been introduced in the LDH layers and even synthesized by hydrothermal methods[94]. This is also the case for $[Li_{1-x}Al_x(OH)_2][OH]_{2x-1}$[95], which is shown in Figure 4 to have a favorable Gibbs free energy of reaction (for x = 0.66, $\Delta_{HR}G^o_m\{298.15$ K, MLC$\}$ = –19.9 kJ mol^{-1}).

LDH reconstruction in the presence of non-hydroxyl anions has been carried out even more often than the preparation of MLCs. This might be due to the increasing interest of this method for environmental applications[58-61, 64] (i.e. anion sequestering) and for the intercalation of organic and inorganic anions in the LDH layers[96-99]. Sato *et al.*[29] reported that the degree of adsorption of $Mg_{1-x}Al_x$ oxides of divalent anions such as CrO_4^{2-}, HPO_4^{2-}, HVO_4^{2-}, SiO_3^{2-}, $HGaO_3^{2-}$ and SO_4^{2-} was higher than that of the monovalent anions Cl^- and MnO_4^-. This conforms with the results in Table 3 and shows that $\Delta_C G^o_m\{298.15$ K, MgA$\}$of SO_4^{2-} is more favorable thermodynamically to the formation of LDH than that of Cl^- ($\Delta_C G^o_m\{298.15$ K, $MgSO_4\}$= 49.4 kJ mol^{-1} < $\Delta_C G^o_m\{298.15$ K, MgCl$\}$ = 94.9 kJ mol^{-1}). Châtelet *et al.*[100] also found similar results.

Table 3 can be also used to predict anion selectivities for the reconstruction of LDHs for a specific divalent-trivalent metal-mixed oxide. However, care should be taken when using these data. For example, Parker *et al.*[63] found anion absorption selectivities for Mg-Al mixed oxides of: $SO_4^{2-} > F^- > Cl^- > NO_3^-$ and the anion selectivities predicted by Table 3 are: $F^- > SO_4^{2-} > NO_3^- > Cl^-$. Although, these predictions contradict the experimental results, these differences may be explained on the basis of the CO_3^{2-} impurities present in the aqueous solution[63] and the oxide adsorption capacities[100], factors not taken into account in the thermodynamic calculations.

Synthesis of LDHs by the coprecipitation (CP) method

As seen in Table 8, there are many possible combinations of metal salts and anions that may be used in the CP method. Therefore, only the most common combinations will be discussed. Since Feitknecht's work[4], hydrotalcite, $[Mg_{1-x}Al_x(OH)_2](A^{n-})_{x/n}$, has been the most studied LDH. According to Cavani *et al.*[9] this may be because hydrotalcite is simple and relatively inexpensive to prepare in the laboratory. Examination of the terms contributing to the total Gibbs free energy in Tables 4 and 5 for Mg and Al, respectively, reveals that Mg and Al salts are the ones with the highest negative contribution value. Hence, the ease of synthesis of hydrotalcite can be understood readily.

There has been a clear preference to use metal chlorides as starting materials for CP synthesis. However, metal nitrates have also been employed[6, 9-10]. Although different kinds of anions have been introduced in LDHs, carbonate anions appear to be the most common[9]. Carbonate anions have also appeared as an impurity in the final LDH, even if a decarbonated synthesis media was used[6]. Detailed calculations of standard Gibbs free energy of the synthesis of some common LDHs are given in Table 9. From these results, some interesting points arise: 1) In all cases, hydrotalcites have relatively high negative Gibbs free energies of reaction; 2) Higher negative Gibbs free energies of CP reaction are obtained when metal chlorides are used as precursors; 3) Carbonate anions are thermodynamically favored in the LDH interlamellar region due to their small $\Delta_C G^o_m\{298.15$ K, $M^{2+}A\}$ values compared to nitrate and chloride anions. These findings agree with the experimental observations.

Solubility of LDHs

In spite of the importance of the solubility of LDHs, related thermodynamic data in the literature are rather scarce[78]. Sato *et al.*[31] calculated the solubilitites of some LDHs (Mg-Al, Mg-Fe, Ni-Al, Ni-Fe and Co-Al). Using K'_{sp} values ($K'_{sp}=[M^{2+}][OH^-]$) they concluded that the solubility of LDHs decreased appreciably when Mg^{2+} was replaced with Ni^{2+} and Co^{2+} and that an appreciable difference was not noted when Al^{3+} was replaced with Fe^{3+}. A similar conclusion can be drawn from the results in Figure 7. Comparing the M^{2+} contributions to the total free energy of dissolution, a decreasing degree of solubility gives the order $Mg^{2+} > Co^{2+} > Ni^{2+}$. This order is based on the fact that the larger the negative value of the free energy of the dissolution reaction the more soluble the LDH. Similarly, it can be seen that Co-Al LDHs will have a lower negative free energy of dissolution than the corresponding cobalt hydroxide, as shown by Thompson *et al.*[101]. Ranges of pH in which some metal hydroxides and LDHs may exist have been reported[10, 102]. Some examples of pH ranges for LDHs are shown in Table 12.

Looking at the results in Figure 7 for LDH combinations in Table 12, a reasonable correlation between the lower pH limit and the free energy change of dissolution is observed. This result is not surprising since LDHs dissolve in acidic media. The standard Gibbs free energies of dissolution have been tabulated in the last column of Table 12. The Zn-Cr compound deviates the most from the correlation, and this may be due to a kinetic effect because of a special stability of the compound. Likewise, Zn-Al, Zn-Cr and Ni-Al LDHs have been used in the synthesis of intercalated catalysts at low pH because of their greater resistance to dissolution compared to Mg-Al LDH[54, 103]. The influence of interlamellar anions on the solubility of LDHs has been little studied. Allada *et al.*[78] reported that nitrate and sulfate anions could increase the solubility of hydrotalcite relative to the carbonate hydrotalcite. The same trend is obtained from $\Delta_C G^o_m\{298.15$ K, MgA$\}$ data for NO_3^-, SO_4^{2-} and CO_3^{2-} in Table 3 ($\Delta_C G^o_m\{298.15$ K, $MgNO_3\}$ = 76.7 kJ mol^{-1} > $\Delta_C G^o_m\{298.15$ K, $MgSO_4\}$ = 49.4 kJ mol^{-1} > $\Delta_C G^o_m\{298.15$ K, $MgNO_3\}$ =17.8 kJ mol^{-1}).

New LDH materials

Numerous LDH materials have been reported so far; however, the number of compositions and possible combinations of metals

Table 12. pH ranges at which some LDHs may exist[10]

LDH	pH Range Low Limit	 High Limit	$\Delta_D G^o_m\{298.15\text{ K, LDH}\}$, kJ mol^{-1}
$[Zn_{1-x}Cr_x(OH)_2](Cl^-)_{x/n}$	4.5	10.0	-74.1
$[Ni_{1-x}Al_x(OH)_2](CO_3^{2-})_{x/n}$	5.0	10.0	-62.4
$[Ni_{1-x}Cr_x(OH)_2](Cl^-)_{x/n}$	5.5	11.5	-69.9
$[Zn_{1-x}Al_x(OH)_2](Cl^-)_{x/n}$	6.0	10.0	-77.4
$[Co_{1-x}Fe_x(OH)_2](Cl^-)_{x/n}$	7.5	10.5	-73.0
$[Mg_{1-x}Al_x(OH)_2](Cl^-)_{x/n}$	8.0	10.5	-107.4

present in the layers and anions in the interlamellar region is almost unlimited. As seen from Figure 1, there are still lots of possibilities to design novel LDH compounds with almost any metal in the periodic table and whose properties have not been yet fully investigated.

The synthesis of LDHs with new divalent and trivalent metals, different from the classically used, represents an open and current field of research. For instance, very few articles referencing LDH materials with lanthanoid and actinoid elements in the LDH layers have been reported[40, 104]. Some monovalent and tetravalent metals have been also used in the synthesis of LDHs. Some examples are Li^+[95], Na^+[41], Ti^{4+}[51] and Zr^{4+}[45, 105]. Other M^{4+} metals with proper ionic radius can be anticipated (i.e. Am^{4+}, V^{4+}, Os^{4+} among others). A different situation occurs with most of the single valent M^+. From Figure 1, it can be seen that the ionic radii of most of the M^+ metals have great differences with the ionic radius of Mg^{2+} (i.e. K^+, Rb^+, Cs^+, Fr^+, Au^+, Tl^+ and Ag^+ among others). This fact might explain in part why they have not been introduced so far in the layers of LDH compounds. The same problem is observed with divalent metals such as Sr^{2+} and Ba^{2+}, although they have been claimed in some patents[46-49].

Using the results of Figures 1 and 4, it can be easily predicted that some combination of metals are highly favored thermodynamically to form LDHs. For example, from the family of LDH compounds: Li^+-M^{3+} LDHs, only the Li^+-Al^{3+} LDH has been reported[95] and attempts to synthesize Li^+-Cr^{3+}, Li^+-Fe^{3+}, Li^+-Ga^{3+} and Li^+-In^{3+} LDHs presumably by coprecipitation methods have failed[106]. In this particular case, hydrothermal methods using metal oxides of Li^+ and Fe^{3+}, Ga^{3+} or In^{3+} as starting materials are thermodynamically favored for the formation of LDHs, as predicted by Figure 4, and could be a route to the successful synthesis of these materials.

The free energy anion contribution term, $\Delta_C G^o_m\{298.15\text{ K}, M^{2+}A\}$, given in Table 3 and used in Equation 25 might be used to predict anion selectivities for the reconstruction of LDH compounds. For example, Fe^{2+}-M^{3+} metal mixed oxides might show monovalent anion selectivities of $OH^- > NO_3^- > F^- > Cl^- > Br^- \approx I^-$ and divalent anion selectivities of $CO_3^{2-} > SO_4^{2-}$. A similar order of stability in acidic solutions is expected for Fe^{2+}-M^{3+} LDHs as calculated by Equation 48. Figure 7 can be used to predict LDH compounds resistant to dissolution; for example, the introduction of metals such as Pt^{2+}, Pd^{2+}, Sn^{2+}, Be^{2+}, Au^{3+}, Am^{4+}, Zr^{4+}, Tl^{3+} and Mn^{3+} among others should improve the stability of LDH materials in acid media.

CONCLUSIONS

From the present thermodynamic review of the synthesis of LDH materials, good qualitative agreement between the estimated standard molar Gibbs free energies and the published experimental data for the synthesis and solubility of LDHs is found. Even though these results are encouraging, care should be taken when interpreting the data, especially when trying to do a quantitative analysis. For instance, carbonate anions are supposed to be highly favorable thermodynamically in the synthesis of LDHs. However, from the results in Table 3, carbonate anions are in some cases slightly unfavorable to the formation of LDHs when compared to hydroxyl anions as in Mg^{2+}-M^{3+} LDHs. Allada *et al.*[78] estimated the errors associated with the predictions of thermodynamic data by the mixture model to be within 5 to 10 kJ mol^{-1}. Therefore, differences found in the anion contributions from Table 3 between carbonate and hydroxyl anions fall within the error range given by the model. Also, the aqueous chemistry of the ions involved in the general reactions may be different and influence the final thermodynamic result.

In general terms, the results reported in the present work represent a valuable tool to assist in the synthesis of LDHs by H-R and CP methods. This study also helps to predict the solubility of LDH compounds, opening up the possibility of creating a great number of new, interesting materials.

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