Layered Double Hydroxide Stability. 1. Relative Stabilities of Layered Double Hydroxides and Their Simple Counterparts

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Solutions containing di- and trivalent metal chlorides [M(II) = Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}; M(III) = Al^{3+}, Fe^{3+}] were titrated with NaOH to yield hydrotalcite-like layered double hydroxides (LDH), $[[M(II)]_{1-x}[M(III)]_x(OH)_2][Cl]_x \cdot yH_2O$, by way of M(III) hydroxide/hydrous oxide intermediates. Analysis of the resultant titration curves yields nominal solubility constants for the LDH. The corresponding LDH stabilities are in the order Mg < Mn < Co ≈ Ni < Zn for M(II) and Al < Fe for M(III). The stability of LDH relative to the separate metal hydroxides/hydrous oxides is discussed.

Introduction

The layered double hydroxides (LDHs) are a family of natural and synthetic materials of general type $[[M(II)]_{1-z}[M(III)]_z(OH)_2][Y_z] \cdot yH_2O$ [Y = e.g. Cl, $^1/_2(CO_3)$], sometimes known as anionic clays.[1–6] These materials are structurally similar to the mineral brucite, $Mg(OH)_2$, with a fraction of M(II) ions replaced by M(III) ions. This replacement results in a net positive charge on the octahedral layers, which is balanced by exchangeable interlayer anions.

Materials of this family have many potential applications, including use as precursors for coatings and catalysts,[7–9] hosts for photoactivation and photocatalysis,[10–13] and anion exchange,[14,15] and have been invoked in the studies of the origins of life.[16] Layered double hydroxides are readily prepared by the addition of base to solutions containing a mixture of M(II) and M(III). Initially, M(III) hydroxides or hydrous oxides are usually formed. Further addition of base results in conversion of the M(III) hydr(ous) oxide to LDH. (In one version of this technique, mixed metal chlorides (at pH ≲ 4, by hydrolysis) are added to a reaction vessel held at a fixed pH, typically 10.[17] Here the trivalent metal hydroxide/hydrous oxide, while not isolated, is presumably formed in the mixing zone and subsequently converted to LDH.) In this paper, we use the pH attained when M(III) hydr(ous) oxide, LDH, and excess solution $M(II)^{2+}$ coexist to estimate nominal LDH solubilities. Knowing the solubility product of "$M(III)(OH)_3$", controlling the concentration of $M(II)^{2+}$, and monitoring the solution pH provide enough information to calculate quantitative solubility data of the precipitated LDH, information which has, hitherto, been lacking. pH methods similar to those used here were, in fact, exploited over 68 years ago to demonstrate the formation of $Mg_2Al(OH)_6X$ as a separate phase, but no quantitative solubility data were derived,[18] although Hansen and co-workers have determined the K_{sp} and $\Delta G°_f$ of the Green Rust sulfate, Fe^{II}_4-$Fe^{III}_2(OH)_{12}(SO_4)$, which is an LDH with M(II) = M(III) = Fe, using a similar pH titration method.[19]

Experimental Section

Pure water (18 MΩ/cm as supplied by Scientific Products), boiled, and purged with nitrogen to remove carbon dioxide, was used throughout this work. Hydrated metal chlorides (ACS reagent grade) were used as supplied by Fisher and Aldrich. Manganese sulfate monohydrate and aluminum sulfate octadecahydrate (ACS reagent grade) were used as supplied by Fisher and Aldrich, respectively. All titrations were performed under a constant stream of nitrogen gas and in a 25 °C constant-temperature bath. Solutions were titrated gravimetrically with certified 50% w/w NaOH solution as

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Table 1. pK_{sp} Values for M(II)(OH)$_2$ and M(III)(OH)$_3$

| ion	this work	literature value	ref
Al^{3+}	31.21	32.90	20
Fe^{3+}	37.24	38.40	21
Mg^{2+}	9.96	10.74	20
Zn^{2+}	16.35	16.92	20
Co^{2+}	14.18	14.80	20
Ni^{2+}	14.04	14.70	20
Mn^{2+}	11.89	12.72	20

supplied by Fisher. The sodium hydroxide solution was periodically standardized against acidimetric grade potassium hydrogen phthalate obtained from E. M. Science. A Fisher Accumet 1002 pH meter and Fisher combination electrode with automated temperature compensation were used for data collection. The pH meter was calibrated using standard buffer solutions at pH values of 4 and 7. Metal contents were determined on a Perkin-Elmer 5500 ICP using standard solutions from Alfa Æsar as calibrants. ICP samples were diluted in a solution approximate 2.5% in both hydrochloric and nitric acids. Metal determinations were run nine times for each sample.

Solutions were prepared by dissolving sufficient amounts of the di- and trivalent metal chlorides and sodium chloride to yield 250 mL of a solution 0.1 M in M(III), 0.2 M in M(II), and 1.0 M in chloride ion. The metal ions studied included Al^{3+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+}. Every titration was performed at least twice, some many more times, to verify the reproducibility of our results. During the titrations, the 50% NaOH solution was added in amounts varying from 0.4 g during the initial plateau to 0.1 g during the first end point and during the second plateau. A stable pH value was determined using the automated stability function on our pH meter.

For product characterization, separate solutions were titrated to approximately 92% of the required end point for the formation of 2:1 M(II):M(III) LDH. At this point, the solid, nominally M(II)$_2$M(III)(OH)$_6$Cl and excess M(III) hydr(ous) oxide, was collected and washed via centrifuge. Approximately 2 g of this solid was then exposed to 100 mL of a 0.1 M Na$_2$SO$_4$ solution overnight to form the LDH sulfate. These solids were also collected and washed via centrifuge. In the case of the Mn(II):Al(III) system, the LDH chloride was air sensitive and the LDH sulfate was prepared directly for XRD characterization. All products were dried at room temperature in an evacuated desiccator. No aging procedures were used on the solids prior to characterization. Separate titrations were performed on 2:1 Mg(II):Al(III) systems wherein the titration was halted near the midpoint of the second plateau. Samples were collected at this point and the liquor examined for metal content by ICP. One titration was performed on a solution having a Mg:Al ratio of 8:1.

To verify the pH relationships studied here, solutions of the individual metal chlorides were also titrated on their own. These solutions were prepared using the same volume and concentrations as the mixed metal solutions. Sodium chloride was added to create ionic strengths matching those present in the mixed metal titrations, to obtain an internally consistent set of data. As in the case of the LDH themselves, we use concentrations rather than activities throughout for all reagents except OH$^-$, so our results do not correspond to ideal thermodynamic quantities; however, this should not affect the interpretation of trends among related materials. In all cases, moreover, our nominal solubility products for the individual hydr(ous) oxides were in good agreement with literature values, given the differences in conditions, and the expected excess solubility of our rapidly formed, poorly crystalline material (Table 1).

Infrared spectra were collected using a Perkin-Elmer 1760X FTIR spectrometer, with computerized data collection and handling. Spectra were obtained using KBr disks containing approximately 1% sample. Powder X-ray diffraction data were collected on a Scintag XDS2000 using Cu Kα radiation. Powder XRD samples contained approximately 5% CaF$_2$ as an internal standard.
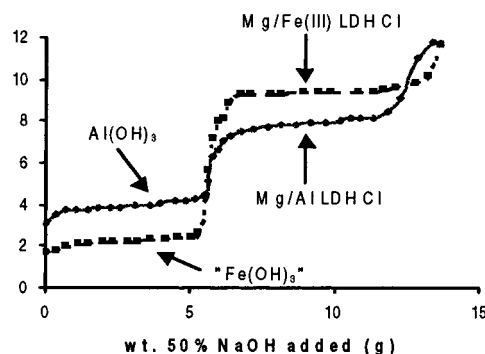

Figure 1. Titration curves of 2:1 MgCl$_2$:AlCl$_3$ and MgCl$_2$:FeCl$_3$ solutions.
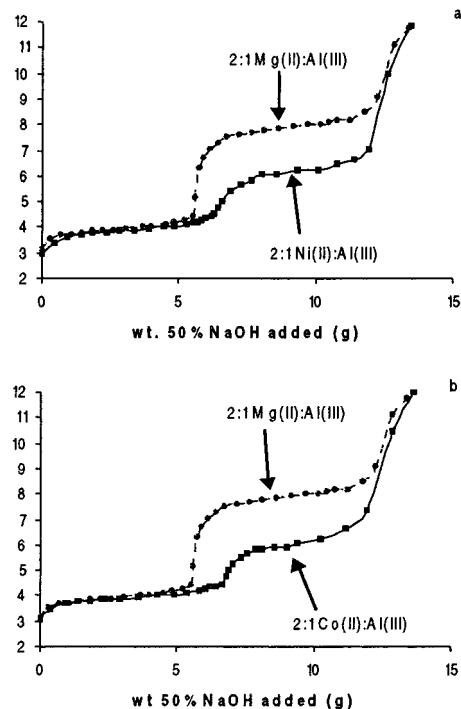
Figure 2. Titration curves of (a) 2:1 CoCl$_2$:AlCl$_3$ and MgCl$_2$:AlCl$_3$ solutions and (b) 2:1 NiCl$_2$:AlCl$_3$ and MgCl$_2$:AlCl$_3$ solutions.

Results and Discussion

The titration curves of the mixed-metal solutions studied here show two distinct buffer regions or plateaus (Figure 1). The transition between these plateaus is generally very sharp. The first, lower pH, buffer region corresponds to formation of the trivalent metal hydroxide or hydrous oxide in the presence of excess M(III)$^{3+}$$_{(aq)}$. The second, higher pH plateau corresponds to formation of the layered double hydroxide from M(III) hydr(ous) oxide in the presence of excess M(II)$^{2+}$$_{(aq)}$. Addition of NaOH past the second end point produces, as expected, a sharp increase in pH associated with the presence of free hydroxide in solution. In some instances, the transition between the two buffer regions is delayed beyond the expected first end point and appears less sharp, phenomena which we attribute to the precipitation of a phase of variable composition. This phenomenon is present in the titration curves of Ni(II):Al(III) and Co(II):Al(III), as seen in Figure 2. In extreme cases, the transition is completely absent and the LDH is formed in preference to M(III)(OH)$_3$ from the start of

the titration, as discussed in the accompanying paper.[22]

The plateau and end point regions are reminiscent of the buffer and end point regions of conventional acid−base titrations. The first plateau corresponds to formation of the trivalent metal hydr(ous) oxide in the presence of excess $M(III)^{3+}_{(aq)}$; the pH of this region should depend only on the activity and identity of the trivalent metal being used and is independent of the identity of the divalent metal, as expected from the equilibrium

$$M(III)^{3+}_{(aq)} + 3OH^-_{(aq)} \rightleftharpoons \text{“}M(III)(OH)_3\text{”} \qquad (1)$$
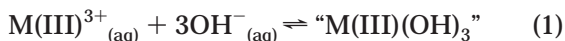
Not only was the form of this region independent of the nature of M(II), but titrations of solutions of the same ionic strength containing only 0.1 M $M(III)Cl_3$ and NaCl showed curves nearly identical with the lower pH portion of a mixed-metal titration curve involving that same M(III). Equilibration in this region was rapid, with a constant pH being reached in a matter of seconds.

Much more information can be gained, however, from the second, higher pH plateau region. In this region, the trivalent metal has been fully precipitated as M(III) hydroxide−hydrous oxide. If further addition of NaOH merely caused precipitation of $M(II)(OH)_2$, the plateau pH would be the same as that for titration of M(II) alone. Such is rarely the case among systems studied. In all the cases described here, the pH of this second plateau is clearly below the pH observed for the corresponding divalent metal alone, showing that the LDH phase is more stable under these conditions than a mixture of "$M(III)(OH)_3$" and $M(II)(OH)_2$. The pH of this LDH formation varies with the identity of both M(II) and M(III), as required by this interpretation:

$$\text{“}M(III)(OH)_3\text{”} + 2M(II)^{2+}_{(aq)} + 3OH^- + Cl^- \rightleftharpoons$$
$$M(III)[M(II)]_2(OH)_6Cl \quad (2)$$
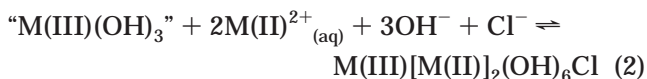
Equilibration in this region is much slower, with a constant pH taking up to 15 min to establish after each addition of hydroxide. This is consistent with a process such as eq 2, involving reaction of a solid rather than a simple precipitation from solution.

Figure 1 shows the titration curves for Mg(II):Al(III) and Mg(II):Fe(III). For each titration, the two buffer regions with the sharp transition can be clearly seen. These curves represent the complete formation of M(III) hydr(ous) oxide, followed by its transformation to the double layer system. As expected from the very low solubility of iron(III) hydr(ous) oxides, the pH of the first plateau for Mg(II):Fe(III) is well below that of Mg(II): Al(III). Correspondingly, the pH of the second plateau for Mg(II):Fe(III) is nearly 0.8 pH units above the second Mg(II):Al(III) plateau (recall that the trivalent metal hydr(ous) oxide is a reactant, not a product, at this second stage) but still 0.5 pH units below the plateau for $Mg(II)(OH)_2$ alone. The titration curves for the Zn-(II):Al(III), Mn(II):Al(III), Zn(II):Fe(III), Ni(II):Fe(III), Co(II):Fe(III), and Mn(II):Fe(III) systems all exhibit

shapes similar to those seen in Figure 1. Figure 2 compares the titration curves for Co(II):Al(III) and Ni-(II):Al(III), respectively, with that of Mg(II):Al(III). In the Co(II):Al(III) and Ni(II):Al(III) systems, the transition from the lower to the higher pH plateau occurs over a range, starting at a point where sodium hydroxide is in excess of the stoichiometric amount necessary for precipitation of aluminum hydroxide. We attribute this to the formation of a variable composition solid, which could be either a solid solution or an adsorbate of M(II)-$(OH)_2$ in $Al(OH)_3$ or a highly Al(III)-rich LDH.

Titration of a solution having Mg(II):Al(III) equal to 8:1 yielded interesting results. In this particular case, the pH of the second plateau remains well below that observed for formation of $Mg(OH)_2$ until the $(OH)^-$:Al-(III) ratio is 8:1, corresponding to a metal ratio Mg(II): Al(III) = 3:1. Addition of base beyond this 3:1 stoichiometry results in a sharp increase in solution pH to a value very near to that for precipitation of $Mg(OH)_2$.

By considering the identity and solubility of the metal hydroxides involved, one can manipulate the pH at which the LDH forms. One can also derive nominal solubility product constants from the solubility of the trivalent metal hydroxide and the pH of the LDH plateau region. Once calculated, these data may be used to quantify the relative stabilities of the layered double hydroxide systems.

We use a simplified model for formation of the layered double hydroxide system to calculate nominal solubility products for our materials. It is assumed that essentially all of the trivalent metal is precipitated as hydr(ous) oxide. Beyond this point, further addition of hydroxide leads to conversion of this hydr(ous) oxide to LDH. This actual process may contain a dependence on the changing charge density of the LDH as it forms, which is ignored in our calculations. The concentration of $M(II)^{2+}$ remaining in solution is inferred on the basis of stoichiometric precipitation of the metal by hydroxide. Given the difficulties of assigning activity coefficients at the high ionic concentrations used, we make no attempt to correct for these. For the purposes of calculation, we assume the simple coexistence of two distinct solid phases, namely "$M(III)(OH)_3$" and $[M(II)]_2M(III)$-$(OH)_6Cl$; this assumption is probably quite realistic for the Mg(II):Al(III) system throughout the second plateau region, but is only valid for those containing Co(II) or Ni(II) and Al(III) under conditions sufficiently far beyond the first end point. Taking these assumptions into consideration, a nominal K_{sp} for the overall dissolution of a layered double hydroxide (as formed under our conditions) into the metal ions, hydroxide, and chloride,

$$M(III)[M(II)]_2(OH)_6Cl \rightleftharpoons$$
$$M(III)^{3+}_{(aq)} + 2M(II)^{2+}_{(aq)} + 6OH^- + Cl^- \quad (3)$$
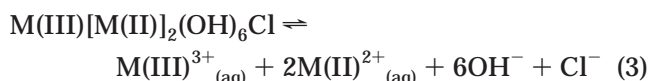
may be inferred from the expression

$$K_{sp,LDH} = K_{sp,M(III)(OH)_3}[M(II)^{2+}]^2[OH^-]^3[Cl^-] \quad (4)$$

We have used both our own nominal K_{sp} values and the corresponding literature values (compared in Table 1) to calculate solubility product constants for the LDH systems described here. In general, our solubilities are

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Table 2. p$K_{sp,LDH}$ Values Inferred for Al(III)- and Fe(III)-Containing LDHs

| p$K_{sp,LDH}$	Mg	Mn	Co	Ni	Zn
			Al^{3+}-Containing		
a	52.12	53.85	57.26	57.79	58.44
b	51.64	53.36	56.77	57.30	57.95
			Fe^{3+}-Containing		
c	54.31	57.14	60.93	60.81	63.84
b	52.99	55.81	59.61	59.49	62.51

[a] Values calculated using $K_{sp,M(OH)_3}$ from ref 20. [b] Using $K_{sp,M(OH)_3}$ as determined in this work. [c] Using $K_{sp,M(OH)_3}$ from ref 21.

somewhat higher than the literature values, as expected for poorly crystalline, initial precipitates and for our use of concentrations for metal ions instead of activities, but these unsurprising differences do not affect our general conclusions.

In addition, the equilibrium constant for reaction 2, the transformation of trivalent metal hydr(ous) oxide to LDH, may be inferred for the second plateau using the expression

$$K_{form,LDH} = \{[M(II)^{2+}]^2[OH^-]^3[Cl^-]\}^{-1} \quad (5)$$

Finally, we note that the equilibrium constant for the reaction

$$M(III)(OH)_3 + 2M(II)(OH)_2 + Cl^- =$$
$$M(III)[M(II)]_2(OH)_6Cl + OH^- \quad (6)$$
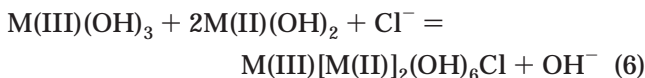
in which a mixture of simple hydroxides that is converted to LDH is given by

$$\log K_{conv,LDH} = \log K_{form,LDH} + 2 \log K_{sp,M(OH)_2} \quad (7)$$

In the second buffer region, pH varied only slowly with the degree of conversion of hydr(ous) oxide to LDH in the region between 30% and 90% conversion. For each titration, therefore, we imposed a linear fit on the data in this region. This fit was then used to calculate a pH value at the 50% conversion point, at which the M(II)$^{2+}$ concentration is 0.1 M. An additional advantage of taking our data from the plateau region is that a small error in the amount of OH$^-$ added does not lead to a large relative error in the inferred concentration of M(II). These inferred pH values were then used with the appropriate concentrations of M(II)$^{2+}$ and Cl$^-$ to obtain the various K values at these points.

Separate titrations were performed on 2:1 Mg(II):Al-(III) solutions which were halted at a point near the midpoint of the LDH-formation plateau. The liquor and resultant solid were separated from each other, and after repeated centrifugation, the liquor was subjected to metal analysis by ICP. The results show no Al(III)$^{3+}$ present in solution and Mg(II)$^{2+}$ values very near the expected 0.1 M value. These results validate our assumption that during the second, higher pH, plateau, we have 2:1 M(II):M(III) LDH forming in the presence of excess M(III) hydr(ous) oxide, since other products would not give the same mass balance.

Results of these calculations are shown in Tables 2 and 3. The values of $K_{form,LDH}$ are derived directly from our experimental LDH data, assuming product stoichiometry, and are independent of the chosen values for the metal hydroxide solubilities, but (as a consequence

Table 3. Inferred Equilibrium Constants for Al(III)- and Fe(III)-Containing LDHs

	Mg	Mn	Co	Ni	Zn
			log $K_{form,LDH}$		
Al^{3+}	20.42	22.15	25.56	26.09	26.74
Fe^{3+}	15.74	18.56	22.37	22.25	25.27
			log $K_{conv,LDH}$		
Al^{3+}	0.50	−1.63	−2.80	−1.99	−5.96
Fe^{3+}	−4.18	−5.22	−5.99	−5.83	−7.43

of this) refer to formation of LDH from our immature "M(OH)$_3$". If desired, a correction can be applied for this using the difference between our K_{sp} values for "M-(OH)$_3$" and those in the literature. $K_{sp,LDH}$ depends, for these materials, on the chosen value of $K_{sp,M(OH)_3}$, while $K_{conv,LDH}$ depends on the chosen value of $K_{sp,M(OH)_2}$. We have, for consistency, calculated our $K_{conv,LDH}$ using our own data for $K_{sp,M(OH)_2}$, so that $K_{conv,LDH}$ and $K_{form,LDH}$ are both relative to immature metal hydr(ous) oxide (and LDH) precipitates. Of the alternatives offered in Table 2, we prefer the values obtained using our own solubility data, since these relate more directly to our conditions for reaction 2.

Titrations were performed on the Mg(II):Al(III) system in the presence of nitrate instead of chloride. The p$K_{sp,LDH}$ and log $K_{form,LDH}$ values obtained from these titrations (51.43 and 20.57) were nearly identical to those inferred from the chloride case (51.64 and 20.42). However, it is known that chloride displaces nitrate from layered double hydroxides, showing that the LDH chloride is more thermodynamically stable than the LDH nitrate. Thus, while our method is able to show differences between the relative stabilities of LDHs of different metals, it is not necessarily sensitive enough to demonstrate thermodynamic stability differences between LDHs of the same metals with differing anions, which must, therefore, be small in comparison.

To verify that the materials produced during the second part of the titration were in fact the desired layered double hydroxides, samples were withdrawn for infrared analysis and their infrared spectra were shown to match those of similar products formed under near-stoichiometric conditions. In addition, the materials were examined by powder XRD and showed the expected[22,23] diffraction patterns of layer materials with basal spacings ranging from 7.38 Å for Zn(II):Al(III) LDH to 7.83 Å for Zn(II):Fe(III) LDH. Finally, the materials were exposed to 0.1 M solutions of sodium sulfate for up to 24 h, to replace Cl$^-$ with $^1/_2$(SO$_4$)$^{2-}$. As expected, the exchanged materials showed new IR bands at 1188, 1109, and 615 cm^{-1}, due to sulfate, and expansion of the interlayer spacings to approximately 9.00 Å, in agreement with literature values.[25] Figure 3 compares the infrared spectra of Co(II):Al(III) LDH chloride and sulfate. The observed XRD spacings for the compounds discussed here, listed in Table 4, are in agreement with the extensive, yet incomplete, data available in the literature.[1-6] Small amounts of carbonate are detectable in the infrared spectra, but compari-

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Figure 3. FTIR spectra of Co(II):Al(III) LDH chloride (a) and sulfate (b).

Table 4. Observed Powder XRD Spacings for Chloride- and Sulfate-Containing LDHs

M(II):M(III)	anion	d_{003}	d_{006}	d_{012}
Mg:Al	Cl^-	7.91	3.92	2.56
	SO_4^{2-}	8.85	4.48	2.56
Zn:Al	Cl^-	7.72	3.88	2.58
	SO_4^{2-}	8.75	4.36	2.58
Co:Al	Cl^-	7.61	3.83	2.59
	SO_4^{2-}	10.51	5.34	2.62
Ni:Al	Cl^-	7.72	3.86	2.54
	SO_4^{2-}	8.82		2.53
Mn:Al[a]	SO_4^{2-}	10.73	5.43	2.45
Mg:Fe	Cl^-	7.60	3.84	
	SO_4^{2-}	8.73	4.42	
Zn:Fe	Cl^-	7.81	3.93	2.65
	SO_4^{2-}	8.73		2.71
Co:Fe	Cl^-	7.89	3.96	2.64
	SO_4^{2-}	8.80		
Ni:Fe	Cl^-	7.87	3.93	2.58
	SO_4^{2-}	8.83		

[a] Material precipitated directly; see the text.

son with fully exchanged carbonate suggests that it amounts to at most 20% of the solids. This carbonate does not affect the mass balances reported in this or the accompanying paper and is, therefore, most probably formed during workup and not during the titrations. In any case, since the carbonate is less soluble than the other materials present, it should not affect our conclusions.

The results of this work show that the relative stabilities of layered double hydroxides and the pH at which they form are related to the stabilities of the corresponding metal hydroxides. For a given M(II), the lower the solubility of $M(II)(OH)_2$, the lower the pH required to form $M(III)[M(II)]_2(OH)_6X$. This is as expected, since the immediate environments of M(II) in LDH and in $M(II)(OH)_2$ are clearly similar. For a given M(III), the lower the solubility of "$M(III)(OH)_3$", the higher the pH required for the formation of the LDH. This is because "$M(III)(OH)_3$" plays the part of reactant, not product, in eq 2. Simple calculations, based on pH

titration data, may be used to calculate the relative stabilities of various layered double hydroxide systems as they form from solution. Thus, the information obtained from such titration curves refers to the stability of this freshly formed precipitate, rather than to the ripened or annealed materials commonly used in the studies of physical properties. However, the XRD, IR, and anion exchange properties of these fresh materials are, apart from the greater XRD line widths resulting from small particle size and order-dependent features in the M$-$O$-$M region,[26,27] almost indistinguishable from those of more mature materials. Generally, the stability of the LDH, relative to its component ions, increases with the stability of both the tri- and divalent metal hydroxides in the order $Al^{3+} < Fe^{3+}$ and $Mg^{2+} < Mn^{2+} < Co^{2+} \approx Ni^{2+} < Zn^{2+}$. LDHs were strongly thermodynamically favored over the separate hydroxides under the conditions studied here (high chloride and low hydroxide ion concentration, the latter being itself a function of the metals), this preference also increasing in the order $Mg^{2+} < Mn^{2+} < Co^{2+} \approx Ni^{2+} < Zn^{2+}$, but being stronger for Al^{3+} than for Fe^{3+}. The pK_{sp} values range from 52.12 for Mg(II):Al(III) to 63.84 for Zn(II):Fe(III). The stabilities of the LDH with respect to solution follow the same trends as the stabilities of the metal hydroxides themselves. Less predictably, this trend is even followed by the stabilities with respect to the separate metal hydroxides.

Finally, we wish to comment on the stability of the LDH relative to mixtures of $M(II)(OH)_2$ and "$M(III)-(OH)_3$." As Table 3 shows, many LDH are, in a sense, less stable than mixtures of simple hydroxides. Reaction 4, however, is driven forward under most conditions of interest by mass action effects, since the concentrations of chloride (or whatever counteranion is used) will usually vastly exceed that of hydroxide. An important exception is the system Mg(II):Al(III). It may be relevant that while many M(II):M(III) combinations are found in naturally occurring LDHs, the Mg(II):Al(III) system is the only one that occurs as a layered double hydroxide, the mineral meixnerite, $[Mg_6Al_2(OH)_{16}(OH)_2\cdot 4H_2O]$.[28] Under strongly alkaline conditions, where hydroxide concentrations begin to approach those of the other ions present, the other LDHs considered here will indeed be unstable relative to the separated metal hydroxides.

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