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Energetic Insight into the Formation of Solids from Aluminum Polyoxocations**

Dana Reusser, William H. Casey, and Alexandra Navrotsky*

Abstract: *The ε-Keggin $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ion ($AlAl_{12}^{7+}$) is a metastable precursor in the formation of aluminum oxyhydroxide solids. It also serves as a useful model for the chemistry of aluminous mineral surfaces. Herein we calculate the enthalpies of formation for this aqueous ion and its heterometal-substituted forms, $GaAl_{12}^{7+}$ and $GeAl_{12}^{8+}$, using solution calorimetry. Rather than measuring the enthalpies of the $MAl_{12}^{7/8+}$ ions directly from solution hydrolysis, we measured the metathesis reaction of the crystallized forms with barium chloride creating an aqueous aluminum solution monospecific in $MAl_{12}^{7/8+}$. Then, the contributions to the heat of formation from the crystallized forms were subtracted using referenced states. When comparing the aqueous $AlAl_{12}^{7+}$ ion to solid aluminum (oxy)-hydroxide phases, we found that this ion lies closer in energy to solid phases than to aqueous aluminum monomers, thus explaining its role as a precursor to amorphous aluminum hydroxide phases.*

The $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ polyoxocation[1] ($AlAl_{12}^{7+}$) in the ε-isomer of the Baker–Figgis–Keggin series[2] is the primary hydrolytic product of partially neutralized aluminum solutions.[1a,2] This ε-$AlAl_{12}^{7+}$ ion is not only an important component in wastewater treatment and catalyst technologies, but also appears to be a key intermediate in the formation of amorphous aluminum oxyhydroxide flocs in polluted streams[3] as the tetrahedrally coordinated $Al(O)_4$ centers can be detected.

Herein we show that the ε-$AlAl_{12}^{7+}$ ion actually lies close in energy to these amorphous oxyhydroxides and other related solids, supporting it as a likely precursor in the formation of these flocs as suggested by Furrer et al.[3] We present the enthalpies of formation using a thermodynamic description independent of formation pathway for this species and other heterometal-substituted forms: $[GaO_4Al_{12}(OH)_{24}$-

$(H_2O)_{12}]^{7+}_{(aq)}$[4] ($GaAl_{12}^{7+}$) and $[GeO_4Al_{12}(OH)_{24}$-$(H_2O)_{12}]^{8+}_{(aq)}$[5] ($GeAl_{12}^{8+}$). Though just applied to aluminum hydroxides, the approach may be useful for other molecular clusters including the newly appreciated prenucleation clusters,[6] if these can be similarly isolated as monospecific solutions.

Instead of estimating formation energetics of the $MAl_{12}^{7/8+}$ ions directly from solution hydrolysis, we used aqueous solution calorimetry to measure the metathesis reaction of the crystallized forms having selenate counterions with barium chloride. Using thermodynamic cycles (see Tables S1–S4 in the Supporting Information), we then calculated the standard enthalpies of formation, $\Delta H°_{f,el}$, for these aqueous $MAl_{12}^{7/8+}$ ions, where $M = Al^{III}$, Ga^{III}, or Ge^{IV}, and used these values to compare their energetics in aqueous exchange reactions. Table 1 summarizes the enthalpies of formation from the elements at 298 K, $\Delta H°_{f,el}$, for each aqueous $MAl_{12}^{7/8+}$ ion.

Table 1: Summary of enthalpy of formation, $\Delta H°_{f,el}$, results for each aqueous $MAl_{12}^{7/8+}$ ion, where $M = Al^{III}$, Ga^{III}, or Ge^{IV}.

ε-$MAl_{12}^{7/8+}$ ion	Stoichiometry	$\Delta H°_{f,el}$ [kJ mol^{-1}]
$AlAl_{12}^{7+}$	$[(AlO_4)Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$	-17067.85 ± 36.90
$GaAl_{12}^{7+}$	$[(GaO_4)Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$	-16809.11 ± 37.41
$GeAl_{12}^{8+}$	$[(GeO_4)Al_{12}(OH)_{24}(H_2O)_{12}]^{8+}$	-16618.59 ± 33.66

As these $MAl_{12}^{7/8+}$ ions contain similar structural features as their parent oxides and hydroxides,[7] collectively this series of heterometal-substituted ions are useful spectroscopic probes for understanding reactions that occur at the mineral-water interface.[8] Isotopic exchange rate data on this series show that the exchange rates of hydroxy bridges are extraordinarily sensitive to heterometal substitution.[9] This finding has led to a proposed mechanism describing oxygen exchange into bridging oxygen atoms as proceeding via partial detachment of aluminum atoms from the internal structural oxygen atoms[8c] to form a dimer-like cap. The extent to which these partially detached intermediates form depends on the heterometal, and proceeds in increasing order from $GaAl_{12}^{7+}$ to $AlAl_{12}^{7+}$ to $GeAl_{12}^{8+}$.[8c]

In previous studies, we examined the energetics of heterometal substitution in the MAl_{12} selenate solids by calculating the enthalpies and free energies of formation for these materials based on solution calorimetric data.[10] While we found the thermodynamic stabilities of the solids corresponded to the order of reactivity at hydroxo bridges in the ions, we could not assess the degree of which differing $MAl_{12}^{7/8+}$ ions interact with the surrounding lattice and influence the resultant enthalpies. Now with the enthalpy values for the
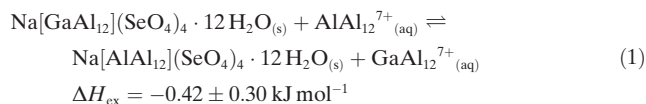
[*] Dr. D. Reusser, Prof. A. Navrotsky
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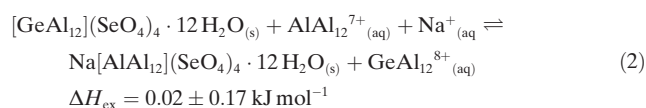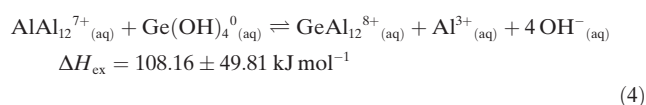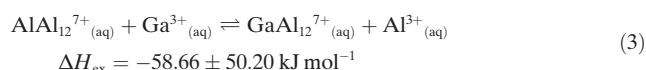Sciences, University of California Davis (USA)

aqueous $MAl_{12}^{7/8+}$ ions, we can examine how these ions affect the energetic stability of the solid forms. Using the calorimetrically measured enthalpies of reaction, ΔH_{rxn}, (see Reaction 1 in Tables S1 and S2) the reaction below [Eq. (1)] calculates the enthalpy of exchange, ΔH_{ex}, between the isovalent MAl_{12}^{7+} aqueous clusters for $M = Al^{III}$ and Ga^{III} and the crystalline forms.

$$Na[GaAl_{12}](SeO_4)_4 \cdot 12\,H_2O_{(s)} + AlAl_{12}^{7+}{}_{(aq)} \rightleftharpoons$$
$$Na[AlAl_{12}](SeO_4)_4 \cdot 12\,H_2O_{(s)} + GaAl_{12}^{7+}{}_{(aq)} \quad (1)$$
$$\Delta H_{ex} = -0.42 \pm 0.30 \text{ kJ mol}^{-1}$$

Likewise, the ΔH_{ex} between the MAl_{12} crystalline selenates and the $MAl_{12}^{7/8+}$ aqueous clusters for $M = Al^{III}$ and Ge^{IV} is calculated [Eq. (2)].

$$[GeAl_{12}](SeO_4)_4 \cdot 12\,H_2O_{(s)} + AlAl_{12}^{7+}{}_{(aq)} + Na^+{}_{(aq)} \rightleftharpoons$$
$$Na[AlAl_{12}](SeO_4)_4 \cdot 12\,H_2O_{(s)} + GeAl_{12}^{8+}{}_{(aq)} \quad (2)$$
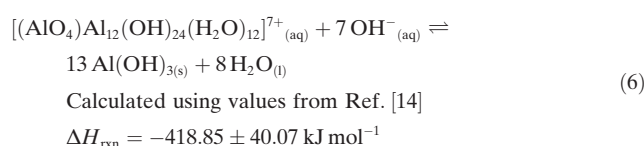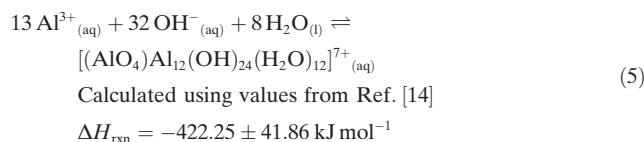$$\Delta H_{ex} = 0.02 \pm 0.17 \text{ kJ mol}^{-1}$$

These enthalpies of exchange, ΔH_{ex}, suggest the $MAl_{12}^{7/8+}$ ions exhibit no preference for either the solid or the aqueous state. Thus the difference in ion charge between the $AlAl_{12}^{7+}$ and $GeAl_{12}^{8+}$ cluster does not seem to influence the observed differences in the enthalpies of these species in the solid form. This suggests that the crystalline materials are good energetic models for the species in solution and vice versa. These new results confirm our previous arguments showing that the order of stability in these $MAl_{12}^{7/8+}$ ions increases from $GeAl_{12}^{8+}$ to $AlAl_{12}^{7+}$ to $GaAl_{12}^{7+}$ and this can also be seen when calculating the enthalpies of exchange, ΔH_{ex}, of one $MAl_{12}^{7/8+}$ ion with another heterometal, such as in Equation (3) and Equation (4). Additionally, because these species are isostructural, or nearly so, these ΔH_{ex} provide a measure for the amount of strain in these ions caused by the presence of different heterometal atoms, Al^{III}, Ga^{III}, or Ge^{IV}, in the tetrahedral site in the molecule. Previously we established these strained sites as a key to their metastability.[9]

$$AlAl_{12}^{7+}{}_{(aq)} + Ga^{3+}{}_{(aq)} \rightleftharpoons GaAl_{12}^{7+}{}_{(aq)} + Al^{3+}{}_{(aq)}$$
$$\Delta H_{ex} = -58.66 \pm 50.20 \text{ kJ mol}^{-1} \quad (3)$$

$$AlAl_{12}^{7+}{}_{(aq)} + Ge(OH)_4^{0}{}_{(aq)} \rightleftharpoons GeAl_{12}^{8+}{}_{(aq)} + Al^{3+}{}_{(aq)} + 4\,OH^-{}_{(aq)}$$
$$\Delta H_{ex} = 108.16 \pm 49.81 \text{ kJ mol}^{-1}$$
$$(4)$$

Unique to the $AlAl_{12}^{7+}$ species, in contrast to the other heterometal-substituted forms, is its capability to polymerize further into a massive $[Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ (Al_{30}) molecule[11] consisting of two δ-Al_{13} units bridged by a tetra-aluminate group. Reasons for this continual progression in the Al^{III} species also appear to be correlated with the nature of the heterometal atom,[9d, 12] where thus far, only the $AlAl_{12}^{7+}$ species has been isolated in other isomers of the Baker–Figgis–Keggin series.[11b, 13] Thermodynamically favorable formation of the $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ polyoxocation from monomeric aluminum aqueous species is generally recognized as likely in solutions to which base is added. Our data confirm

the strongly exothermic nature of this formation reaction [Eq. (5)] and also confirm the metastability of the polyoxocation with respect to the formation of gibbsite (as well as diaspore) as more base is added [Eq. (6)]. The $MAl_{12}^{7/8+}$ polyoxocation is also kinetically inert at the tetrahedral bonding oxygen atoms within the structure, going through numerous exchanges at the exterior with the bulk solution before dissociating or condensing to form solid phases.[9] Thus aggregation and continual evolution of the polyoxocation to form solid phases is an energetically downhill transformation.

$$13\,Al^{3+}{}_{(aq)} + 32\,OH^-{}_{(aq)} + 8\,H_2O_{(l)} \rightleftharpoons$$
$$[(AlO_4)Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}{}_{(aq)}$$
Calculated using values from Ref. [14]
$$\Delta H_{rxn} = -422.25 \pm 41.86 \text{ kJ mol}^{-1}$$
$$(5)$$

$$[(AlO_4)Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}{}_{(aq)} + 7\,OH^-{}_{(aq)} \rightleftharpoons$$
$$13\,Al(OH)_{3(s)} + 8\,H_2O_{(l)}$$
Calculated using values from Ref. [14]
$$\Delta H_{rxn} = -418.85 \pm 40.07 \text{ kJ mol}^{-1}$$
$$(6)$$

To examine the energetic relationship between this $AlAl_{12}^{7+}$ ion and other aluminum oxides and hydroxides, we plot the enthalpy of formation from α-Al_2O_3 and water versus the water content for several aluminum phases, including the $AlAl_{12}^{7+}$ ion in Figure 1. All enthalpies in Figure 1 are normalized to one mole of aluminum.

Unlike monomers of aluminum, for example, $[Al(H_2O)_6]^{3+}{}_{(aq)}$ or $[Al(OH)_4]^-{}_{(aq)}$, which for similar formation reactions have enthalpies of formation from α-Al_2O_3 and water that are positive by 38.0 ± 1.7 and 50.4 ± 2.1 kJ mol^{-1}, respectively, the $AlAl_{12}^{7+}$ polyoxocation lies close in enthalpy to the solid phases. As an aqueous species, however, contribution to stability from entropy may become more significant. While there is no direct measurement of the absolute entropy, $S°$, of the $AlAl_{12}^{7+}$ ion, we can estimate a range of values. Knowing that the entropy of the reaction, ΔS_{rxn}, to form the crystalline $AlAl_{12}$ selenate [Eq. (7)] should
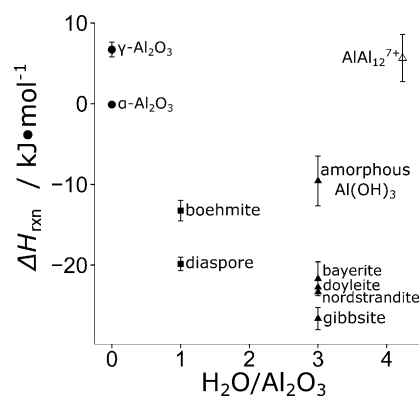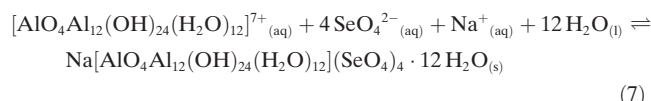

Figure 1. Enthalpy of formation from 0.5 α-Al_2O_3 and water (ΔH_{rxn}) for various Al^{III} phases versus water content. Data from Refs. [14–16]. Error bars are generated from the uncertainties associated with the reaction to form each product from 0.5 α-Al_2O_3 and water. They are calculated as the square root of the sum of squares for the reaction.

be negative and using reference values for the other species in the reaction, we find that the $S°$ of the AlAl$_{12}^{7+}$ should be greater than $+1095.7 \pm 66.3\ \mathrm{J\,mol^{-1}\,K^{-1}}$.

$$[\mathrm{AlO_4Al_{12}(OH)_{24}(H_2O)_{12}}]^{7+}_{\mathrm{(aq)}} + 4\,\mathrm{SeO_4}^{2-}_{\mathrm{(aq)}} + \mathrm{Na^+}_{\mathrm{(aq)}} + 12\,\mathrm{H_2O_{(l)}} \rightleftharpoons$$
$$\mathrm{Na[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SeO_4)_4 \cdot 12\,H_2O_{(s)}}$$

$$(7)$$

Similarly, the decomposition of the AlAl$_{12}^{7+}$ ion to α-Al$_2$O$_3$ and water [Eq. (8)] yielding a positive ΔS_{rxn} constrains the $S°$ to below $+1765.9 \pm 2.2\ \mathrm{J\,mol^{-1}\,K^{-1}}$, thus the $S°$ should fall between $+1095.7 \pm 66.3$ and $+1765.9 \pm 2.2\ \mathrm{J\,mol^{-1}\,K^{-1}}$.

$$[\mathrm{AlO_4Al_{12}(OH)_{24}(H_2O)_{12}}]^{7+}_{\mathrm{(aq)}} \rightleftharpoons$$
$$6.5\,\alpha\text{-}\mathrm{Al_2O_{3(s)}} + 20.5\,\mathrm{H_2O_{(l)}} + 7\,\mathrm{H^+}_{\mathrm{(aq)}}$$

$$(8)$$
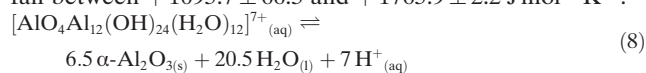
Figure 2 plots the free energy of formation from α-Al$_2$O$_3$ and water in the same manner as with the enthalpy but now incorporating the estimated entropy in the stability of the AlAl$_{12}^{7+}$ polyoxocation. The free energy of formation from α-Al$_2$O$_3$ and water for the monomers, $[\mathrm{Al(H_2O)_6}]^{3+}_{\mathrm{(aq)}}$ and $[\mathrm{Al(OH)_4}]^{-}_{\mathrm{(aq)}}$, puts them even further from the stabilities of the solids with a ΔG_{rxn} equal to $+185.5 \pm 3.4$ and $+77.9 \pm 6.3\ \mathrm{kJ\,mol^{-1}\,K^{-1}}$ respectively. A downhill sequence in free energy from the AlAl$_{12}^{7+}$ ion to amorphous aluminum hydroxide to gibbsite can be inferred from this figure. Figure 2 also suggests an interplay of dehydration events affecting phase formation, where more hydrous, less-crystalline phases appear closest to the stability of the polyoxocation and progressive dehydration proceeds towards more negative free energies of formation and increased crystallinity.

Measuring the heat effect of the metathesis reaction between ε-MAl$_{12}^{7/8+}$ selenates and barium chloride allowed us to calculate $\Delta H°_{\mathrm{f,el}}$ for aqueous ε-MAl$_{12}^{7/8+}$ ions, where M = Al$^{\mathrm{III}}$, Ga$^{\mathrm{III}}$, or Ge$^{\mathrm{IV}}$. We are unaware of this approach being used previously to collect such thermodynamic data on this or other large aqueous polyvalent ions, such as the ε-AlAl$_{12}^{7+}$ species. Indeed this metathesis calorimetry method may be general for studying the enthalpies of formation of dissolved molecular clusters and provides an useful alternative to 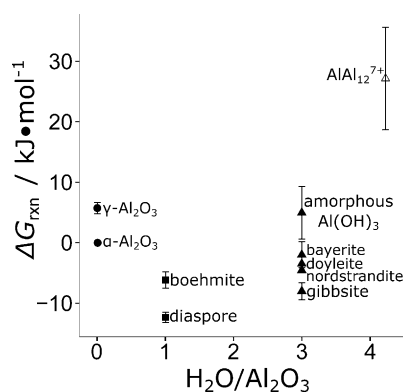collect thermodynamic data for these and many other aqueous species that is independent of formation pathway. Currently our group is working on expanding this approach to other aluminum clusters such as Johansson's aluminum dimer,[17] $[\mathrm{Al_2(OH)_2(H_2O)_8}]^{4+}$, the large aforementioned Al$_{30}$ molecule,[11b,c] $[\mathrm{Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}}]^{18+}$, and the other main class of aluminum hydroxide species—those containing solely octahedrally coordinated aluminum atoms[18].

Experimental Section

A CSC 4400 isothermal microcalorimeter (Calorimetry Sciences Corporation) was used to measure the enthalpies of reaction, ΔH_{rxn}, of the MAl$_{12}$ selenates and reference materials. Solid samples were weighed and mixed with excess BaCl$_2$·2H$_2$O. These mixtures were pelletized and dropped from room temperature directly into 13.00 g of millipore (resistance of 18 MΩ) water held isothermally at 299 K, providing a final molality of 3.16 ± 0.01 mM and a final selenium concentration of 9.55 ± 0.01 μM. Additionally, the amount of added excess BaCl$_2$·2H$_2$O was controlled to 8.05 ± 0.05 mg for each run in all the samples and the sodium selenate reference phase to account for any contribution to the heat effect from solvation of this species in solution. Mechanical stirring was used for the entire duration of the experiment. The calorimeter was calibrated prior to experimentation using the heat effect of KCl (NIST SRM 1655) in deionized water. After each run, the contents of the sample chamber were filtered through a 0.22 μm filter and the precipitate and filtrate were retained for further analysis. Inductively coupled plasma quadrupole mass spectrometry (ICP-MS) for total selenium concentration was run on each filtrate to check for any unreacted MAl$_{12}$ or sodium selenate and powder X-ray diffraction (PXRD) was performed on the collected precipitate to check for undissolved starting materials. PXRD of the precipitate collected from the metathesis reactions was matched to BaSeO$_4$[19] with no additional impurities (Figure S1). The ICP-MS analyses for total selenium concentration showed that all reaction filtrates contained less than 5% residual selenium (Table S5). This confirms that the method used was effective in measuring the metathesis reaction of each selenate with barium chloride. Additional details on the materials characterization and experimental details can be found in the supporting information.

Figure 2. Free energy of formation from 0.5 α-Al$_2$O$_3$ and water (ΔG_{rxn}) for various Al$^{\mathrm{III}}$ phases versus water content. Data from Refs. [14–16]. Error bars are generated from the uncertainties associated with the reaction to form each product from 0.5 α-Al$_2$O$_3$ and water. They are calculated as the square root of the sum of squares for the reaction.

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