

Aquoacidity of cations, in context

When we study basic chemistry, we learn about acids, such as sulfuric and nitric acid. When we at a more advanced level study aqueous geochemistry, we hear about aquoacidity of cations, which seems to be a special or strange form of acidity. The point of this page is to show that the acidity of the common strong acids and the aquoacidity of cations is one and the same thing. To do so, this page looks at acidity in the context of a bit of the periodic table (the gray under-pinnings of the diagram below).

When we study about conventional acidity, we often study about acids with the general

formula H_nXO_m , which in their first dissociation yield H^+ and the conjugate base $H_{n-1}XO_m^{1-}$. In such cases, we can envision the large positive charge of the X atom in the XO_m^{n-} group repelling the H^+ ions that are acidity. Among the acids highlighted below, sulfuric and phosphoric acids would be good examples, with S^{6+} and P^{5+} as the "cations" at their core. As we move to the left to cations of lesser ionic potential, and thus lesser propensity of repel H^+ , we come to Si^{4+} , which we think of as forming a weak acid that we call silicic acid.

When we learn about aquoacidity, we learn about hydrated cations around which water

molecules can lose H^+ ions to form OH^- and thus generate hydroxo complexes. The usual example about which we learn is Al^{3+} , which hydrates to form $Al(H_2O)_6^{3+}$ and then yields aquoacidity by dissociating to $AlOH(H_2O)_5^{2+}$ and H^+ . Further dissociation gets us to $Al(OH)_2(H_2O)_4^{1+}$, $Al(OH)_3(H_2O)_3^0$, etc.

The point of this page is that these two styles of acidity are the same thing in the spectrum from a cation of relatively low ionic potential like Al^{3+} to a cation of very high ionic potential like S^{6+} . In the examples in red below, the upper row of chemical reactions is written as if we were thinking of dissociation of a strong acid like sulfuric acid. The bottom row of reactions is written as if we were thinking of the

aquoacidity of a cation. However, the form is the same throughout: in the top row an acid of the form H_nXO_m dissociates, and in the bottom row a cation coordinated with some combination of H_2O , OH^- , and O^{2-} loses an H^+ ion. The only change across this spectrum is that the cations of lower ionic potential have less power to reject H^+ (they have a smaller K_a and thus larger pK_a) and the cations of greater ionic potential have greater power to reject H^+ (they have a larger K_a and thus smaller pK_a). That change across the spectrum is why we speak of the aquoacidity of Al^{3+} and not "aluminic acid", and why we speak of sulfuric acid and not of "the aquoacidity of S^{6+} ". However, as this shows, it's all the same thing: repulsion of H^+ ions from an $X^{(2m-n)+}$ -centered, H_2O -and/or- OH^- -bearing, chemical entity.

