

# Periodicity in the Acid-Base Behavior of Oxides and Hydroxides

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The oxides and hydroxides for most elements are among their most important compounds. For these compounds the reactions with acids and bases are among the most important ones. And for these reactions we look to the periodic table to reveal some regularities that can facilitate the teaching of fundamental chemistry. Possibly our first (and last?) step is to draw diagonal lines in the table from the upper left to the lower right and to make some broad generalizations in relation to those lines. It may be useful, however, to have a series of graphs that could provide the basis for more precise and varied studies for students.

In this article the aqueous solubilities of many important hydrous oxides and hydroxides are displayed, for the various elements, as functions primarily of pH. These graphs are then arranged in groups to facilitate studies of the effects of oxidation state, electron structure, and position in the periodic table, along with, say, size and coordination number. Some patterns discovered might be superficial, since the present diagrams cannot show the great variety of underlying solution phenomena; however, many uses remain, even, for example, just the estimation of the initial pH of a precipitation.

The graphs show calculated values of solubilities, at or near 25°C and with ionic strength at or near 1.0 M, using equilibrium quotients and constants mainly from Baes and Mesmer<sup>1</sup> and Kragten.<sup>2</sup> (Note that, at least at a pH 0 or 14, the

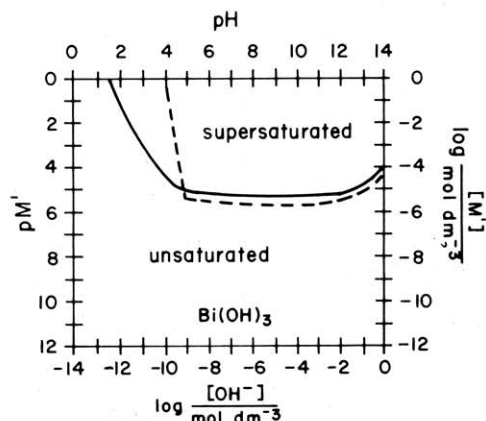


Figure 1. Key to graphs in Figures 2-7.

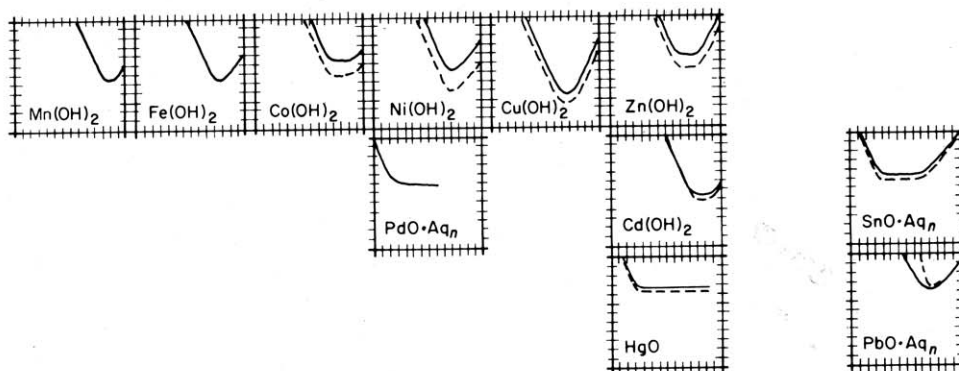


Figure 2. Solubility versus pH graphs for hydroxides and hydrous oxides of elements in oxidation state II.

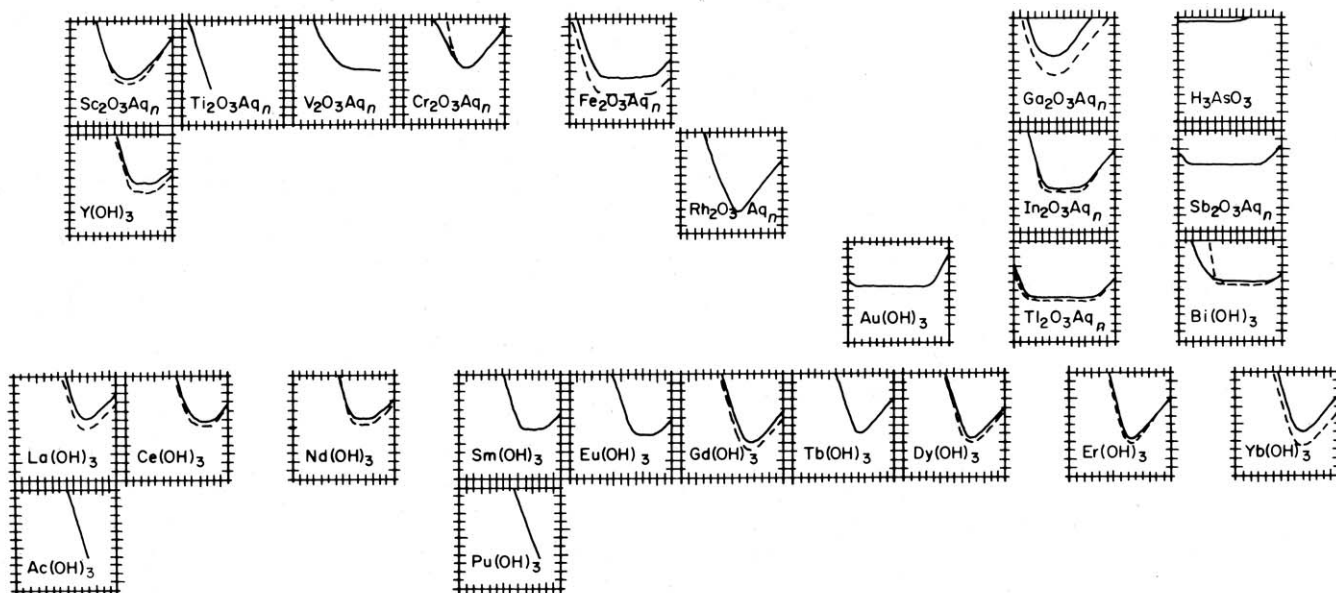


Figure 3. Solubility versus pH graphs for hydroxides and hydrous oxides of elements in oxidation State III.

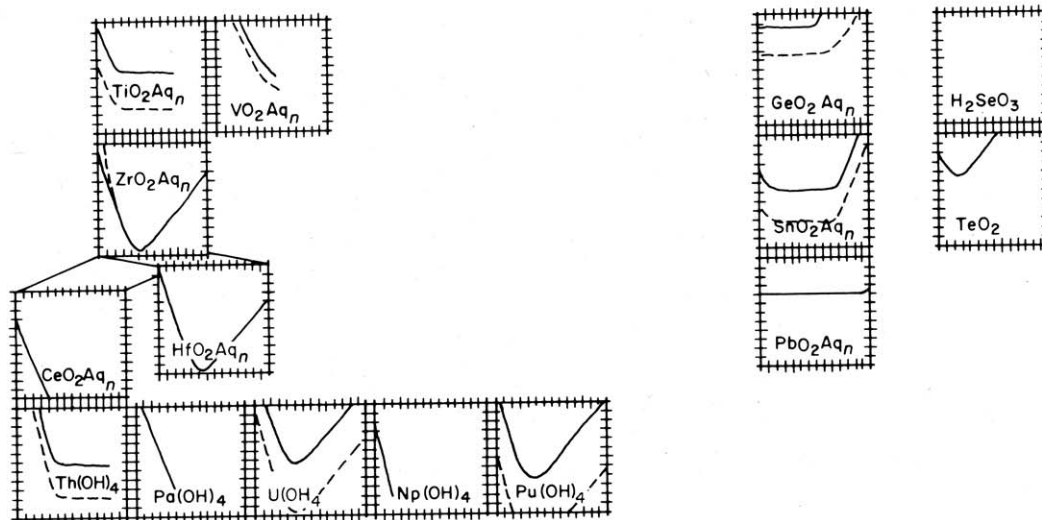


Figure 4. Solubility versus pH graphs for hydroxides and hydrous oxides of elements in oxidation State IV.

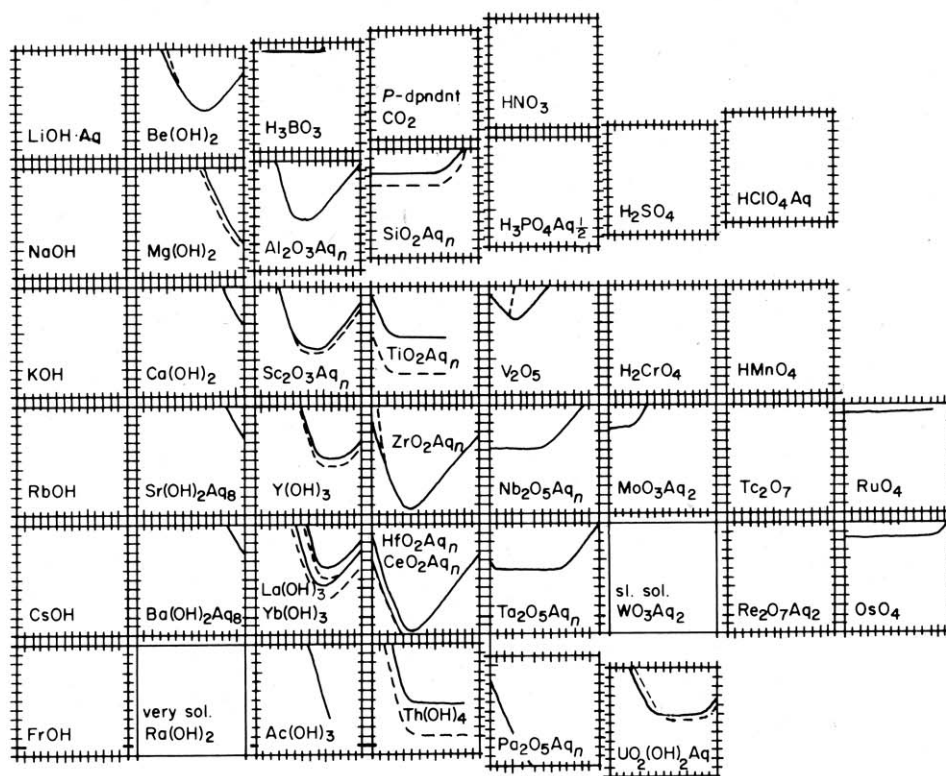


Figure 5. Solubility versus pH graphs for compounds of noble-gas ions.

ionic strength may be at least a bit over 1.0 M, depending on solubility.) The original graphs of concentrations, re-drawn here, were produced by a Tosbac-40 computer and plotter at International Christian University, Tokyo.

Figure 1 is the key. Figures 2, 3, and 4 show the results for oxidation states (II), (III), and (IV), respectively. Figures 5, 6, and 7 concern central "cations" with noble-gas electron structures (Fig. 5), with mainly pseudo-noble-gas structures (Fig. 6), and with "inert" electron pairs (Fig. 7). Aq in the formulas represents (H<sub>2</sub>O). Frames without tick marks indicate inadequate data. Frames with ticks but no curves represent either high solubilities or, for gases, pressure dependency.

Many of the graphs include two curves, and most of these mainly reflect, especially at intermediate pH's, the range of stabilities reported for the solids. The differences result not only from experimental error, however, but frequently also from the lowering of solubility due to the aging of precipitates during the approach to true equilibrium. Thus, the usually upper, solid curves represent more closely the behavior observed in relatively rapid precipitations and changes of pH; they do not include data for soluble polynuclear species, since these equilibrate *comparatively* slowly (but their wide range of rates is not indicated here). The usually lower, dashed curves include all the selected data; they represent the most stable solutions and the most stable solids and, thus, the true

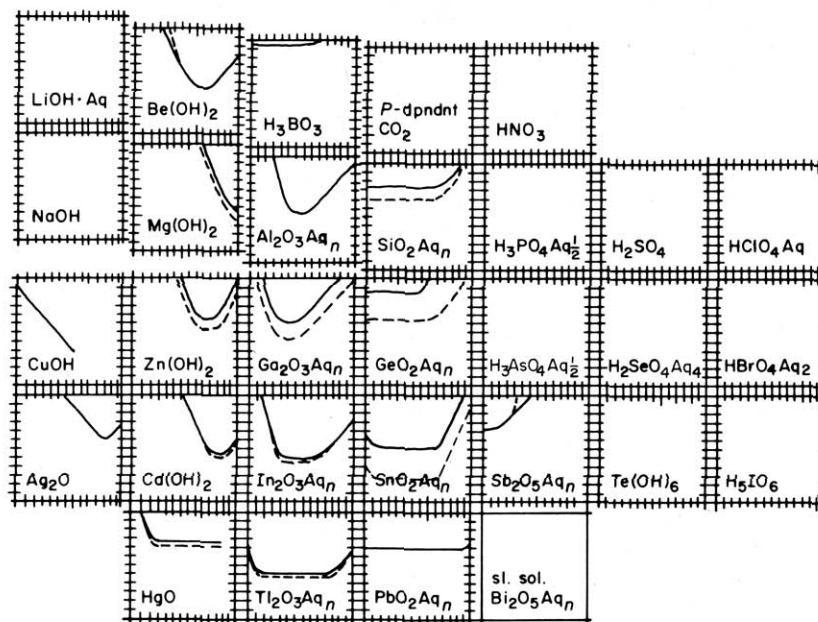


Figure 6. Solubility versus pH graphs for compounds of mainly pseudo-noble-gas ions.

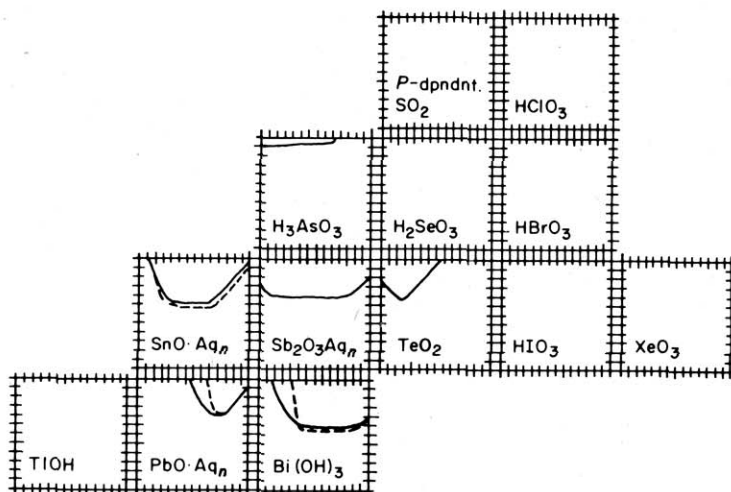


Figure 7. Solubility versus pH graphs for compounds of ions having inert pairs.

equilibria—to the extent that they can be calculated this way. Graphs having single curves likewise include all the chosen data.

The lower curves cross over to become the upper ones in the left-hand regions for Be(II), Pb(II), Cr(III), Bi(III), Zr(IV), and U(VI), and in the right-hand regions for V(V) and Sb(V). The reason is that the soluble polynuclear complexes for which we have equilibrium constant are important enough in these cases to raise the solubilities above those in the other curves. As in any branch of science it would not be surprising if further data were to reveal similar phenomena in other cases. This does not mean that polynuclear complexes are significant only in such cases; they seem in fact to be rather or quite significant more often than not.<sup>1,2</sup> No attempts have been made to correct curves for which additional qualitative, but not suitable quantitative, information is now available.

<sup>1</sup> Baes, Charles F., Jr., and Mesmer, Robert E., "The Hydrolysis of Cations," John Wiley, New York, 1976.

<sup>2</sup> Kragten, J., "Atlas of Metal-Ligand Equilibria in Aqueous Solution," Ellis Horwood (John Wiley), New York, 1978.