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## DEMONSTRATION OF UNSTABLE ANIONIC COMPLEX FORMATION BY THE METHOD OF ELECTROMETRIC TITRATION

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Although the pH value at which the precipitation of a given hydrous oxide or hydroxide occurs is in general independent of the type of anion present, in those instances where the anion is capable of coordinating with the cation, the concentration of the latter may be reduced to such an extent that excessive quantities of alkali must be added to induce precipitation. In other words under these conditions the precipitation pH is appreciably raised, and in instances where the complex is either inherently sufficiently stable or is stabilized by excessive quantities of the added anion, precipitation can be completely inhibited.

Thus it has been demonstrated (1, 2) that not only can the precipitation of hydrous mercuric oxide be completely inhibited by added chloride, bromide, or iodide but also that the dry oxide can itself be dissolved in solutions of the potassium halides with the quantitative liberation of titratable potassium hydroxide. Similar phenomena are encountered with the corresponding cadmium materials (3) although the lesser stabilities of the cadmium complexes necessitate the presence of excessively high quantities of the potassium halides to prevent the precipitation of the hydrous hydroxide.

The effects of anionic complex formation upon subsequent hydroxide precipitation can be readily followed by an electrometric titration technique which involves treatment of the salt solution in question with successive increments of standard alkali, the changes in pH being

followed by means of a suitable glass, quinhydrone, or hydrogen electrode assembly. Displacement of the resultant titration curve toward higher pH values can then be taken as being indicative of complex formation, and the instability of the complex is shown not only by the magnitude of the pH displacement but by the similarity existing between the displaced curve and the normal curve for the uncomplexed cation. Procedures of this sort do not, however, give information as to the structures of any complexes which may arise.

Thus when solutions of such strong electrolytes as lanthanum bromide and neodymium chloride are titrated with alkali in the presence of successively increasing quantities of alkali bromide and chloride respectively, the titration curves show no displacement from those obtained with the pure salts alone even at such high ratios of alkali halide to rare earth halide as one hundred twenty to one. These not unexpected results indicate the complete lack of coordination between the halide and rare earth ions by proving that the concentrations of the lanthanum and neodymium ions are unaffected by added halide.

With the elements immediately following the transition elements in the periodic system, however, anionic complex formation is commonplace as is indicated by the poor conductivities of many of the salt solutions (particularly those of the soluble halides). Thus the inhibitions of oxide and hydroxide formation is mercuric and cadmium salt solutions containing added halides can be

ascribed to the formation of complex anions of the form  $[MX_n]^-$  in accordance with the coordination number of four usually exhibited by these elements.

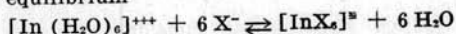
The method of electrometric titration could readily be extended to studies upon the effects upon hydroxide precipitation exerted by similar complexes of many of the elements in this general region of the periodic arrangement. Such an element is indium, halo complexes of which have been indicated by various other methods.

Alkali titrations of indium salt solutions containing added alkali salts indicate displacements of the precipitation regions of the titration curves to higher and higher pH values in the series iodide to bromide to chloride to fluoride, the fluoride thus giving the most stable complex. The weakly coordinating nitrate ion has no effect when added, but the sulfate raises the precipitation region somewhat farther than does the chloride.

That the resultant indium complexes are sufficiently unstable (except with the fluoride) to effect only slight reductions in indium ion concentration is apparent from the fact that only at halide to indium ratios of around one hundred to one do curve displacements become appreciable. Precipitation of hydrous indium hydroxide is completely inhibited by none of these anions, probably because of the instabilities of the complexes and

of the fact that the precipitation pH of the hydroxide is so low at 3.41 (4) that an extremely large pH shift would be necessary.

Inasmuch as the coordination number of indium in its compounds is generally six, anionic complex formation can be regarded as resulting according to the equilibrium



That the equilibrium constants for the reactions in question are small is attested by the excessively large amounts of  $\text{X}^-$  needed to bring about effective equilibrium displacements.

The stabilities of halo anions in general are functions of both the cation and the anion. Thus the order of decreasing stability runs from iodide to fluoride with the members of the "B" families of Periodic Groups I and II but from the fluoride to the iodide in Groups III and IV. The smaller ionic radii of the members of the latter two groups apparently offset the tendency of the more covalent iodide to enter into such complex formation.

#### REFERENCES

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4. Moeller, *J. Am. Chem. Soc.*, 63, 2625 (1941).