On the Hydrothermal Behavior of the Solutions of Some Metal Complexes Observed by Means of Visual Autoclaving

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Visual autoclaving, a method of direct observation of autoclaving process, was worked out for the purpose of following the hydrothermal changes which take place during the course of autoclaving. The method turned out to be very effective, and the principal achievements so far obtained are (1) discovery of new examples of thermochromism,[1-3] (2) establishment of optimum concentration effect in hydrothermal precipitation,[4] (3) synthesis of a new magnetic compound Fe_3S_4, identified with the new mineral *greigite,* thiospinel of iron.[5,6] Study by means of this method is in progress. Some recent results which do not seem to have been reported so far are given in the following.

1. Ethylenediaminetetracetate (EDTA) Complexes. In order to see the effect of EDTA, a representative chelate-forming agent, on the hydrothermal behavior of heavy ions, *ca.* 0.1 M solutions of the chelate complexes of EDTA with bivalent Mn, Co, Ni, Cu, Zn, Pb, Hg and tervalent Fe were subjected to autoclaving at 200°C for one

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hour.[*1] No noticeable change was observed in the solutions except in that of Hg(II) complex. No thermochromism was observed in the solutions of the complexes of Co(II), Ni(II) and Cu(II). This behavior is different from that of the simple salts of these bivalent metals, indicating the higher hydrothermal stability of the complex compounds. The stabilization caused by EDTA is particularly notable in the case of the Fe(III) complex, if we recall the fact that the solutions of the simple salts as well as those of the cyano-complexes of Fe(II) and of Fe(III) undergo decomposition above 100°C.7)

A peculiar decomposition takes place in the case of Hg(II) complex. The colorless and transparent 0.1 M solution changes into a white suspension at 130°C. Coagulation is accelerated with the rise of temperature, and the suspension separates finally into two phases, *viz.* the shining Hg drops at the bottom and the brown supernatant liquid. Contrary to this, the 0.1 M solution of $HgCl_2$ remains intact at 200°C. This suggests that chelate formation diminishes the hydrothermal stability of the solution. In connection with this, it should be mentioned that the formation of metallic gold takes place when a Au(III) salt reacts with EDTA at room temperature.8)

II. Halogeno-complexes of Some Noble Metals. In order to study the hydrothermal stability of noble-metal complexes, the 0.01 M and 0.1 M solutions of the following compounds were autoclaved up to 200°C and the resulting change was observed: Hexachloroplatinic(IV) acid $H_2[PtCl_6]$, potassium hexachloroplatinate(IV) $K_2[PtCl_6]$, tetrachloroauric(III) acid $H[AuCl_4]$, potassium tetrachloroaurate(III) $K[AuCl_4]$. It was found that all the solutions are thermochromic. The yellow color of these solutions turns red above 140°C. The change is enhanced with the rise of temperature. On cooling the colorations return to the original state. The change is thus reversible with respect to temperature.

The cause of the thermochromism might be attributed to the partial reversible hydrolysis of these chloro-complexes. We realize the facts herewith that the color of the solution of platinum(IV) chloride $H_2[Pt(OH)_2Cl_4]$ changes from greenish yellow to orange red with the progress of hydrolysis and that the solution of gold(III) chloride $H[Au(OH)Cl_3]$ is reddish yellow.9) We see thus that the thermochrmomism of these noble-metal complexes and that of the solutions of Co(II), Ni(II) and Cu(II) chlorides are caused by different mechanisms. In the latter case, the cause is attributed to the formation of chloro complexes at elevated temperatures.

It should be added that the solutions of potassium tetrachloroplatinate(II) $K_2[PtCl_4]$ and potassium tetrachloropalladate(II) $K_2[PdCl_4]$ are both unstable above 100°C, and dark brown precipitates are formed at *ca.* 150°C.

[*1] The general formulas of the reagents: $Na_2Me^{II}(EDTA)\cdot 3\text{-}4H_2O$, $NaFe^{III}(EDTA)\cdot 2{-}3H_2O$. "Dotite" products were used.

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