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AURUM (V) FLUORIDES REACTIONS WITH WATER AND THEIR THERMOCHEMISTRY.

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The enthalpies of reactions in water of solid $Ba(AuF_6)_2 \cdot 4KrF_2$ and $Ba(AuF_6)_2$ were measured at 298.2 K using an air tight liquid isotermal calorimeter. These enthalpies were used to obtain an alternate set of formation standard enthalpies for these compounds.

The analogous to these measurings for ${\rm AuF}_5$ and ${\rm MAuF}_6$ (M=Na, K, Rb) and also ${\rm AuF}_3$ were conducted earlier. Recommended values for ${\rm \Delta H^O}_{\rm f298}$ mentioned solid fluorides are: ${\rm AuF}_5 = -413.2 \pm 5$; ${\rm NaAuF}_6 = -1094.5 \pm 6.5$; ${\rm KAuF}_6 = -1158.8 \pm 6.5$; ${\rm RbAuF}_6 = -1145.2 \pm 6.5$; ${\rm AuF}_3 = -473.4 \pm 5$ kJ·mole⁻¹. For ${\rm \Delta H^O}_{\rm f298}$ Au(OH) $_3$ was decided the value -433 ± 6.5 kJ·mole⁻¹.

All compounds were prepared by fluorination of gold in ${\rm KrF}_2$ in solutions in HF (Kel-F reactor). ${\rm Ba(AuF_6)}_2\cdot 4{\rm KrF}_2$ was prepared in conditions of a large excess of ${\rm KrF}_2$.

It is interesting to note that the reaction AuF_5 in water and aqueous sodium hydroxide (0.05 N) went to precipitation of metallic gold, for example:

 $AuF_5 + 3.475H_2O = 0.35Au_{(s)} + 0.65Au_{(OH)_3(s)} + 5HF_{(sol)} + 0.7625O_{2(g)}$ $\Delta H_{298} = -491.9 \pm 1.6 \text{ kJ} \cdot \text{mole}^{-1}$

The separate measurements gave values of ~2442 \pm 15 and ~3132 \pm 15 kJ·mole⁻¹ for $\Delta {\rm H^0}_{\rm f298}$ Ba($\Delta {\rm uF_6}$)₂ and Ba($\Delta {\rm uF_6}$)₂·KrF₂ respectively, yielding.

 $Ba(AuF_6)_2 + 8H_20 = BaF_2(s) + 2Au(OH)_3(s) + 10HF(sol) + O_2(g)$ $\Delta H_{298} = -729\pm6 \text{ kJ} \cdot \text{mole}^{-1}$

 $Ba(AuF_6)_2 \cdot 4KrF_2 + 12H_20 = BaF_2(s) + 2Au(OH)_3(s) + 18HF(sol) + 3O_2(g) + 4Kr(g)$ $\Delta H_{298} = -1548 \pm 10 \text{ kJ} \cdot \text{mole}^{-1}$

The reaction enthalpy of the process $\mathrm{AuF_{3(s)}} + \mathrm{F_{2(g)}} = \mathrm{AuF_{5(s)}}$ was estimated. $\mathrm{AuF_{5}}$ was synthesised by this reaction.