THE CALORIMETRY OF SOME XENON FLUORIDE COMPLEXES

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The enthalpies of solution in water and in 1-M alkali of the complexes $XeF_2.CrF_4$ and $XeF_2.VF_5$ have been measured, and from the results the enthalpies of formation are estimated to be -1438 and -1673 kJ mol^{-1} respectively. The values imply that $XeF_2.CrF_4$ is formed slightly endothermally from XeF_2(c) and CrF_4(c), whereas $XeF_2.VF_5$ is formed exothermically with respect to XeF_2(c) and VF_5(ℓ); this result is consistent with the existence of $XeF_2.VF_5$ in the vapour phase.

Measurement of the enthalpy of hydrolysis of $XeF_2.MnF_4$ in 1-M alkali gives a value of Δ(hydr.) of -720 kJ mol^{-1}, from which the enthalpy of formation of the compound is estimated to be -1288 kJ mol^{-1}. $XeF_2.MnF_4$ is, therefore, formed exothermally from XeF_2(c) and MnF_4(c).

The complex $XeF_6.CrF_4$ hydrolyses violently in water; the stoichiometry of the reaction is nearly in accordance with the equation:

$$3XeF_6.CrF_4 + 15H_2O \rightarrow 3CrO_3aq + 30HFaq + 2Xeaq + XeO_3aq + \tfrac{3}{2}O_2$$

From the enthalpy of hydrolysis (-660 kJ mol^{-1}) the enthalpy of formation of the complex is estimated to be about -1620 kJ mol^{-1}, which implies that for the reaction $CrF_4(s) + XeF_6(s) \rightarrow XeF_6.CrF_4$, $\Delta H \cong 0$.