Formation and thermal stability of neodymium hydroxychloride

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It is well known [1,2] that rare earth (RE) chlorides $LnCl_3$ form various hydrates with water which give on heating oxychlorides LnOCl and hydroxychlorides $Ln(OH)_2Cl$. All these compounds are very important for chemistry and technology of RE metals, because they are intermediate products in the metallurgy of these metals using a relatively low-temperature chloride technology. Thus on heating of $LnCl_3$ hydrates in order to obtain the necessary anhydrous chlorides, a complex system is formed that includes several solid phases, as well as a gas phase containing water vapour and hydrogen chloride in various ratios. In order to understand the chemical processes in such a complex system, the method of chemical thermodynamics can be effectively used, but this requires sufficiently reliable thermodynamic information about all the components of this system. Work [1] presents the results of a detailed study of formation and decomposition of the chloride hydrates and hydroxychloride of neodymium – one of the most widely used rare earth metal (strong magnets). The hydroxychloride decomposition temperature according to the reaction

$$Nd(OH)_2Cl(s) \leftrightarrow NdOCl\ s + H_2O(g)$$

was determined by the DTA method in the atmosphere of Ar, it is equal to 376 ° C.

However, the water vapour pressure was unknown in this case, apparently, it was very low. Its heat of decomposition, equal to 98.2 kJ /mol, was obtained by the DSC method. However, the latter value differs significantly from the value, corresponding to its enthalpy of formation, found in the dissertation work [2] by the method of dissolution calorimetry. In addition, the analysis of chemical equilibria carried out in [1] did not give an answer to the most important question – by which reaction and at what temperatures the intermediate compound $Nd(OH)_2Cl$ is formed. Therefore we recalculated the equilibria of $Nd(OH)_2Cl$ formation and decomposition reactions. These calculations are based on 2 experimental values: $\Delta H°_{649}$ of reaction (1), equal to 98.2 kJ /mol [1], and the decomposition temperature (669 K) of $Nd(OH)_2Cl$ at the water vapour pressure equal to 1 atm [3]; the approximate value of reaction (1) $\Delta Cp°$ (– 7.3 J/mol•K) was also used. These calculations may be useful for planning and explaining the results of subsequent scientific and technological investigations of such RE systems.

References

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