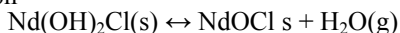


Formation and thermal stability of neodymium hydroxychloride

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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 $\text{Ln}(\text{OH})_2\text{Cl}$. 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



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 $\text{Nd}(\text{OH})_2\text{Cl}$ is formed. Therefore we recalculated the equilibria of $\text{Nd}(\text{OH})_2\text{Cl}$ formation and decomposition reactions. These calculations are based on 2 experimental values: $\Delta H^\circ 649$ of reaction (1), equal to 98.2 kJ/mol [1], and the decomposition temperature (669 K) of $\text{Nd}(\text{OH})_2\text{Cl}$ at the water vapour pressure equal to 1 atm [3]; the approximate value of reaction (1) ΔCp° (– 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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