Thermodynamics of the Pt-Cl System

Z.I. Semenova, V.A. Titov[C, S] and T.P. Chusova
A.V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia
tv@che.nsk.su

Modern technologies of platinum affinage and secondary raw materials processing aimed at extracting noble metals are based on specific features of platinum chlorides. The phase diagram of the system Pt-Cl was studied. Using: the static method with diaphragm zero-pressure gauges; the method of phase tempering with following x-ray diffraction analysis; the differential thermal analysis, we have proved existence three individual compounds in this system: $PtCl_4$, $PtCl_3$ and $PtCl_2$. The results of other authors about existence PtCl were refuted. For the first time it was established that high - temperature modification $PtCl_2$ undergoes reversible monotropical phase transformation at 665 K and with the thermal effect 170 J/mol. The dissociation of platinum chlorides has studied. The dissociation pressure was equilibrated for a very long time; hence, we could approach the equilibrium only from the side of lower pressures. The approximating equations for the temperature dependences on the dissociation pressure were found. The enthalpies and entropies of dissociation were calculated. Using the running calorimeter we were measured the heats of platinum chloride reduction. We were calculated the heats of formation and the enthalpies of platinum chlorides dissociation, using the heats of platinum chlorides reduction and the heat of formation of HCl(g). Based on an analysis of the obtained tensimetric and calorimetric data we have proposed the set of key thermodynamic characteristics of platinum chlorides at 298.15 K: standard enthalpies of formation, $kJ \cdot mol^{-1}$ (-136.3, -194.1, - 246.3) and absolute entropies, $J \cdot mol^{-1} \cdot K^{-1}$ (100.9, 117.7, 150.4) of $PtCl_2$, $PtCl_3$ and $PtCl_4$ correspondingly.