THERMOCHEMICAL PROPERTIES OF SOME METHANESULFONATES OF TRANSITION METALS

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This work continues the systematic investigation of the thermodynamic properties of methanesulfonic acid's salts. It is devoted to the study of the thermochemical properties of $Mn(CH_3SO_3)\cdot 2H_2O$, $Co(CH_3SO_3)\cdot 4H_2O$ and $Ni(CH_3SO_3)\cdot 4H_2O$. Methanesulfonates of 3d-metals can be used in their electrodeposition and extraction of manganese, cobalt and nickel from spent lithium-ion batteries and alloys containing these elements. Data on their enthalpies formation are necessary for correct modeling of phase equilibria.

Manganese methanesulfonate was obtained via reaction of $MnCO_3\cdot Mn(OH)_2$ and CH_3SO_3H in an aqueous solution. Tetrahydrates of nickel and cobalt methanesulfonates $Co(CH_3SO_3)\cdot 4H_2O$ and $Ni(CH_3SO_3)\cdot 4H_2O$ were synthesized according to the substitution reaction of barium methanesulfonate in an aqueous solution. The obtained samples were identified by X-ray, ICP-OES and TG analysis.

The thermochemical properties of methanesulfonates were investigated by method of solution calorimetry. The enthalpies of solution of $Mn(CH_3SO_3)\cdot 2H_2O$, $Co(CH_3SO_3)\cdot 4H_2O$ and $Ni(CH_3SO_3)\cdot 4H_2O$ were measured in water at 298.15 K in calorimeter Parr 6755 (Parr Instrument Company). The temperature rise in each run was measured by resistance thermometer (Parr 6772). The thermometric sensitivity was $2\cdot 10^{-4}$ K. The enthalpies of formation of methanesulfonates at 298.15 K were calculated on the basis of the experimental data and $Mn^{2+}(aq)$, $Co^{2+}(aq)$, $Ni^{2+}(aq)$ and $SO_3CH_3^-(aq)$ enthalpies of formation. The results are presented in Table. The enthalpy of formation of methanesulfonate ion in solid state was estimated according to the Mostafa's scheme on the basis of the obtained data for all studied methanesulfonates.

Thermochemical properties of methanesulfonates at 298.15 K

Sample	$\Delta_{sol}H^o_{298.15}$, $kJ\cdot mol^{-1}$	$\Delta_fH^o_{298.15}$, $kJ\cdot mol^{-1}$
$Mn(CH_3SO_3)\cdot 2H_2O$	–24.1 ± 0.5	–2138 ± 9
$Co(CH_3SO_3)\cdot 4H_2O$	–6.3 ± 0.4	–2564 ± 9
$Ni(CH_3SO_3)\cdot 4H_2O$	–15.6 ± 0.3	–2552 ± 9

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