STUDY OF THE SUBLIMATION AND VAPORIZATION OF ALKALI METAL PERTECHNETATES, $MTcO_4$ (M = K, Cs)

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Volatility data on ^{99}Tc(VII) compounds are of high importance for two main reasons. The first is the understanding of Tc behavior in the procedures of radioactive wastes vitrification. The second is the basis for estimating of possible environmental contamination during accidental nuclear reactors. The data on the Tc rejects from Chernobyl accident are sometimes contradictory [1] and indicate the importance of more systematic study of sublimation and volatilization of different ^{99}Tc species under high temperature conditions. Among the Tc compounds, the volatility of oxides is the best studied. At low concentrations of Tc formation of TcO_3 was postulated [2], while at relatively high concentrations, Tc forms Tc_2O_7 with high volatility starting from 100^{o}C. Some kinetic data are available on oxidation of Tc metal [3] and sublimation of ÒñÎ$_3$ from UO_2 ceramics [4]. Volatile Tc oxides and hydroxides are discussed in [5]. The data on sublimation of $KTcO_4$ at 1000 $^{\hat{i}}$Ñ without decomposition is due to terminology misusing in [6] (in fact they observed evaporation) because the congruent fusion temperature of $KTcO_4$ is 803 K [7]. For $NaTcO_4$ and $CsTcO_4$ fusion points are at 1063 K [8] and 863 K [9] correspondingly. Considerable information is found on volatility of Tc during radioactive wastes vitrification [10, 11, 12]. Data on the volatility of Tc salts are limited by few works: evaporation rate for $NaTcO_4$ was reported to be 0.37 mg$*$cm$^{-2}*$min^{-1} at 700 $^{\hat{i}}$Ñ and increased to 3.2 mg$*$cm$^{-2}*$min^{-1} at 1050 $^{\hat{i}}$Ñ [13]. Kuranov with co-authors has determined by effusion mass-spectrometry from Knudsen camera that ΔH_{evap} ($KTcO_4$) = 213 kJ/M and ΔH_{evap} (($KTcO_4$)$_2$) = 282 kJ/M [14]. Gibson has confirmed that evaporation gives gaseous $KTcO_4$ and ($KTcO_4$)$_2$ in vacuum at 500 - 550 ^{o}C [15].

We studied the high-temperature evaporation of $MTcO_4$ (M= K, Cs) from chemically pure compounds by thermogravimetry analyses (TGA) using a Q-1500D derivatograph (system F.Paulik-J.Paulik-L.Erday) in 300 – 1300 K temperature region. Dynamic and quazi-isothermal modes were used. Some experiments were also carried out by effusion mass-spectrometry (EMS).
In TGA tests (with lower sensitivity if compared to EMS), no evaporation of solid $KTcO_4$ and $CsTcO_4$ from crucible was noted. The detectable changes in the $KTcO_4$ and $CsTcO_4$ sample masses

were noted only after 995 K and 950 K correspondingly (that means after salt fusion) while the Tc_2O_7 oxide is known to exhibit noticeable volatility even at 475 K.

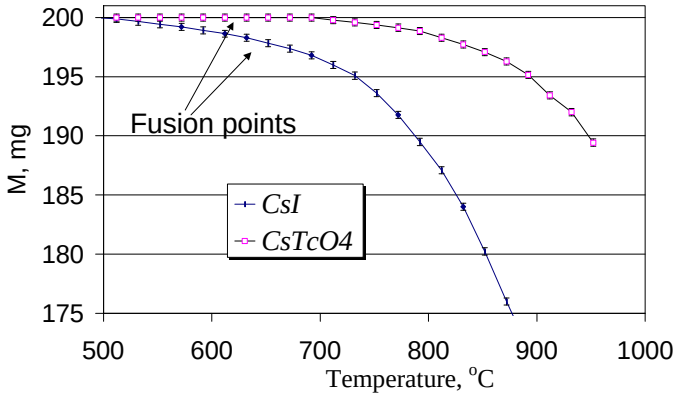

Fig.1. Experimental thermogrammes of CsTcO4 and CsI in dynamic TGA mode (pre-fused samples, temperature increase rate 10 deg/min, sample evaporating surface 1 cm^2, initial sample mass 200 mg)

X-ray diffraction test of the rest in the crucible was done after evaporation 20% of the sample. The patterns were identified as identical to initial compounds, i.e. $KTcO_4$ and $CsTcO_4$. The same composition was found by X-ray diffraction after condensation of vapors. The $KTcO_4$ and $CsTcO_4$ evaporation rate increase monotonically with temperature. For comparison similar tests were caried out with CsI sample (Fig. 2).

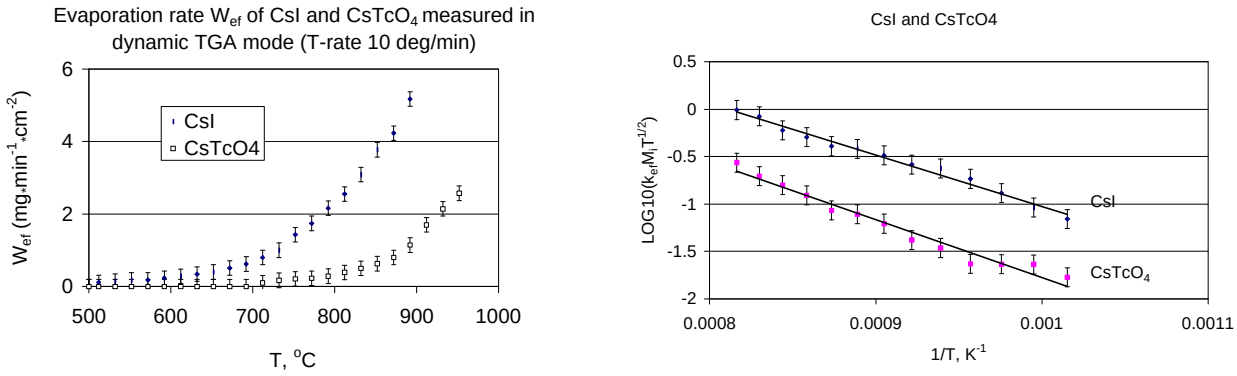

Fig.2. Evaporation rate and its linearization for fused salt sample of CsI and $CsTcO_4$ in dynamic TGA mode (pre-fused samples, temperature increase rate 10 deg/min, sample evaporating surface 1 cm^2, initial sample mass 200 mg)

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