
Thermochemistry of gaseous ruthenium compounds in case of severe accident in a nuclear pressurized water reactor

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Résumé

During a severe accident in a pressurized water reactor with an air ingress in the core fuel, ruthenium compounds can be released in large amount through oxides formation. Regarding nuclear safety, ruthenium compounds are high radio-contaminants which are important at short and medium time scale. In case of outside releases, the behavior of ruthenium tetroxide (RuO₄), highly volatile, is of great importance and has to be well understood and modelled. The outside releases evaluation is greatly uncertain due to a lack of data. One point of improvement is to consolidate the thermochemical data (ΔH_o298K, S_o298K, Cp=f(T)) relative to gaseous Ru oxides, hydroxides and oxy-hydroxides. One mean is to use quantum chemistry tools combined with statistical thermodynamics to get such parameters.

This work deals with the determination of geometrical parameters as well as of thermodynamics for ruthenium-containing species [RuO_x (x = 1-4) and RuO_y(OH)_z (y,z ≤ 3)].

In order to find a suitable methodology, we performed on target species DFT calculations with Gaussian 09 code, using TPSS and TPSSh functional with basis set aug-cc-pVXZ (X=T,Q,5) and the CBS extrapolation. The ruthenium atom was described by the pseudopotential ECP28MDF. We found structural and geometries parameters which allow us to calculate entropies and Cp. Standard enthalpies of formation of ruthenium gaseous oxides at 298 K have been calculated from four reactions. Results are compared to post HF theory CCSD(T). In addition, due to ruthenium multireference states, multireference configuration interactions: MRCI, AQCC, ACPF, CASPT2, NEVPT2 and QDNEVPT2 were also performed in dual level method to evaluate correlation and spin orbit effect with MOLPRO software. Data obtained are discussed and compared to the few available data in literature. These thermodynamic data will be used to simulate the results of experimental tests dedicated to the transport of Ru through RCS conditions.

Mots-Clés: ruthenium, thermochemistry, nuclear, oxides

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