LETTERS TO THE EDITOR

COMMENTS ON "THERMODYNAMICAL CALCULATIONS ON THE BEHAVIOR OF GASEOUS IODINE SPECIES FOLLOWING A HYPOTHETICAL SEVERE LIGHT WATER REACTOR ACCIDENT"

In their paper,[1] Hahn and Ache reported the results of equilibrium chemical calculations on fission product iodine (and cesium) and control rod material silver and argued that AgI is the most abundant iodine-containing species in the temperature range near 1700 K. Although this paper is valuable in that it warns against the neglect of AgI in similar analyses, the stability of AgI is overstated by mistakes in handling thermodynamic data (H_f and S_f). By comparing their data set (Table I in Ref. 1) with their original data book,[2] we can indicate where the mistakes exist (see Table I).

In their analysis, the thermodynamic values for nine species are defined based on inconsistent sets of reference states. For seven compounds that include CsI and AgI, the reference states chosen are silver, cesium, I_2, H_2, and O_2 (all gaseous states at 2000 K except for silver for which the gaseous state at 2437 K is the reference state). It follows that, to be consistent, H_f and S_f must be zero for these elemental species. For cesium, however, finite values have been used that are presumed to be enthalpy and entropy changes for the solid-to-gas phase change at 298 K. Furthermore, for silver, integral enthalpy and entropy changes from 298 to 2437 K have been used.

TABLE I

Enthalpies and Entropies of Formation at 2000 K

Species	Original Data		Corrected Data	
	ΔH_f^0 (kJ/mol)	ΔS_f^0 (J/mol·K)	ΔH_f^0 (kJ/mol)	ΔS_f^0 (J/mol·K)
Silver	333.18	175.4	0.0	0.0
Cesium	76.65	91.1	0.0	0.0
Iodine	78.90	54.2	78.90	54.2
H_2	0.0	0.0	0.0	0.0
O_2	0.0	0.0	0.0	0.0
AgI	−205.11	−53.8	−193.51	−47.2
CsI	−228.90	−13.7	−228.90	−13.7
HI	−6.76	6.8	−6.96	6.8
H_2O	−252.67	−58.3	−252.67	−58.3
CsOH	---	---	−333.35	−85.9

The overstated stability of AgI in their calculation results from overstatement of the instability of elemental silver due to this inconsistency in reference states. The composition of the species was recalculated by SOLGASMIX-PV (Ref. 3) and MPEC (Ref. 4) using the corrected set of H_f and S_f data. The result was that CsI was always found to be more abundant than AgI under their compositions of elements. If CsOH is included, an important species they have neglected, the abundance of AgI increases, but CsI remains the most abundant.

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