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CHEMICAL THERMODYNAMICS OF COMPLEX SYSTEMS: FISSION-PRODUCT BEHAVIOR IN LWR FUEL ELEMENTS

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CHEMICAL THERMODYNAMICS OF COMPLEX SYSTEMS:

FISSION-PRODUCT BEHAVIOR IN LWR FUEL ELEMENTS

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ABSTRACT

A detailed thermodynamic assessment has been made of the chemical reactions of fission products in LWR fuel rods. Using recent thermodynamic data and the in-reactor oxygen potential and temperature range of LWRs, equilibrium thermodynamic calculations were performed for the most plausible reactions of the fission products. The emphasis in this model is on the chemistry of cesium and rubidium and their reactions with the fuel, other fission products, and the zircaloy cladding. The model predictions are discussed for their implications in fuel-cladding interactions.

INTRODUCTION

It is commonly agreed [1] that the presence of both stress and an aggressive environment is necessary to induce cladding failure in LWR fuel rods. Thus, the nature of the chemical environment in the vicinity of PCI-failures (Pellet-Clad-Interaction) is probably the key to interpreting the mechanisms involved in such failures. In order to do this, it is necessary to consider the reactions of the fission products with each other, the fuel, and the zircaloy cladding.

Large amounts of oxygen and fission products are generated during irradiation of the fuel rods. Since the affinity of the fission products for oxygen is less than for uranium (the rare earths form more stable oxides; but they form solid solutions with UO_{2+x} and will not exist as separate phases), the large excess of oxygen ensures that not all of it is combined with the fission products. Thus, the chemical states of the fission products will be effectively set by the oxygen potential ($\Delta\bar{G} = RT\ln p_{O_2}$) of the system. Furthermore, for a reaction to occur, migration of the fission products across the fuel to the cladding must take place. In the presence of the strong temperature gradients in the fuel rod (2500K at the centerline, 600K at the cladding), volatile fission product species will migrate to the cladding. Hence, the oxygen potential and the temperature are the two key parameters in the subsequent thermodynamic analysis.

A preliminary thermodynamic model has been published previously [2]. The purpose of this paper is to present a more detailed analysis of fission product reaction behavior in LWR fuel rods.

Using recent thermochemical data (Appendix 1) and the in-reactor oxygen potential range of LWR fuel rods, -100 to -130 kcal/mol [3,4], equilibrium thermodynamic calculations were performed for complex reactions of the fission products. The emphasis here is on the chemistry of cesium and rubidium, since cesium (and, to a lesser extent, rubidium) has always been observed in the fuel-cladding gap. In addition, these elements form a number of very stable compounds. This suggests that the chemical activity of other aggressive fission products such as iodine and bromine [5], tellurium and selenium [6], and, possibly, molybdenum [7], may well be determined by cesium and rubdium.

COMPOSITION OF THE VAPOR

As Cs(g) and Rb(g) are released from the fuel during irradiation, they could react with oxygen to form the various oxides. It is assumed that the partial pressure of cesium, p_{Cs}, is less than its vapor pressure at the cladding temperature, approximately 10^{-2}atm. Thus, for $p_{Cs} = 10^{-2}$ atm, the partial pressures of the other oxide species in the vapor are estimated to be

$$p_{Cs_2O} = 1.17 \times 10^{-27} \text{atm}$$

$$p_{CsO} = 1.61 \times 10^{-23} \text{atm} \quad .$$

Similar values can be estimated for the rubidium oxide species in the vapor. The partial pressure of rubidium, p_{Rb}, is assumed to be in the same ratio to p_{Cs} as the ratio of their fission yields, that is, $p_{Rb} \sim 10^{-3}$ atm. Hence, the equilibrium form of the vapor will be

predominantly elemental Cs and Rb.

REACTIONS WITH THE FUEL

Cs(g) and Rb(g) can react with the fuel to form a series of uranates [8]. At the oxygen potentials of interest in LWRs (-100 to -130 kcal/mol), the uranates most likely to form are $Cs_2UO_4(s)$, $Cs_2U_2O_7(s)$, and possibly $Cs_2U_4O_{12}(s)$, according to the reactions:

$$2Cs(g) + UO_2(s) + O_2(g) = Cs_2UO_4(s) \quad (1)$$

$$2Cs_2UO_4(s) = Cs_2U_2O_7(s) + 2Cs(g) + \frac{1}{2}\ O_2(g) \quad (2)$$

$$2Cs(g) + 4UO_2(s) + 2O_2(g) = Cs_2U_4O_{12}(s) \quad (3)$$

The partial pressures of Cs(g) associated with these reactions have been calculated for oxygen potential and temperature conditions typical of the fuel-cladding gap and are shown in Table 1.

Inspection of the values for p_{Cs} suggests that $Cs_2UO_4(s)$ and $Cs_2U_2O_7(s)$ are most likely to form. However, the activity of $Cs_2U_2O_7(s)$ is estimated to be negligible and $Cs_2UO_4(s)$ should be the principal uranate. Figure 1 shows isobars for Cs(g) in the $Cs_2UO_4(s)$ + $UO_{2+x}(s)$ system. This suggests that significant pressures of cesium will develop only in the immediate vicinity of the fuel periphery. The pressure decreases dramatically across the gap.

The oxygen potentials associated with the formation of $Cs_2UO_4(s)$ and for $UO_{2+x}(s)$ are shown in Fig. 2 for a cesium pressure of 10^{-2} atm. This diagram provides an extremely effective basis for comparing the stability of the various compounds. For oxygen potentials above the Cs_2UO_4-line in Fig. 2, $Cs_2UO_4(s)$ is stable as a separate phase.

Table 1. Partial Pressures of Cs(g) Associated with Uranate-Forming Reactions

Compound	Temp K	p_{Cs} (atm) at $\Delta G(O_2)$ kcal/mol -110	-130
Cs_2UO_4	600	3.7×10^{-13}	1.6×10^{-9}
	1000	7.2×10^{-4}	0.11
$Cs_2U_2O_7$	600	1.5×10^{-17}	6.3×10^{-15}
	1000	1.0×10^{-6}	1.2×10^{-5}
$Cs_2U_4O_{12}$	600	8.0×10^{-7}	15.5
	1000	17.5	4.1×10^{8}

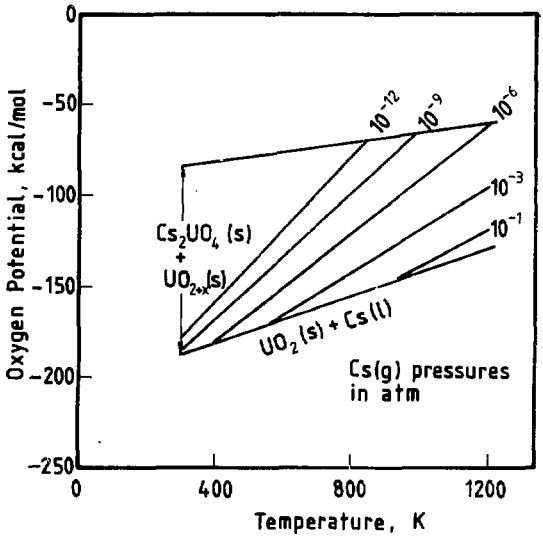

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Fig. 1. Oxygen potential as a function of temperature for the $UO_{2+x}(s) + Cs_2UO_4(s)$ region with isobars of Cs(g).

The behavior of Rb(g) in the $Rb_2UO_4(s) + UO_{2+x}(s)$ system is similar and the pressures of rubidium are estimated to be less than 10^{-3} atm in the fuel-cladding gap. Also, the oxygen potentials associated with the formation of $Rb_2UO_4(s)$ are shown in Fig. 3, which can also be used to compare the stabilities of the various rubidium compounds.

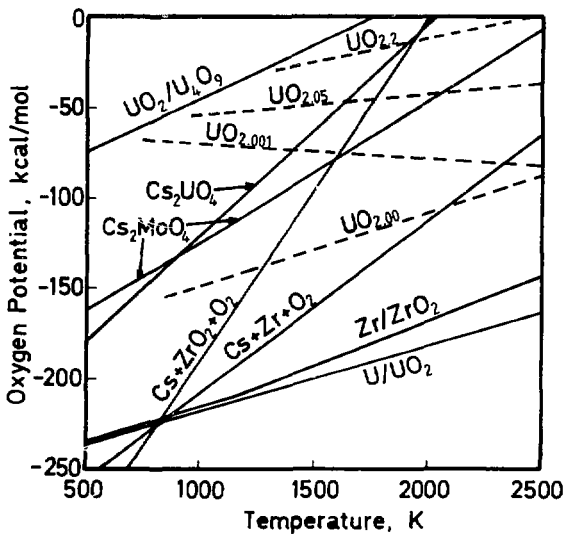

Fig. 2. Oxygen potentials associated with the formation of various ternary cesium compounds for a cesium partial pressure of 10^{-2} atm.

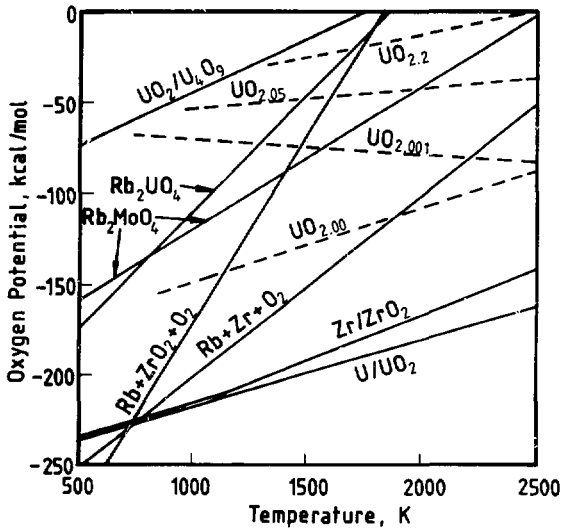

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Fig. 3. Oxygen potentials associated with the formation of various ternary rubidium compounds for a rubidium partial pressure of 10^{-3} atm.

FORMATION OF MOLYBDATES

Cesium and rubidium form a number of molybdates [9]. As in the case of the uranates, Cs_2MoO_4(s) and Rb_2MoO_4(s) are the most probable compounds formed at the oxygen potentials and temperatures of interest. All other molybdates are calculated to have very low

activities. The oxygen potentials associated with the formation of $Cs_2MoO_4(s)$ and $Rb_2MoO_4(s)$ are also shown in Figs. 2 and 3, respectively. Inspection of the values indicates that at higher temperatures (>900K) the molybdates are more stable than the uranates. This suggests that comigration of cesium and molybdenum as $Cs_2MoO_4(g)$ from the hot center to the fuel-cladding gap will occur (the volatility of $Rb_2MoO_4(s)$ is not known, but it is assumed to behave similarly). However, condensed phase $Cs_2MoO_4(s)$ or $Rb_2MoO_4(s)$ is less stable than the corresponding uranates, thereby suggesting that the latter will be the predominant phases in the vicinity of the fuel-cladding gap. On the other hand, for Cs(g) or Rb(g) pressures less than 10^{-10} atm the molybdates are more stable than the uranates over the entire temperature range, as Figs. 4 and 5 show.

FORMATION OF ZIRCONATES

Fission-product Zr reacts with oxygen in the fuel rod to form a very stable oxide, $ZrO_2(s)$, which also forms a solid solution with $UO_{2+x}(s)$. Even so, its high yield suggests that Zr and/or ZrO_2 might also react with Cs(g) and Rb(g) to yield the respective zirconates:*

$$2Cs(g) + Zr(s) + \frac{3}{2} O_2 = Cs_2ZrO_3(s) \quad (4)$$

$$2Cs(g) + ZrO_2(s) + \frac{1}{2} O_2 = Cs_2ZrO_3(s) \quad (5)$$

* The compound Rb_2ZrO_3 is known [10] but Cs_2ZrO_3 has not been described in the literature. Post-irradiation examination of spent LWR fuel rods [4,11] has shown the presence of a Cs-Zr-O compound in the fuel-cladding gap. We, therefore, assume that Cs_2ZrO_3 can exist.

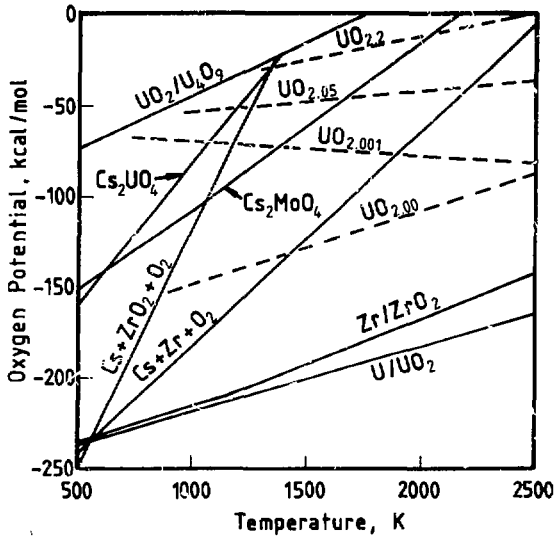

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Fig. 4. Oxygen potentials associated with the formation of various ternary cesium compounds for a cesium partial pressure of 10^{-6} atm.

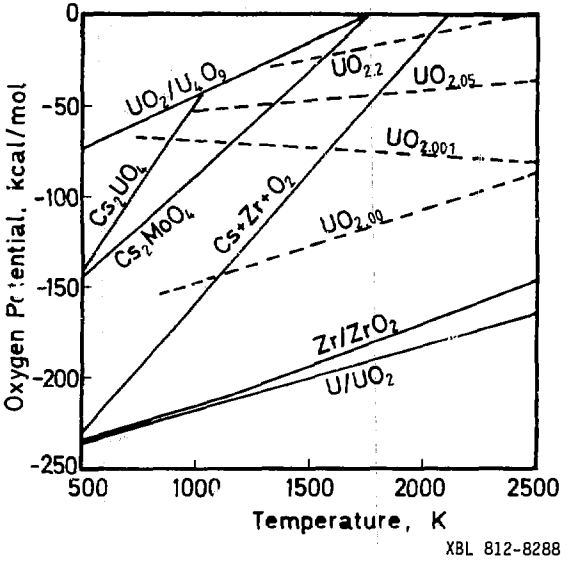

Fig. 5. Oxygen potentials associated with the formation of various ternary cesium compounds for a cesium partial pressure of 10^{-10} atm.

Using the estimated values in Appendix 1, the oxygen potentials for both reactions were calculated and are shown in Figs. 2 and 3. Clearly, the formation of zirconates is thermodynamically more favorable than either the uranates, or the molybdates at temperatures below 1500K. On the other hand, the zirconates are only likely to exist as

separate phases at oxygen potentials below -220 kcal/mol and temperatures below 800K, conditions unlikely to be found in the fuel rod. The situation in the fuel-cladding gap, however, is favorable to zirconate formation: even for p_{Cs} of the order of 10^{-6} or 10^{-10} atm, $Cs_2ZrO_3(s)$ is more stable than either $Cs_2MoO_4(s)$ or $Cs_2UO_4(s)$ (see Figs. 4 and 5). Thus, Cs or Rb reaching the inner surface of the cladding will react to form the respective zirconates, which should also be the predominant phases in the fuel-cladding gap.

REACTIONS WITH IMPURITIES IN THE FUEL

Two manufacturing impurities in the fuel, Al_2O_3 and SiO_2, could strongly affect the chemistry of cesium and rubidium. Calculations of the oxygen potentials associated with the formation of $CsAlO_2(s)$/ $RbAlO_2(s)$ and $Cs_2SiO_3(s)$ were performed using the estimated values in Appendix 1 and these are shown in Fig. 6 for the cesium compounds. A comparison of the values in Figs. 2 and 6 shows that only $Cs_2SiO_3(s)$ is more stable than $Cs_2UO_4(s)$ or $Cs_2MoO_4(s)$, but less than $Cs_2ZrO_3(s)$ {the aluminates are unstable above 1373K [12]}. This suggests that deliberate additions of Si or SiO_2 to the fuel might inhibit Cs(g) and Rb(g) migration. The simultaneous presence of Al_2O_3 and SiO_2 in the fuel could well lead to the formation of the complex aluminosilicate, $CsAlSi_2O_6$. Calculations using recent thermochemical data for $CsAlSi_2O_6$ [13], however, showed that its stability is comparable with that of $Cs_2SiO_3(s)$. Thus, simultaneous addition of Al or Al_2O_3 to the fuel would not enhance the effectiveness of Si or SiO_2 in inhibiting the migration of cesium and rubidium.

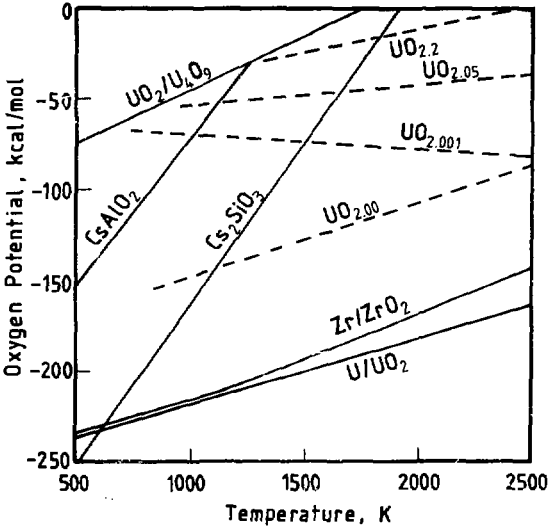

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Fig. 6. Oxygen potentials associated with the formation of $CsAlO_2(s)$ and $Cs_2SiO_3(s)$ for a cesium partial pressure of 10^{-2} atm.

Table 2 compares the stabilities of all the ternary cesium compounds based on equilibrium cesium partial pressures for typical temperatures and oxygen potential conditions existing in the fuel-cladding gap.

Table 2. Partial Pressures of Cs(g) Associated with Various Ternary Compounds

Compound	Temp K	p_{Cs}(atm) at $\Delta\bar{G}(O_2)$ kcal/mol -110	-130
Cs_2UO_4	600	3.7×10^{-13}	1.6×10^{-9}
	1000	7.2×10^{-4}	0.11
Cs_2MoO_4	600	3.8×10^{-19}	7.3×10^{-12}
	1000	3.9×10^{-6}	9.2×10^{-2}
Cs_2ZrO_3	600	5.1×10^{-40}	1.5×10^{-34}
(from Zr)	1000	6.9×10^{-19}	1.3×10^{-15}
$CsAlO_2$	600	3.2×10^{-5}	2.1×10^{-5}
	1000	1.2	13.8
Cs_2SiO_3	600	1.7×10^{-14}	1.2×10^{-12}
	1000	3.8×10^{-9}	1.1×10^{-4}

REACTIONS WITH THE HALOGENS

The fission yields of the halogens are significantly less than Cs and Rb, and all the fission-product iodine and bromine are expected to be tied up as the respective halides, which are among the most stable compounds known. In the strong temperature gradient, the halides will evaporate from the hot center and condense in the cooler fuel-cladding

gap. In this case the partial pressures of gas-phase iodine species can be calculated for the $Cs_2UO_4(s) + UO_{2+x}(s) + Zr(s) + CsI(s)$ system. The results of one such calculation for an oxygen potential of -130 kcal/mol are shown in Fig. 7. Clearly, the predominant equilibrium species should be CsI(g), the pressures of the other iodine-bearing species are negligibly small.

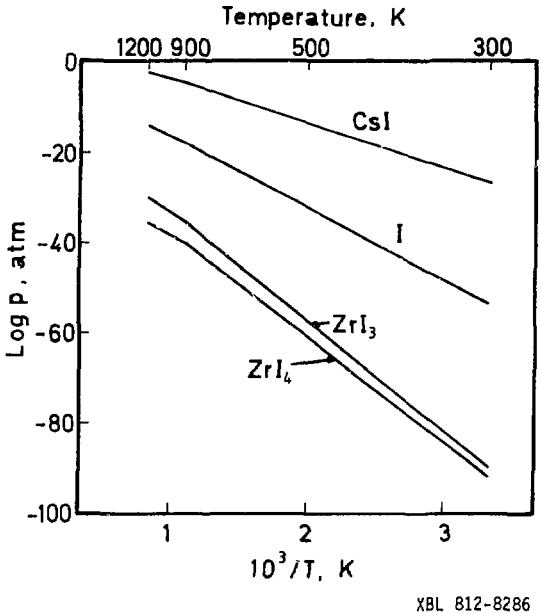

Fig. 7. Partial pressures of various iodine-bearing species as a function of temperature for conditions in the fuel-cladding gap.

The thermodynamics of reaction of the halides with zircaloy are unfavorable, since for the reaction

$$4CsI(s) + Zr(s) = 4Cs(g) + ZrI_4(s) \quad (6)$$

the calculated thermodynamic activity of $ZrI_4(s)$ is about 10^{-40} for cesium partial pressures as low as 10^{-10} atm. If, however, as suggested in the literature [1] iodine (and, possibly, bromine) is an active agent in the PCI failure of zircaloy cladding, its activity at the cladding inner surface must be sufficient to cause such failure. In the fuel-cladding gap iodine may be generated by the reaction

$$CsI(s) + \frac{1}{2}\ O_2(g) + \frac{1}{2}\ UO_2(s) = \frac{1}{2}\ Cs_2UO_4(s) + I(g) \quad (7)$$

from which the iodine partial pressure can be calculated to be 10^{-21} atm at 600K for an oxygen potential of -110 kcal/mol, large enough for monolayer iodine coverage of the zircaloy cladding [14]. Whether this is sufficient to cause the observed PCI-failures in fuel rods is still an open question. Peehs et al [15] have found in laboratory tests that solid iodides on the zircaloy surface are involved in stress corrosion cracking (SCC) and that the minimum surface concentration required for SCC is about 3×10^{-6} grams iodine per square centimeter area. This represents about 30 monolayers of iodine over the entire surface. Some recent research [16] has shown that iodine SCC of zircaloy will not occur below iodine partial pressures of 10^{-8} atm. On the other hand, radiolytic decomposition of CsI(s) might liberate sufficient iodine to enhance the activity at the cladding inner surface, although there is evidence that no iodine

is released from CsI(s) crystals exposed to a γ-radiation field in a liquid cesium source with $p_{Cs} \sim 10^{-9}$ atm [17]. Further, rubidium will also be actively competing for both iodine and bromine, so that supposedly the activity of the halogens at the cladding inner surface will be even lower. Hence, it seems highly unlikely that the halogens play a major role in PCI failures.

REACTIONS OF THE CHALCOGENS

As in the case of the halogens, the large excess of cesium (and rubidium) should tie up fission-product tellurium and selenium as the respective chalcogenides. However, these compounds may be thermally unstable above 1000K [18]. On the other hand, with the exception of the rare earths and the alkaline earths, other fission-product chalcogenides are thermodynamically much less stable. Thus, tellurium and selenium should migrate in the elemental state to the fuel-cladding gap.* However, lack of thermodynamic information on complex chalcogenides makes detailed predictions about the chemical state of these elements difficult. Te and Se are very reactive towards zircaloy [6] and may be potentially embrittling. Their role in PCI failure is probably a minor one, but needs to be defined more closely.

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* The rare earths and the alkaline earth metals form very stable oxides [2] and are not expected to be available to transport tellurium and selenium. However, recent evidence [18] from post-irradiation examination of mixed-oxide fuel indicates that barium and tellurium comigrate, possibly as Ba-Te-O compound.

Based on the above analysis, it is suggested that cesium and rubidium as they are generated will react with the fuel, halogens, molybdenum, and possibly, fission-product zirconium. Since there are no significant gaseous species in the Cs-U-O or Rb-U-O systems, cesium and rubidium are expected to migrate as the halides and the molybdates to the fuel periphery. Tellurium and selenium should migrate there in their elemental states. In the fuel-cladding gap a number of solid phases will be present. Whether under in-reactor conditions such a chemical environment in the gap is entirely favorable to PCI failure of zircaloy cladding needs to be explored further. The halogens appear to play a relatively minor role in PCI failure and currently accepted mechanisms based on iodine-induced cracking need to be reevaluated. The deliberate addition of Si or SiO_2 to the fuel might inhibit cesium and rubidium migration to the cladding.

Though the analysis as proposed here is comprehensive, it is based on equilibrium calculations using mainly room temperature thermochemical data. For more accurate calculations, data on most of the complex fission-product compounds is needed in the temperature range 300-1000K. A research program has been initiated to obtain high temperature thermodynamic data on cesium and rubdium chromates, molybdates, zirconates, and the chalcogenides. First results appear to be in good agreement with the sparse data available in the literature.

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REFERENCES

1. F. Garzarolli, R. von Jan, and H. Stehle, "The Main Causes of Fuel Element Failure in Water-Cooled Power Reactors," At. Energy Rev., 17, (1979) 31.

2. R. Kohli, "Ein thermodynamischer Beitrag zum Verständnis des Vielstoff-systems Urandioxid-Spaltprodukte-Zircaloy," Report No. SGAE-3014, Austrian Research Center Seibersdorf, Austria, December 1978 (in German).

3. M. G. Adamson, E. A. Aitken, S. K. Evans, and J. H. Davies, "Oxygen Redistribution and its Measurement in Irradiated Oxide Fuels," p. 59 in Proc. Symp. Thermodynamics of Nuclear Materials 1974, International Atomic Energy Agency, Vienna, 1975.

4. H. Kleykamp, "The Chemical State of LWR High Power Rods Under Irradiation," J. Nucl. Mater., 84 (1979) 109.

5. B. Cox, "Environmentally Induced Cracking of Zirconium Alloys," Rev. Coatings Corros., 1 (1975) 367.

6. R. Kohli, "Reaction Behavior of Zircaloy with Simulated Fission Products," Report No. LBL-12069, Lawrence Berkeley Laboratory, University of California, January 1981.

7. R. Kohli and F. Holub, "Effects of Simulated Fission Products on the Mechanical Properties of Zircaloy-2," Nucl. Technol., 48 (1980) 70.

8. D. C. Fee and C. E. Johnson, "Phase Equilibria in the Cs-U-O System in the Temperature Range from 873 to 1273K," J. Inorg. Nucl. Chem., 40 (1978) 1375.

9. H. R. Hoekstra, "The Cs_2MoO_4-MoO_3 System," Inorg. Nucl. Chem. Letters, 9 (1973) 1291.

10. R. Hoppe and K. Seeger, "Zur Kenntnis des Rb_2PbO_3Typs: Über Rb_2ZrO_3, Rb_2ZnO_3 and Rb_2TbO_3," Z. anorg. allgem. Chemie, 375 (1970) 266.

11. J. Bazin, J. Jouan, and N. Vignesoult, "Behavior and Physico-Chemical State of Fission Products in Fuel Elements for Pressurized Water Reactor," Trans. Am. Nucl. Soc., 20 (1975) 235.

12. G. Langlet, "Synthèse et étude cristallographique des composés du système Cs_2O-Al_2O_3-SiO_2, "Report No. CEA-R-3853, COMMISSARIAT A L'ENERGIE ATOMIQUE, France, May 1969 (in French).

13. R. Odoj and K. Hilpert, "Mass spectrometric study of the evaporation of crystalline compounds in the Cs_2O-Al_2O_3-SiO_2 system. 1. The synthetic compound $CsAlSi_2O_6$ and the mineral pollucite," High Temp-High Press., 12 (1980) 93.

14. D. Cubicciotti, R. L. Jones, and B. C. Syrett, "Chemical Aspects of Iodine-Induced Stress Corrosion Cracking of Zircaloys," in Proc. 5th ASTM Intern. Conf. on Zirconium in the Nuclear Industry, Boston, Massachusetts, August 1980.

15. M. Peehs, F. Garzarolli, R. Hahn, and E. Steinberg, "Diskussion möglicher Mechanismen von PCI-Defekten," J. Nucl. Mater., 87 (1979) 276.

16. Private communication, D. R. Olander, University of California, Berkeley, January 1981.

17. D. Cubicciotti and J. H. Davies, "Release of Iodine from Iodide Salts by Gamma Radiolysis," Nucl. Sci. Eng., 60 (1976) 314.

18. Private communication, H. Kleykamp, Kernforschungszentrum Karlsruhe, West Germany, January 1981.

19. CODATA Recommended Key Values for Thermodynamics, April, 1978, ICSU Central Office, Frankfurt/Main, West Germany.

20. I. Barin, O. Knacke, and O. Kubaschewski, Thermochemical Properties of Inorganic Substances, Springer-Verlag, New York, 1973 and 1977.

21. D. R. Hull and H. Prophet, Project Directors, JANAF Thermochemical Tables, 2nd ed., NSRDS-NBS 37, National Bureau of Standards, 1971.

22. O. Kubaschewski and C. B. Alcock, Metallurgical Thermochemistry, 5th ed., Pergamon Press, New York, 1979.

23. J. L. Settle, G. K. Johnson, and W. N. Hubbard, "The Enthalpy of Formation of Dicesium Monoxide (Cs_2O)," J. Chem. Thermodynamics, 6 (1976) 263.

24. H. E. Flotow and D. W. Osborne, "The Heat Capacity of Dicesium Monoxide (Cs_2O) from 5 to 350K and the Gibbs Energy of Formation to 763K," J. Chem. Thermodynamics, 6 (1979) 135.

25. E.H.P. Cordfunke and P.A.G. O'Hare, The Chemical Thermodynamics of Actinide Elements and Compounds, Part 3, International Atomic Energy Agency, Vienna, 1978.

26. E.H.P. Cordfunke and E. F. Westrum, Jr., "Investigations on Cesium Uranates VII. Thermochemical Properties of $Cs_2U_4O_{12}$," Intern. Symp. on Thermodynamics of Nuclear Materials, Jülich West Germany, 1979, Paper No. IAEA-SM-236/34.

27. P.A.G. O'Hare, K. J. Jensen, and H. R. Hoekstra, "Thermochemistry of Molybdates. IV. Standard Enthalpy of Formation of Lithium Molybdate, Thermodynamic Properties of the Aqueous Molybdate Ion, and Thermodynamic Stabilities of the Alkali-Metal Molybdates, "J. Chem. Thermodynamics, 6 (1976) 681.

28. Estimated Values.

29. R. C. Feber, "Thermodynamic Data for Selected Gas Impurities in the Primary Coolant of High-Temperature Gas-Cooled Reactors," Report No. LA-NUREG-6634, Los Alamos Scientific Laboratory, New Mexico, April 1977.

30. M. W. Chase, Jr., J. L. Curnutt, R. A. McDonald, and A. N. Syverud, "JANAF Thermochemical Tables 1978 Supplement," J. Phys. Chem. Ref. Data, 7 (1978) 793.

Appendix 1. Thermodynamic Data

Compound	$-\Delta H_f^o$, 298 kcal/mol	Ref.	S^o,298 cal/mol	Ref.
$UO_2(s)$	259.32	19	18.41	19
$O_2(g)$	0	-	49.005	19
Rb(g)	+19.53	20	40.873	20
Cs(g)	+18.68	21	41.962	21
$Rb_2O(s)$	78.9	22	25.1	22
$Cs_2O(s)$	82.69	23	35.1	24
CsO(g)	+15.00	21	134.25	21
$Cs_2O(g)$	22.00	21	119.19	21
$Cs_2UO_4(s)$	460.39	25	52.5	25
$Cs_2U_2O_7(s)$	764.6	25	78.33	25
$Cs_2U_4O_{12}(s)$	1332.22	26	125.82	26
$Rb_2UO_4(s)$	457.3	25	48.5	25
$Cs_2MoO_4(s)$	362.00	27	59.36	27
$Rb_2MoO_4(s)$	357.06	27	56.0	27
$Cs_2ZrO_3(s)$	417.83	28	42.62	28
$Rb_2ZrO_3(s)$	413.56	28	39.52	28
$Cs_2Te(s)$	73.12	28	38.1	28
$Cs_2Se(s)$	75.44	28	37.3	28
$Rb_2Te(s)$	74.91	28	34.7	28
$Rb_2Se(s)$	77.28	28	33.9	28

Appendix 1. Thermodynamic Data (continued)

Compound	$-\Delta H_f^o$, 298 kcal/mol	Ref.	S^o,298 cal/mol	Ref.
$CsAlO_2(s)$	240.41	28	28.96	28
$RbAlO_2(s)$	241.72	28	24.51	28
$Cs_2SiO_3(s)$	354.75	28	45.01	28
$Rb_2SiO_3(s)$	353.33	28	37.31	28
CsI(s)	83.9	29	29.2	29
RbI(s)	78.5	20	28.2	20
CsBr(s)	94.3	20	26.0	20
RbBr(s)	93.0	20	26.00	20
I(g)	+25.57	14	43.26	14
$ZrI_4(s)$	116.87	14	59.8	14
$ZrI_3(s)$	93.69	14	47.18	14
$ZrI_4(g)$	84.84	14	106.84	14
$ZrI_3(g)$	30.83	14	97.99	14
$ZrBr_4(s)$	181.8	30	53.7	30
$ZrBr_4(g)$	154.1	30	99.04	30