HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF ALKALI METAL COMPOUNDS. II. ESTIMATION OF THE THERMODYNAMIC PROPERTIES OF CESIUM AND RUBIDIUM ZIRCONATES

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ABSTRACT

The standard enthalpies of formation of the alkali metal zirconates have been estimated using a general parameterization scheme. Details of the calculations are presented. The results are in very good agreement with the available experimental data. The entropies of formation of these compounds have also been estimated and are listed.

INTRODUCTION

One of the interactions that is of considerable interest in light water reactor (LWR) fuel rod performance is the formation of alkali metal zirconates since both the alkali metals and zirconium are generated in large quantitites during irradiation of the fuel rod. Although zirconium forms a very stable oxide, ZrO_2, which is also soluble in the fuel, the possibility remains that the following reaction for zirconate formation may occur

$$2 A(g) + Zr(s) + 3/2 O_2(g) = A_2ZrO_3(s) \tag{1}$$
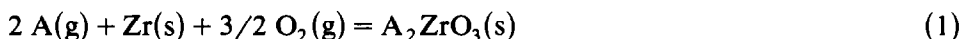
where A is either cesium or rubidium.

On the other hand, fission product cesium or rubidium reaching the zircaloy cladding could react with the oxide on the inside surface to form the respective zirconates in the fuel-cladding gap according to the reaction

$$2 A(g) + ZrO_2(s) + 1/2 O_2(g) = A_2ZrO_3(s) \tag{2}$$

One can also argue that the formation of cesium or rubidium zirconates in the fuel-cladding gap, according to the reactions

$$2 AB(s) + Zr(s) + 3/2 O_2(g) = A_2ZrO_3(s) + 2 B(g) \tag{3}$$

$$2 AB(s) + ZrO_2(s) + 1/2 O_2(g) = A_2ZrO_3(s) + 2 B(g) \tag{4}$$
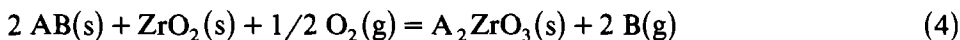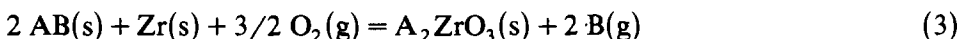
where B is either iodine or bromine, might generate sufficiently large iodine or bromine pressures in the gap to cause PCI failure of the zircaloy cladding

by halogen stress corrosion cracking (SCC).

In order to deduce whether these compounds can form or undergo a specific reaction given a particular set of conditions, reliable thermodynamic data for the zirconates are required. Except for a value for the enthalpy of formation of lithium zirconate, Li_2ZrO_3 [1,2], there are no experimental thermodynamic data on the alkali metal zirconates. For that matter, there is still some uncertainty as to whether cesium zirconate, Cs_2ZrO_3, is stable. Hoppe and Seeger [3] successfully prepared and characterized rubidium zirconate, Rb_2ZrO_3, but failed in their attempts to prepare Cs_2ZrO_3. On the other hand, Alyamovskaya and Chukhlantsev [4] claim to have prepared Cs_2ZrO_3. In the case of the alkali metal uranates, compound stability is strongly correlated with the size of the alkali metal ion. For example, $LiUO_3$, $NaUO_3$, KUO_3, and $RbUO_3$ are stable [5,6], but $CsUO_3$ is not [7]. On this basis, it can be argued that Cs_2ZrO_3 might not be stable. However, in post-irradiation examination of LWR spent fuel rods a cesium–zirconium–oxygen compound has always been observed in the fuel-cladding gap of such rods [8–10].

In view of this, we decided to estimate the thermodynamic properties of the alkali metal zirconates. This paper presents details of the method employed. In addition, the estimated values have been used to predict possible interactions of fission product cesium and rubidium suggested by reactions (1)–(4).

DETAILS OF THE ESTIMATION METHOD

Enthalpy of formation

The estimation technique employed here is based on a method suggested by Brandenburg [11] in a dissertation presented to the University of Amsterdam in 1978. Since Brandenburg's dissertation is not widely available, the estimation method is briefly described here. For a compound M_xN_y, the standard enthalpy of formation, ΔH_f^0, can be estimated by means of substitution of parameter values, assigned to the respective cation and anion, into an estimation equation. The basic estimation equation, in turn, is based on the assumption that ΔH_f^0 is the sum of specific cation and anion contributions to the enthalpy of formation of the compound. Thus, for the compound M_xN_y

$$\Delta H_f^0\left(M_xN_y\right) = x \cdot L(M) + y \cdot L(N) \tag{5}$$

where M is the cation, N is the anion, $L(M)$ is the cation parameter, and $L(N)$ is the anion parameter.

For a large number of ions for which reliable experimental data are available, Brandenburg [11] has shown that the linear estimation eqn. (5)

does not correctly predict the values of ΔH_f^0 for these compounds. Thus, eqn. (5) is modified to include a product term

$$\Delta H_f^0(M_x N_y) = x \cdot L(M) + y \cdot L(N) + x \cdot y \cdot P(M) \cdot P(N) \qquad (6)$$

By correlating a large body of experimental data, Brandenburg [11] has calculated the parameters L and P for a number of ions. These values are listed in Table 1 for selected ions. Using the appropriate values in eqn. (6) we have estimated the heats of formation listed in Table 2 for the alkali metal zirconates.

As can be seen, the one experimental value for lithium zirconate, Li_2ZrO_3, is only about 13 kJ less than the corresponding estimated value. This agreement is very good especially if one considers the very large absolute values of the enthalpies of formation. Thus, we feel that eqn. (6) will give

TABLE 1

Parameters L and P for estimating ΔH_f^0 from eqn. (6)

Ion	L	P [a]
Li^+	-237.65	-1.69
Na^+	-230.10	-3.74
K^+	-234.64	-5.93
Rb^+	-234.61	-6.46
Cs^+	-236.94	-7.05
Ca^{2+}	-473.39	-1.17
Sr^{2+}	-475.87	-2.13
Ba^{2+}	-477.03	-3.10
UO_4^{2-}	-0.20	-0.97
ZrO_3^{2-}	51.40	-0.33
MoO_4^{2-}	103.99	-0.70
CrO_4^{2-}	130.13	-0.36

[a] These values were used to calculate ΔH_f^0 values in Tables 2 and 3 in kcal mole^{-1}, which were then converted to kJ mole^{-1} by multiplying by 4.184.

TABLE 2

Calculated values for the enthalpies of formation of the alkali metal zirconates from eqn. (6)

Zirconate	$-\Delta H_f^0$(kJ mole^{-1})		
	Calcd.	Exptl.	Ref.
Li_2ZrO_3	1768.91	1755.61	2
Na_2ZrO_3	1700.08		
K_2ZrO_3	1732.05		
Rb_2ZrO_3	1730.34		
Cs_2ZrO_3	1748.20		

TABLE 3

Comparison of calculated and experimental values for $-\Delta H_f^0$ (kJ mole^{-1}) for various compounds

Element	Uranates			Zirconates			Molybdates			Chromates		
	Calcd.	Exptl.	Ref.	Calcd.	Exptl.	Ref.	Calcd.	Exptl.	Ref.	Calcd.	Exptl.	Ref.
Li	1975.77	1961.46	16	1768.91	1755.61	2	1543.66	1519.88	20	1439.10	1394.23	21
Na	1895.96	1896.70	17	1700.08			1468.48	1467.33	20	1369.75	1343.98	21
K	1916.17	1911.25	16	1732.05			1493.64	1497.45	20	1400.89	1404.44	21
Rb	1911.62	1913.34	16	1730.34			1490.28	1493.86	20	1399.29	1409.46	21
Cs	1926.33	1926.31	16	1768.20			1506.32	1514.61	20	1417.01	1430.01	21
Ca	1976.75	2001.63	16	1763.99	1766.90	19	1542.22	1541.39	19	1434.44	1426.33	19
Sr	1983.23	1986.56	16	1773.18	1767.32	19	1549.75	1548.08	19	1443.37		
Ba	1984.05	1997.10	18	1776.53	1779.46	19	1551.85	1548.08	19	1446.76	1445.99	19

TABLE 4

Calculated values of the entropies of the alkali metal zirconates

Zirconate	S^0(J K^{-1} mole^{-1})	
	Calcd.	Exptl.
Li_2ZrO_3	88.62	91.63 [a]
Na_2ZrO_3	125.77	
K_2ZrO_3	144.85	
Rb_2ZrO_3	183.31	
Cs_2ZrO_3	197.58	

[a] This value is estimated from experimental heat capacity data on Li_2ZrO_3 given by Barin et al. [22].

reliable estimates of ΔH_f^0. This is further reinforced by the close agreement between estimated and experimental values for other analogous compounds, as Table 3 shows.

Entropy of formation

The entropies of the zirconates were estimated by addition of the entropies of the component oxides, A_2O (A = Li, Na, K, Rb, or Cs) and ZrO_2. The values are listed in Table 4 together with an experimental value for Li_2ZrO_3. Once again, there is close agreement between the estimated and experimental values for Li_2ZrO_3, suggesting that the estimated values for the zirconates are reasonable. We believe that the error introduced in estimating entropies by the additive method will not be too great. In any case, the contribution of the entropy term to the overall free energy of formation of the zirconates is relatively small at lower temperatures compared with the enthalpy term.

APPLICATION TO LWR FUEL ROD CHEMISTRY

As noted earlier, the main reason for this work was to make detailed predictions of fission product interactions in a fuel rod based on reactions (1)–(4).
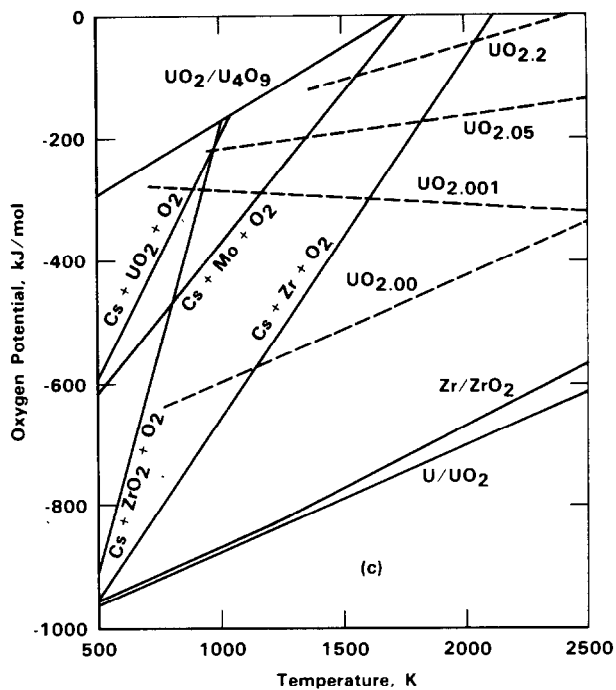
Formation of the zirconates

Consider first the formation of the zirconates. Using the estimated values in Tables 2 and 4 the oxygen potentials associated with reactions (1) and (2) were calculated and are shown in Fig. 1 for various cesium and rubidium
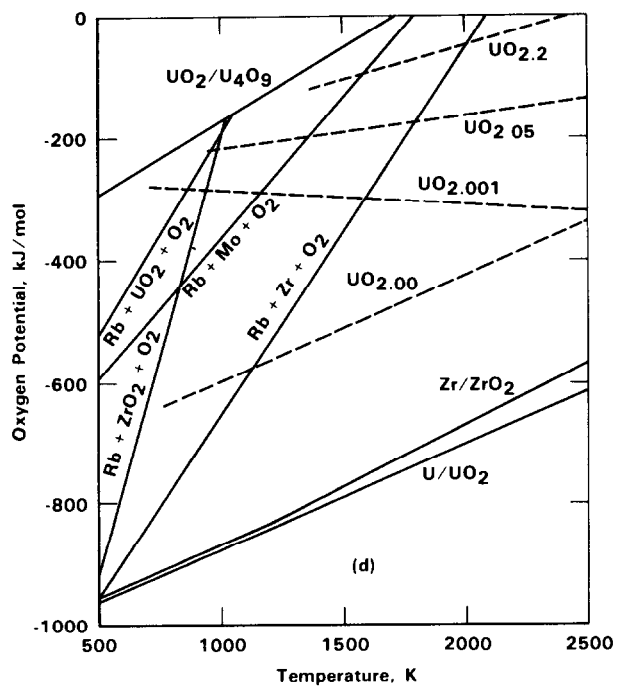
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(a)

A

(b)

B
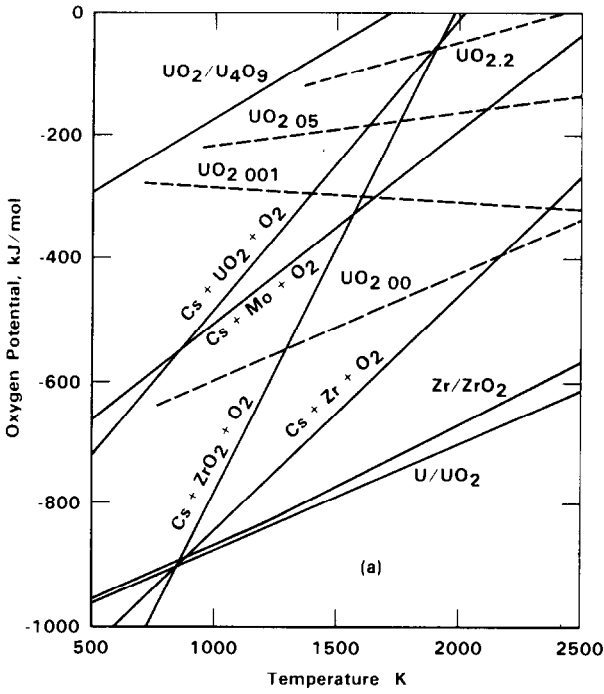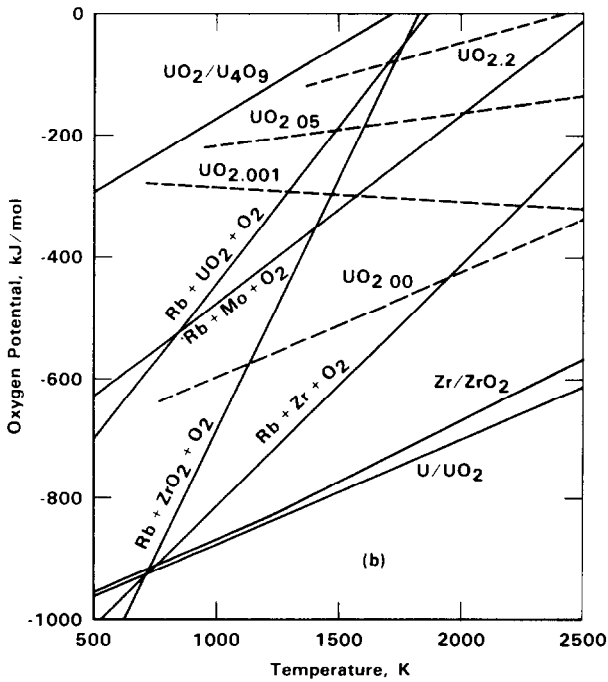
Fig. 1. Oxygen potentials associated with the formation of various ternary compounds for (a) $P_{Cs} = 10^{-3}$ MPa; (b) $P_{Rb} = 10^{-4}$ MPa; (c) $P_{Cs} = 10^{-11}$ MPa; (d) $P_{Rb} = 10^{-11}$ MPa.

partial pressures *, together with those for the formation of the corresponding uranates and molybdates (the necessary data were taken from ref. 13). Inspection of the diagrams clearly shows that the formation of the zirconates is thermodynamically much more favorable than either the uranates or the molybdates at temperatures below about 1500 K. On the other hand, the zirconates are only likely to exist as separate phases at oxygen potentials below -920 kJ mole^{-1} and temperatures below about 800 K, conditions unlikely to be found in the fuel pellet. The situation in the fuel-cladding gap, however, is favorable to zirconate formation: even for cesium pressures as low as 10^{-11} MPa, cesium zirconate is more stable than either cesium molybdate or uranate in the fuel-cladding gap region. Thus, cesium or rubidium reaching the inner surface of the cladding will react to form the respective zirconates, in line with the results of post-irradiation examination of spent fuel rods.

Chemistry of PCI failures

Assuming cesium or rubidium zirconate is the predominant compound formed in the fuel-cladding gap, one can calculate the partial pressures of the halogens expected in the gap from reactions (3) and (4). For cesium iodide the calculation gives an iodine partial pressure of 10^{-9} MPa large enough to react with the zircaloy cladding and, as recent research has shown, iodine SCC of zircaloy takes place at partial pressures above about 10^{-8} MPa [14]. Thus, under conditions that can occur in the fuel-cladding gap sufficiently large iodine pressures can be generated to cause PCI failure of the zircaloy cladding. This is a significant conclusion since it now provides a thermodynamically feasible argument to justify elemental iodine as the principal chemical species involved in PCI.

FUTURE WORK

Estimation of the thermodynamic properties of the zirconates presented here is part of a larger experimental program on high temperature heat capacity measurements on alkali metal compounds: molybdates, chromates, zirconates, dimolybdates, dichromates, and chalcogenides. Data on the molybdates have been published earlier [15]. Measurements on the chromates and zirconates are in progress.

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* We assume that the average partial pressures of cesium and rubidium in a fuel rod will be less than 10^{-3} and 10^{-4} MPa, respectively [12,13].

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