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Estimation of oxygen potential for U–Pu–O mixed oxide fuel

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ABSTRACT

A thermochemical analysis of the estimation of oxygen potential for mixed oxide fuel is presented. The MOX fuel is treated as a pseudo-quaternary solid solution of UO_2–U_cO_d–PuO_2–Pu_aO_b with $b = 1.5a$ and $d = 2.25c$. The hypo-stoichiometric fuel is viewed as UO_2–$(1/a)Pu_aO_b$–PuO_2 pseudo-ternary system and the hyper-stoichiometric fuel is viewed as UO_2–$(1/c)U_cO_d$–PuO_2 pseudo-ternary system and the graphical representation is visualized as a 'diamond plot'. The oxygen potential for MOX is determined either by PuO_2–Pu_aO_b equilibria or by the UO_2–U_cO_d equilibria subject to the constraint that the oxygen potential is equal both in Pu–O subsystem and in U–O subsystem. The choice of stoichiometric parameters a and c affects the relative contribution of configurational entropy to the oxygen potential which determines the shape of the 'S'-type curve near exact stoichiometry. From the analysis of literature data, $a = 2$ and $c = 8$ was derived at for the 'diamond plot' model. Oxygen potentials for MOX fuel with 21, 28% and 44% plutonia was estimated using the 'diamond plot' model. A simplified nomograph for the oxygen potential of MOX is presented.

1. Introduction

Uranium–plutonium mixed oxide (MOX) is being considered as fuel for the Prototype Fast Breeder Reactor (PFBR) at Kalpakkam, India. A two region core consisting of MOX with 21% plutonia as the inner core and MOX with 28% plutonia as the outer core is envisaged. Irradiation studies on high plutonium MOX fuel such as $(U_{0.56}Pu_{0.44})O_{2-x}$ are also planned in the Fast Breeder Test Reactor (FBTR), Kalpakkam, India. The irradiation testing in FBTR and usage of urania–plutonia oxide fuel in PFBR needs an understanding of the physicochemical properties of the fuel at these compositions. The behaviour of an oxide fuel during irradiation is dependent on its oxygen potential. The oxygen potential controls the chemical state of fission products, the interaction of fission products with the fuel and redistribution of fuel and fission product constituents and also influences fuel–clad chemical interaction. Experimental results on the oxygen potentials of mixed oxide with PFBR fuel compositions were reported earlier [1]. The present study attempts to provide a simple model correlating the oxygen potential of MOX with the stoichiometry of plutonium and oxygen as well as with temperature. The model is applied for the estimation of oxygen potentials for MOX fuel compositions of 21, 28% and 44% plutonia.

Several approaches are found in the literature for the estimation of oxygen potential of U–Pu–O mixed oxide fuel system. Some of them are based on defects [2,3] and some on average valency for plutonium or uranium in the solid solution [4,5]. Krishnaiah and Sriramamurti [6] as well as Besmann and Lindemer [7] used the thermochemical approach for the estimation without invoking either the presence of defects or average valency. Krishnaiah and Sriramamurti [6] employed equilibrium constant approach, in which expressions for two independent and simultaneous equilibria among plutonium oxides and among uranium oxides were set-up. By invoking the condition that the oxygen potential in the Pu–O pseudo-binary system is equal to that in the U–O pseudo-binary, the non-linear expressions are solved for the respective unknowns using iterative procedures. Besmann and Lindemer [7] had used SOLGASMIX computer code built on free energy minimization approach in which the MOX fuel was modeled as a solid solution of UO_2–$U_2O_{4.5}$–PuO_2–$Pu_{(4/3)}O_2$. The equilibrium constant method permits development of a compact computer code which can be integrated into any fuel modeling code.

2. U–Pu–O system

The present work attempts to generalize the thermochemical approaches [6,7]. The MOX fuel is treated as a pseudo-quaternary solid solution of UO_2–U_cO_d–PuO_2–Pu_aO_b, where a, b, c and d are stoichiometric coefficients. Pu_aO_b is typically a Pu_2O_3-type oxide ($b = 1.5a$) predominant in the description of hypo-stoichiometry fuel and U_cO_d is U_4O_9-type oxide ($d = 2.25c$) predominant in the description of hyper-stoichiometric fuel. For these oxides, the coefficient a can assume values 1, (4/3) [7], 2 [6] or higher and the coefficient c can assume values 1, 2 [7], 4 [6] or higher.

Consider one mole of the mixed oxide solid solution, $U_{1-p}Pu_pO_{2+z}$. Let the solid solution be comprised of two

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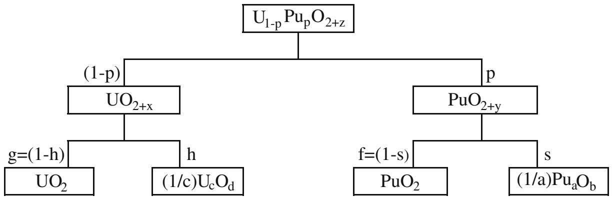

Fig. 1. Schematic representation of the mixed oxide fuel solid solution and its components.

subsystems, namely UO_{2+x} and PuO_{2+y} solid solutions. The parameters *z*, *x* and *y* account for the deviation from stoichiometry of the respective oxide solid solutions. The variable *p* represents the fraction of plutonium present in the fuel, Pu/(U + Pu). Further the UO_{2+x} are treated as solid solution of UO_2 and U_cO_d while PuO_{2+y} is treated as solid solution of PuO_2 and Pu_aO_b. The MOX $U_{1-p}Pu_pO_{2+z}$ is represented as a pseudo-quaternary system and the schema is shown in Fig. 1. All the solid solutions were assumed ideal except when Besmann and Lindemer [7] model is used.

The factor *s* gives the fraction of plutonium present in the form of $(1/a)Pu_aO_b$ and the factor *h* is the fraction of uranium present in the form of $(1/c)U_cO_d$. Note that the species Pu_aO_b is weighed by $(1/a)$ and the species U_cO_d is weighed by $(1/c)$. Such normalizations are typically used in the representations of ternary systems, for example, ½ (O_2).

It can be shown from stoichiometric considerations that

$$h = 4x; \quad s = -2y \quad \text{and} \quad 4z = (1-p)h - 2ps \tag{1}$$

The parameters *h* and *s* are the unknowns. Using the stoichiometric correlations the number of moles, *m*, of species of interest and their mole fractions, *N*, can be derived

$$m\mathrm{UO_2} = (1-p)(1-h); \quad m\mathrm{U_cO_d} = (1-p)h/c$$
$$m\mathrm{PuO_2} = p(1-s); \quad m\mathrm{Pu_aO_b} = ps/a \quad \text{and} \tag{2}$$
$$m_{\text{tot}} = 1 - ps(a-1)/a - (1-p)h(c-1)/c \tag{3}$$

Conversion of mole fraction to moles yields

$$m\mathrm{Pu_aO_b} = N\mathrm{Pu_aO_b}[1-(c-1)m\mathrm{U_cO_d}]/[1+(a-1)N\mathrm{Pu_aO_b}]$$
$$m\mathrm{U_cO_d} = N\mathrm{U_cO_d}[1-(a-1)m\mathrm{Pu_aO_b}]/[1+(c-1)N\mathrm{U_cO_d}] \tag{4}$$

Expressions (1)–(4) are used for generating the initial guess values for the relative compositions which are refined further using iterative procedure.

3. Diamond plot

In this simplified representation, the hypo-stoichiometric fuel is viewed as UO_2–PuO_2–$(1/a)Pu_aO_b$ pseudo-ternary system and the hyper-stoichiometric fuel is viewed as UO_2–$(1/c)U_cO_d$–PuO_2 pseudo-ternary system. The 'diamond plot' is a graphical representation in which the pseudo-ternaries are adjoined at UO_2–PuO_2 binary (Fig. 2). Several stoichiometric correlations are readily inferred from the diamond plot. For example, the UO_2–$(1/a)Pu_aO_b$ boundary line gives the lowest possible O/M for a given Pu fraction of the fuel, (2-*p*/2). Likewise, the $(1/c)U_cO_d$–PuO_2 boundary line gives the maximum possible O/M for a given Pu fraction of the fuel, (2.25-*p*/4). Lines parallel to UO_2–PuO_2 pseudo-binary represent isograms of constant O/M ratio. Line connecting UO_2 and fuel composition of interest, can be extended to meet the PuO_2–$(1/a)Pu_aO_b$ line. The point of intersection shall define the initial composition for the hypo-stoichiometric fuel. For compositions away from *z* = 0, the initial composition estimated from the diamond plot is adequate for the oxygen potential calculations. Only when O/M approaches the exact stoichiometry, about 1.99, the iterative procedure provides any refinement on the initial composition values.

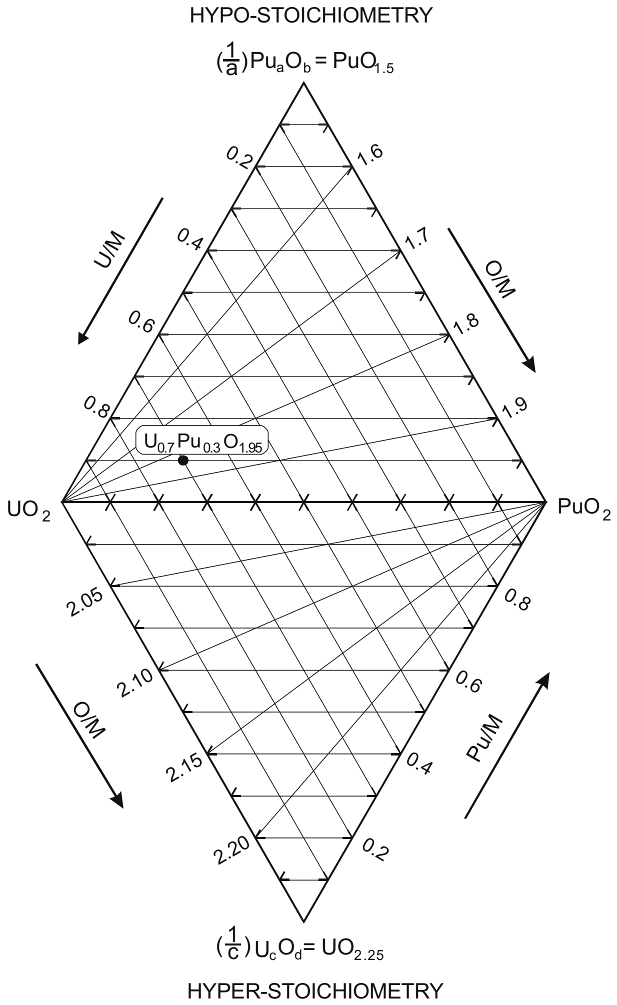

Fig. 2. The 'diamond plot' describing hyper and hypo-stoichiometric MOX fuel.

4. Oxygen potential

The oxygen potential can be calculated using PuO_2–Pu_aO_b equilibrium or UO_2–U_cO_d equilibrium. For the PuO_2–Pu_aO_b equilibrium

$$Pu_a\mathrm{O}_b + (a/4)\mathrm{O_2} = a\mathrm{PuO_2}$$

$$\Delta\overline{G}_{\mathrm{O_2}} = (4/a)\left\{\begin{array}{c} a\Delta G_f^o < \mathrm{PuO_2} > -\Delta G_f^o < \mathrm{Pu}_a\mathrm{O}_b > +RT\ln\left(\frac{N^a_{\mathrm{PuO_2}}}{N_{\mathrm{Pu}_a\mathrm{O}_b}}\right) \\ +\{a(1-N_{\mathrm{PuO_2}})N_{\mathrm{Pu}_a\mathrm{O}_b} - (N_{\mathrm{PuO_2}}(1-N_{\mathrm{Pu}_a\mathrm{O}_b})\}\Omega \end{array}\right\} \tag{5}$$

where N_i is the mole fraction of species *i*; Ω is the regular solution interaction parameter employed for estimations using Besmann and Lindemer [7] model, which is set to zero for ideal cases. For the UO_2–U_cO_d equilibrium:

$$c\mathrm{UO_2} + (c/8)\mathrm{O_2} = \mathrm{U}_c\mathrm{O}_d$$

$$\Delta G_{O_2} = \left(\frac{8}{c}\right)\left[\Delta G^o_{U_cO_d} - c\Delta G^o_{UO_2} + RT\ln\left(\frac{N_{U_cO_d}}{N^c_{UO_2}}\right) + 4(N_{Pu_aO_b}N_{PuO_2})\Omega\right] \tag{6}$$

Though Eq. (5) is predominant in the hypo-stoichiometric fuel and Eq. (6) is predominant in the hyper-stoichiometric fuel, both equilibria prevail at all compositions. Since Pu–O and U–O systems are in simultaneous equilibrium in the fuel, the oxygen potentials

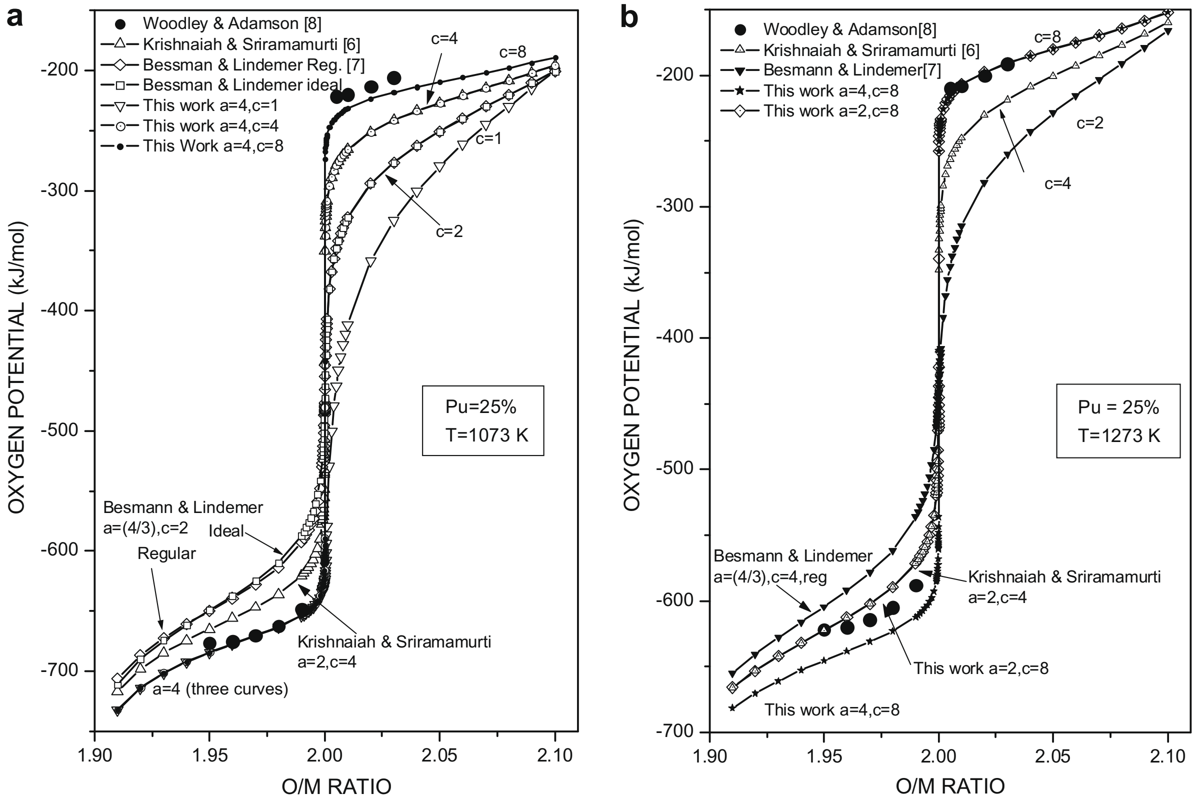

Fig. 3. Variation of oxygen potential as a function of O/M for MOX with 25% plutonia at (a) 1073 and (b) 1273 K.

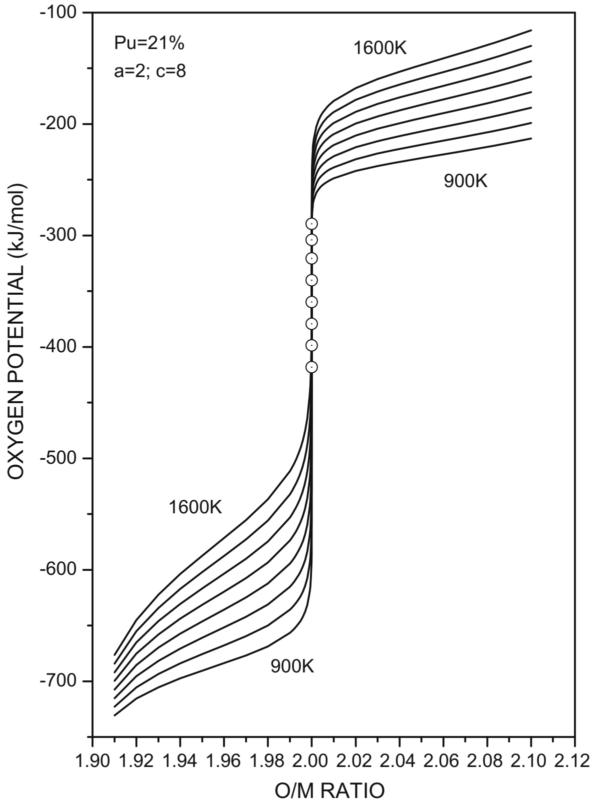

Fig. 4. Variation of oxygen potential for MOX with 21% plutonia as a function of O/M. The effect of temperature is also shown. Oxygen potential at exact stoichiometry is marked by circle.

of Pu–O system and U–O system are equated as the equilibrium constraint. The Eqs. (1)–(6) are solved iteratively to arrive at the equilibrium composition and the oxygen potential. In this scheme there is a finite possibility for the presence of U_cO_d-type oxide in the hypo-stoichiometric fuel and for the presence of Pu_aO_b-type oxide in the hyper-stoichiometric fuel [6].

5. Configurational entropy

The oxygen potential expressions derived in Eqs. (5) and (6) have both thermal contributions and configurational contributions. The thermal contributions are independent of the values of the stoichiometric coefficients *a* and *c*. For example, invoking the thermochemical data employed by Besmann and Lindemer [7], the thermal term can be shown to be

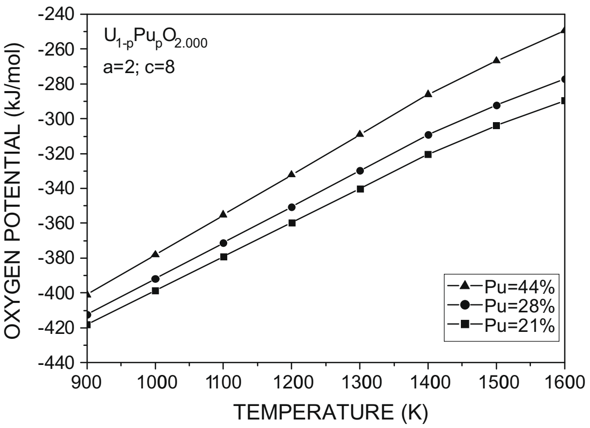

Fig. 5. The oxygen potential variation at exact stoichiometry for MOX with 21, 28 and 44% plutonia.

$$\left(\tfrac{4}{a}\right)\left[a\Delta G^0_{PuO_2} - \Delta G^0_{Pu_aO_b}\right] = -821000 + 168.48T(\mathrm{J/mol}) \quad \text{and}$$

$$\left(\tfrac{8}{c}\right)\left[\Delta G^o_{U_cO_d} - c\Delta G^0_{UO_2}\right] = -338000 + 126.2T(\mathrm{J/mol})$$

The configurational term in Eq. (5) is given by $\Delta S^{conf} = \left(\frac{4}{a}\right)RT\ln\left(\frac{N^a_{PuO_2}}{N_{Pu_aO_b}}\right)$ and the configurational term in Eq. (6) is given by $\Delta S^{conf} = \left(\frac{8}{c}\right)RT\ln\left(\frac{N_{U_cO_d}}{N^c_{UO_2}}\right)$

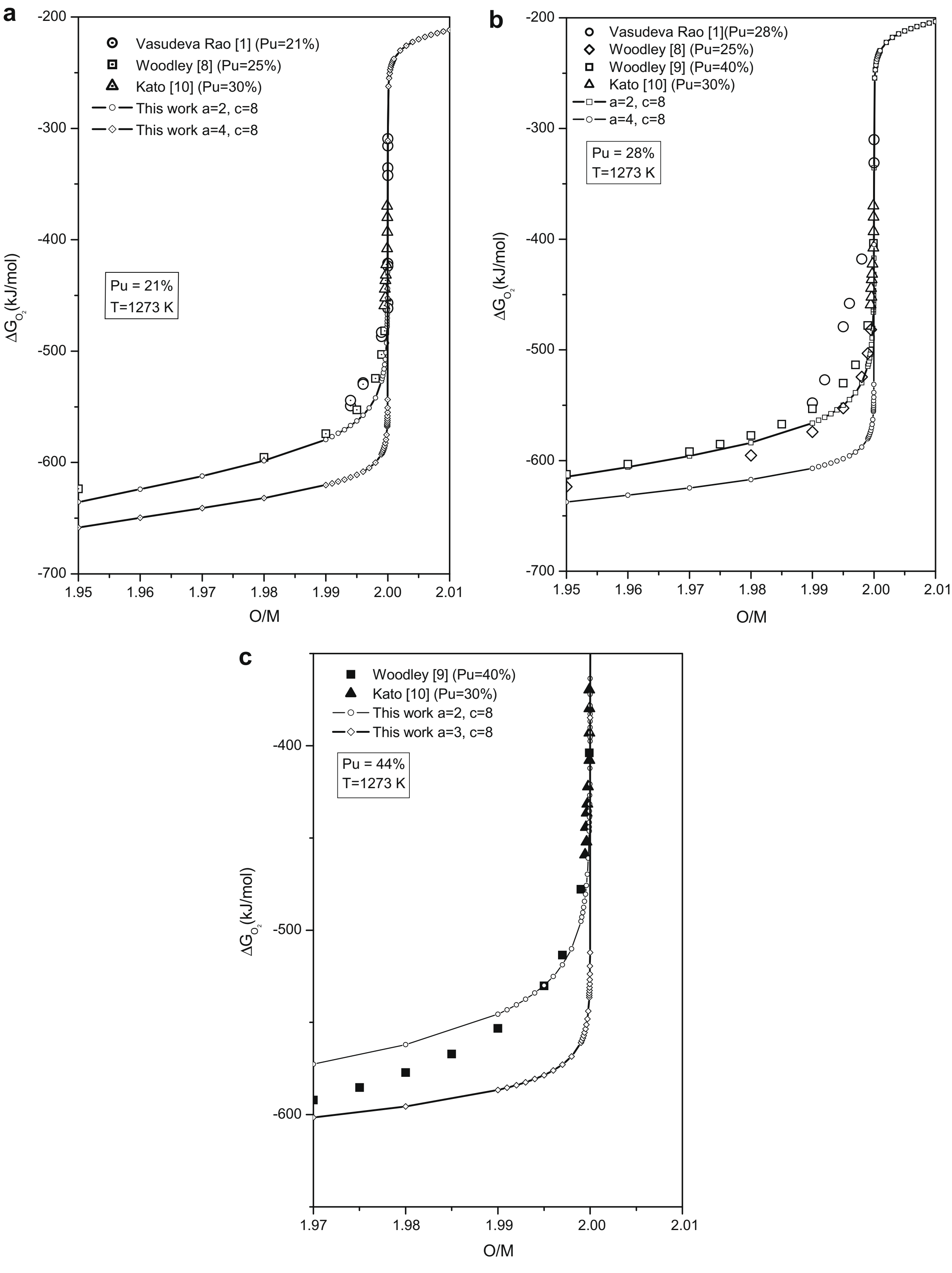

Fig. 6. The variation of oxygen potential as a function of O/M at 1273 K for Pu=21, 28 and 44%.

The choice of stoichiometric parameters a and c affects the relative contribution of the configurational entropy to the oxygen potential. Krishnaiah and Sriramamurti [6] have used $a = 2$ and $c = 4$ and Besmann and Lindemer [7] have used $a = (4/3)$ and $c = 2$. Effect of these parameters on the predicted oxygen potentials is shown in Fig. 3 and compared with the experimental data of Woodley and Adamson [8]. It is seen that $a = 2$ or 4 and $c = 8$ provides a closer representation of experimental data. The uncertainty on the estimated values is traceable to the uncertainties in the basic Gibbs energy data and is given as ±4 kJ/mol.

5.1. O/M variation

The model is applied for MOX fuel with 21, 28% and 44% plutonia and the typical results are shown in Fig. 4 for 21% plutonia. As expected, the oxygen potential exhibits a typical 'S' curve which shifts towards higher oxygen potential as temperature increases. As plutonium fraction is increased from 0.21 to 0.28 and to 0.44, the curves shift towards higher oxygen potential values.

5.2. Temperature variation

In general, the temperature variation of oxygen potential is expected to show a linear correlation for solids ($\Delta Cp = 0$, assumed). If one uses $a = (4/3)$, a small curvature was observed on these curves above O/M>~1.99 due to the configurational contribution. The curvature, closer to O/M = 2.00, was illustrated earlier by Besmann and Lindemer [7].

5.3. At exact stoichiometry

The oxygen potential variation at exact stoichiometry is shown in Fig. 5 for MOX with 21, 28% and 44% plutonia respectively. As expected the increase in plutonium fraction resulted in higher oxygen potential at all temperatures. As temperature increases from 900 to 1600 K, the moles of Pu_aO_b increases from $\sim 10^{-12}$ to $\sim 10^{-5.5}$ and U_cO_d increases only from $\sim 10^{-6.3}$ to $\sim 10^{-5.5}$ at exact stoichiometery. The effect of increase in plutonium fraction is only marginal.

5.4. Effect of regular solution behaviour

The effect of regular solution parameter is illustrated with Besmann and Lidemer [7] model. Oxygen potential was estimated with $a = (4/3)$ and $c = 2$, for hypo-stoichiometric fuel assuming ideal and regular solution behavior. Thermochemical data suggested by Besmann and Lindemer [7] are used in this calculation. The introduction of regular solution behavior to the Pu–O pseudo-binary had only a marginal impact on the estimated oxygen potential.

6. Application

The 'diamond plot' model was applied to the MOX fuel compositions of interest to PFBR and FBTR. The estimated values are compared with a few literature data [1,8–10], Fig. 6. In each case, the estimated oxygen potential reasonably represents the reported values.

7. Nomograph of oxygen potential for hypo-stoichiometric MOX fuel

Fig. 7 represents a simplified nomograph for oxygen potential of MOX fuel. The UO_2–PuO_2–$(1/a)Pu_aO_b$ triangle represents the hypo-stoichiometric fuel. Pu/M scale is marked at UO_2–$(1/a)Pu_aO_b$ boundary and O/M scale is marked at PuO_2–$(1/a)Pu_aO_b$ boundary. Any Colinet isogram[1] [11,12], parallel to the UO_2–PuO_2 boundary, indicates constant O/M. Any Colinet isogram, parallel to PuO_2–$(1/a)Pu_aO_b$ indicates constant Pu/M. Any Kohler isogram[2] originating from UO_2 apex can be extended to intersect the PuO_2–$(1/a)Pu_aO_b$ boundary; the point of intersection provides the relative ratio of PuO_2:$(1/a)Pu_aO_b$ for all the fuel compositions lying on that Kohler isogram [12,13]. These lines represent constant valency for plutonium [4]. In order to be consistent with the ternary representation, the oxygen potential scale was calculated using $a = 1$ and $c = 1$.

The indexed region outside this triangle provides the scale for oxygen potential for temperatures from 900 to 1500 K in steps of 100 K. In this region, the lines parallel to PuO_2–$(1/a)Pu_aO_b$ indicate fixed temperatures. The Kohler isogram is projected to this region to provide oxygen potential at respective temperatures. For O/M close to 2.000 this representation may have limitations which are attributed to the following: (i) contribution by U_cO_d becomes significant and (ii) configurational entropy influences oxygen potential. One can read the oxygen potential for a given MOX composition from the nomograph. For example, for $U_{0.75}Pu_{0.25}O_{1.95}$ has an oxygen potential of −724 kJ/mol at 1000 K. The fuel $U_{0.6}Pu_{0.4}O_{1.92}$ also has the same oxygen potential at 1000 K as that of $U_{0.75}Pu_{0.25}O_{1.95}$, since both the compositions lie on the same Kohler isogram.

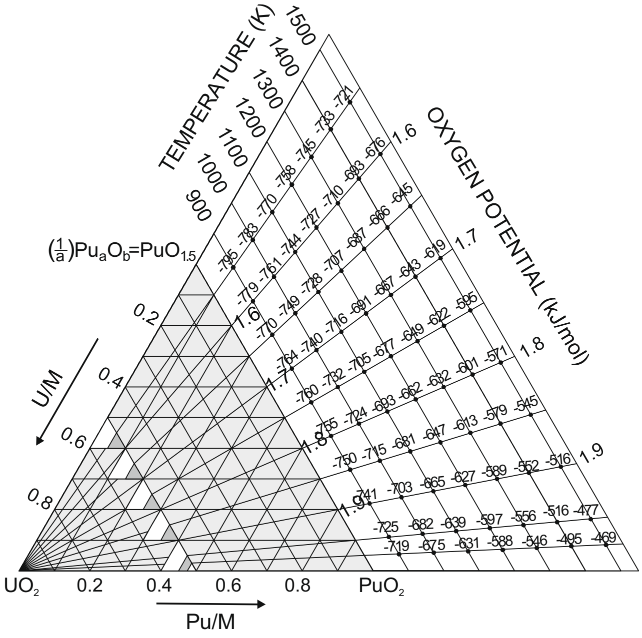

Fig. 7. Nomograph of oxygen potential for hypo-stoichiometric MOX fuel.

8. Conclusions

Thermochemical approaches for the estimation of oxygen potential for MOX fuel system were generalized using the stoichiometric parameters a and c. The choice of the parameters influences the configurational entropy contribution to the estimate. The choice of $a = 2$ and $c = 8$ provides reasonable estimates for MOX

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[1] Colinet isogram is a pseudo-binary line connecting two constituent binary systems in a ternary phase diagram such that the mole fraction of the common component present in both the binaries remains constant [12].

[2] Kohler isogram is a pseudo-binary line connecting one apex of the Gibbs triangle to the opposite binary system. Along a Kohler isogram, originating from UO_2 apex, the ratio of the components on the baseline binary, $N_{(1/a)Pu_aO_b}/N_{PuO_2}$, remains constant [12].

fuel with 21, 28% and 44% plutonia. A simplified nomograph for the oxygen potential hypo-stoichiometric fuel is presented.

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