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ON THE CHEMISTRY OF THE REACTIONS BETWEEN LIQUID SODIUM AND URANIA–PLUTONIA FUEL FOR FAST BREEDER NUCLEAR REACTORS

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ABSTRACT

Aspects of the phase equilibria and thermodynamic quantities for the various chemical reactions which can occur between sodium and irradiated oxide fuel for fast breeder reactors are discussed in detail in terms of the individual oxide and fission product systems. The contamination of the primary circuit by dissolved fission product species and particulate matter is also discussed in terms of the appropriate phase equilibria.

INTRODUCTION

In this paper, some aspects of the phase equilibria and thermodynamic properties of systems and compounds of relevance to the reactions between liquid sodium and some actinide and lanthanide oxides are discussed. Such systems are of great significance to an understanding of the behaviour of irradiated uranium oxide–plutonium oxide nuclear fuel in a liquid sodium cooled fast breeder reactor. The fuel for such a nuclear power reactor consists of dense pellets of urania–plutonia ($U_{1-x}Pu_xO_{2-y}$, $0.2 < x < 0.3$, $0.01 < y < 0.03$) clad in stainless steel. If the cladding were breached, the irradiated fuel could react with the coolant. Therefore much attention has been focused on such reactions, in order that the consequences on the operation of a fast reactor may be established.

An essential feature for the determination of such consequences has been the study of the phase equilibria and thermodynamic quantities of the systems of liquid sodium with urania and plutonia, and with the lanthanide oxides. The lighter lanthanide elements are fission products and a significant quantity of their cations enter the lattice of the actinide oxide during irradiation in the core of the reactor. Up to nearly 20% of the actinide atoms could undergo fission in the fuel for a fast breeder reactor.

Dedicated to Professor Oswald Kubaschewski in honour of his contribution to thermochemistry.

This paper is dedicated to Professor O. Kubaschewski who has provided so much stimulus to so many of us working on the chemical behaviour of nuclear materials by his generous counsel and his many contributions to the publications of the International Atomic Energy Agency on the thermodynamics of nuclear materials.

THE REACTIONS OF LIQUID SODIUM WITH THE COMPONENTS OF OXIDE FUEL

Reactions with urania

An isothermal section of the ternary phase diagram Na–U–O is shown in Fig. 1 and the equilibrium phase field of major interest is that containing UO_2(s), Na(l, O in solution) and Na_3UO_4(s) (s and l represent the solid and liquid states). The overall reaction involving hyperstoichiometric urania can be represented by

$$3x\text{Na(l, O in solution)} + 2\text{UO}_{2+x}\text{(s)} \rightarrow x\text{Na}_3\text{UO}_4 + (2-x)\text{UO}_{2.00}\text{(s)} \qquad (1)$$

and the equilibrium reaction is

$$3\text{Na(l, O in solution)} + \text{UO}_2\text{(s)} + \text{O}_2\text{(dissolved in oxide or Na)} \rightleftarrows \text{Na}_3\text{UO}_4\text{(s)} \qquad (2)$$

The threshold O : U ratio for the reaction is very close to 2.00 and the

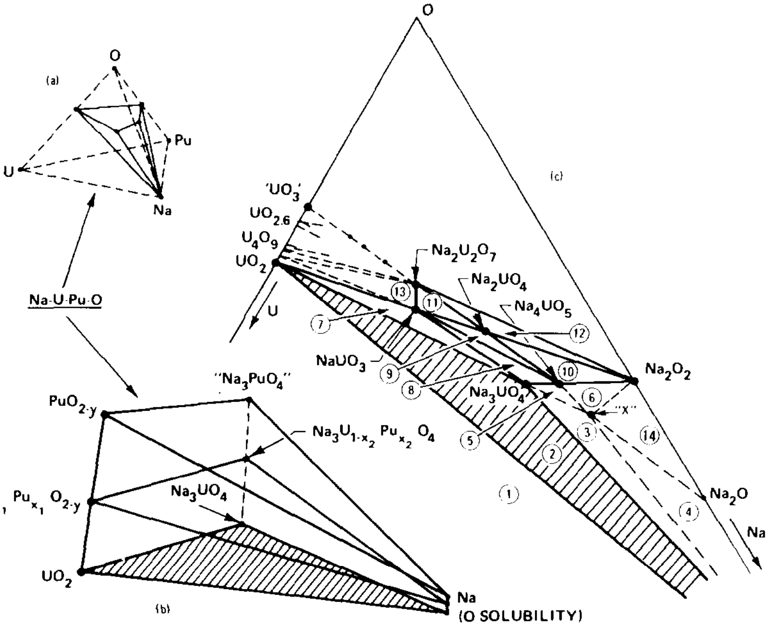

Fig. 1. Sections of phase diagrams for the Na–U–Pu–O and Na–U–O systems at 1000 K.

threshold oxygen concentration in sodium is < 1 w.p.p.m. at 1073 K [1]. A detailed study on the effect of increasing both the O : U ratio and the oxygen content of the sodium on this reaction has been reported [2]. The kinetics of the reaction between liquid sodium and pellets of hyperstoichiometric urania has been investigated over the temperature range 723 K to 1173 K and the mechanism of the reaction has been proposed [2].

It should be noted that for the reaction between sodium and hyperstoichiometric urania (UO_{2+x}) different mechanisms occur at low and high temperatures. The more destructive reaction between sodium and pellets of urania can possibly be attributed to the formation of the low-density product sodium monoxide (Na_2O) within the grain boundaries at temperatures less than 400 °C. This has been observed when the reactants are in contact during the initial period of heating up to the final reaction temperature. As the temperature is raised (above 450 °C), the thermodynamically more stable sodium uranate (Na_2UO_4) is formed. The reaction of sodium with pellets of hyperstoichiometric urania, without the reactants being in contact prior to attaining the reaction temperature, results in swelling which almost corresponds to the calculated value for the formation of Na_3UO_4.

It was also shown that pellets of stoichiometric urania do not undergo a destructive reaction when in contact with sodium which contains a significant amount of oxygen. A layer of reaction product tends to be loosely held to the surface of the pellet and consists of a high proportion of the phase Na_3UO_4.

The equilibrium oxygen potential $\bar{G}_{O_2}^{eq}$ for reaction (2) is given by

$$\bar{G}_{O_2}^{eq} = \Delta_f G^0(Na_3UO_4(s)) - \Delta_f G^0(UO_2(s)) - 3\bar{G}(Na(l)) \qquad (3)$$

where $\Delta_f G^0(Na_3UO_4(s))$ and $\Delta_f G^0(UO_2(s))$ are the Gibbs energies of formation of Na_3UO_4 and UO_2, respectively and $\bar{G}(Na(l))$ is the partial molar Gibbs energy of liquid sodium which, because of the small quantities of oxygen present, can be taken as zero.

The values for the equilibrium oxygen potential for the Na–U–O system were obtained from measurements with an e.m.f. cell. The cell was based on a thoria–yttria electrolyte and the e.m.f. was measured with a slurry of Na(l), UO_2 and Na_3UO_4 at one electrode and a mixture of In and In_2O_3 as the reference electrode. The oxygen potential can be expressed by the equation

$$\bar{G}_{O_2}\left(J\ (mol\ O_2)^{-1}\right) = -949789 + 253.1\,T \qquad (4)$$

for which the estimated uncertainty, including the error in the values for $\Delta_f G^0(In_2O_3(s))$ is ± 2.7 kJ $(mol\ O_2)^{-1}$. These data are in good agreement with those determined by Adamson et al. [3]. These experimentally determined values of $\bar{G}_{O_2}$ for the phase field Na(l), $UO_2(s)$, $Na_3UO_4(s)$ are all more negative than the values calculated from the Gibbs energies of forma-

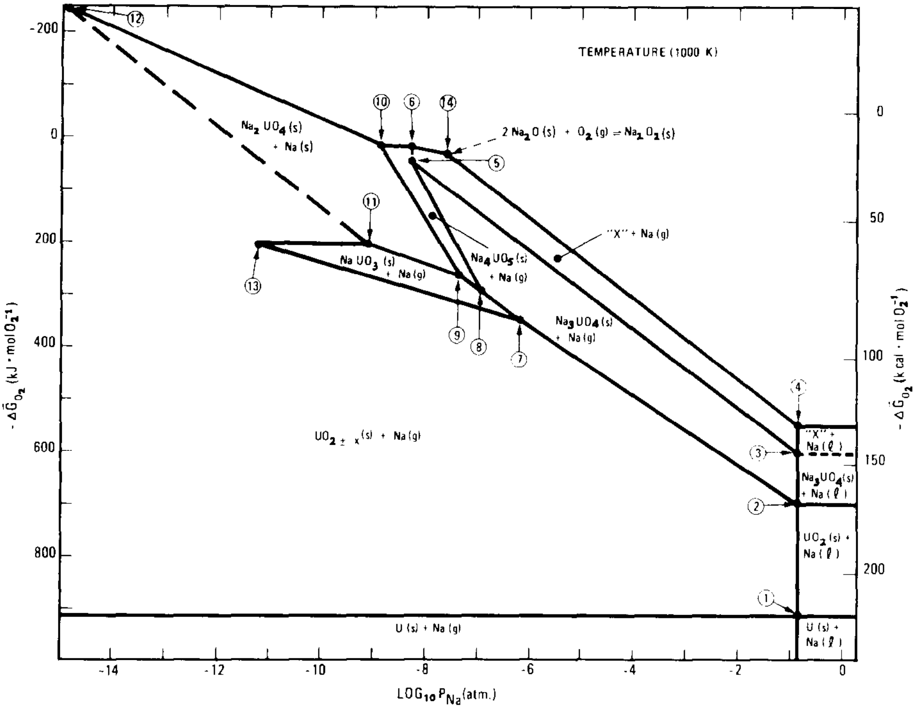

Fig. 2. Oxygen potentials and sodium vapour pressure in the Na–U–O system at 1000 K. The phase fields are numbered as in Fig. 1.

tion, although the partial molar entropies of oxygen ($\bar{S}_{O_2}$) are identical. It is possible therefore that the discrepancy could be due to a small error in the experimentally determined value for the enthalpy of formation of Na_3UO_4.

In addition to a possible isothermal section of the Na–U–O phase diagram shown in Fig. 1, a predominance area diagram for the system is shown in Fig. 2. This latter diagram indicates the regions of existence of the phases of the system in terms of the thermodynamic potentials of oxygen and sodium. Thus if the sodium pressure is set at one temperature, we can immediately determine the conditions required to form the various ternary phases. For example, for the formation of $NaUO_3$, we require progressively increasing potentials of oxygen with decreasing pressures of sodium. Thus if the vapour pressure of sodium is set at a lower temperature in a region of the fuel, the potential of oxygen which is required for the conformation of the phase $NaUO_3$ at a higher temperature can readily be obtained.

Reactions with plutonia

When sintered pellets of plutonia reacted with liquid sodium at 700 °C for 24 h considerable swelling of the pellets occurred due to the formation of the compound Na_3PuO_4 [4]. This compound is isomorphous with Na_3UO_4

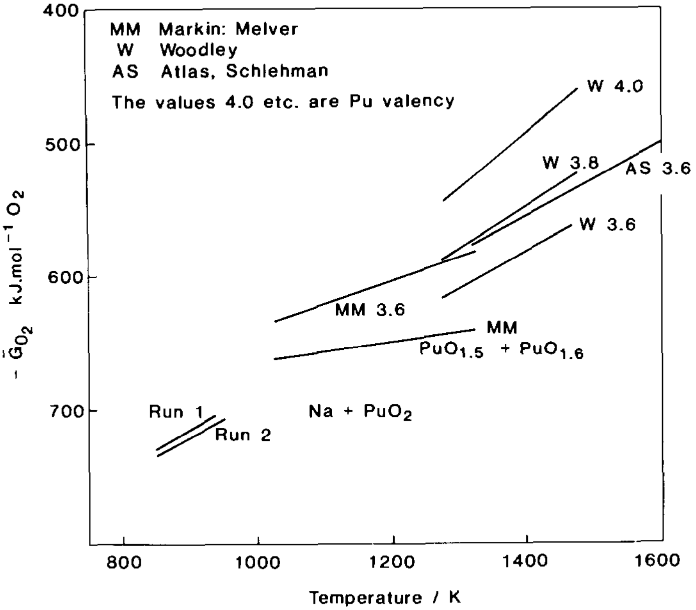

Fig. 3. $\bar{G}_{O_2}$ for the sodium–plutonia reaction and for the plutonium–oxygen system.

with a slightly smaller lattice parameter (Na_3PuO_4: $a_0 = 0.486$ nm [4], $a_0 = 0.488$ nm [5]; Na_3UO_4: $a_0 = 0.479$ nm). The remaining phases were a mixture of PuO_2 and $PuO_{1.61}$ which formed by the disproportionation of hypostoichiometric plutonia (PuO_{2-z}) [3]; the proportion of these phases suggested that the threshold plutonium valency for reaction was between 3.45 and 3.55. Subsequent studies with powders of plutonia heated with liquid sodium at 580–680 °C for 120 h indicated that the threshold valency of plutonium was about 3.0. We have measured [6,7] the partial molar Gibbs energy of oxygen for the phase field appropriate to the overall reaction

$$3Na(l) + (1 + 2/z)PuO_2(s) \rightarrow Na_3PuO_4(s) + (2/z)PuO_{2-z}(s) \qquad (5)$$

for which the equilibrium reaction is given by

$$3Na(l, O \text{ in solution}) + PuO_{2-z}(s) + (1 + z/2)O_2(\text{in oxide}) \rightleftarrows Na_3PuO_4 \qquad (6)$$

The determination of $\bar{G}_{O_2}$ was made using an e.m.f. cell based on a thoria–yttria electrolyte; the e.m.f. of the cell was measured with a slurry of Na(l), Na_3PuO_4 and PuO_{2-z} at one electrode, and a mixture of In and In_2O_3 as the reference electrode.

Measurements of oxygen potential were made with two separate batches of PuO_2 powder (run 1 and run 2) the results of which are shown in Fig. 3. These two sets of data are not in agreement within the experimental uncertainty and the source of the discrepancy is not clear. Our data for $\bar{G}_{O_2}$

for the three-phase field are compared with data for $\bar{G}_{O_2}$ of the binary plutonium–oxygen system in Fig. 3. The observation that the oxide is reduced by liquid sodium to the hexagonal-structured Pu_2O_3 phase indicated that the data for $\bar{G}_{O_2}$ of the binary system extrapolated from the measurements of Woodley [8] and Atlas and Schlehman [9] are inconsistent with our measurements. Our data are more compatible with the determinations of $\bar{G}_{O_2}$ of Martin and McIver [10] for this binary system.

Reactions with urania–plutonia solid solutions

For this system, the overall reaction can be expressed by

$$\begin{aligned}&3(y-z)\mathrm{Na}(\mathrm{l,\ O\ dissolved}) + (2+y)\mathrm{U}_{1-x_3}\mathrm{Pu}_{x_3}\mathrm{O}_{2-z}(\mathrm{s})\\ &\quad\rightarrow (y-z)\mathrm{Na}_3\mathrm{U}_{1-x_2}\mathrm{Pu}_{x_2}\mathrm{O}_4(\mathrm{s}) + (2+z)\mathrm{U}_{1-x_1}\mathrm{Pu}_{x_1}\mathrm{O}_{2-y}(\mathrm{s})\end{aligned} \tag{7}$$

We showed earlier [1] that when the three condensed phases ($U_{1-x_1}Pu_{x_1}O_{2-y}(s)$, $Na_3U_{1-x_2}Pu_{x_2}O_4(s)$ and Na(l)) given in the overall reaction above, are in equilibrium, then the equilibrium reactions can be considered in terms of the separate reactions for the uranium and plutonium components of the system. The equilibrium reaction for the uranium component is

$$\begin{aligned}&3\mathrm{Na}(\mathrm{l,\ O\ dissolved}) + \mathrm{UO}_2(\mathrm{dissolved\ in\ PuO}_{[2-(y/x)]}) + \mathrm{O}_2(\mathrm{dissolved})\\ &\quad\rightleftarrows \mathrm{Na}_3\mathrm{UO}_4(\mathrm{dissolved\ in\ Na}_3\mathrm{PuO}_4)\end{aligned} \tag{8}$$

The valency of plutonium in the oxide solid solution is $2[2-(y/x)]$.

It was shown that the oxygen potentials in the phase field of the quaternary system could be expressed in terms of those for the analogous phase field in the ternary uranium system, namely

$$\bar{G}^{\mathrm{eq}}_{O_2}(\text{quaternary system}) = \bar{G}^{\mathrm{eq}}_{O_2}(\text{ternary system}) + RT\ \ln\left(a_{\mathrm{Na_3UO_4}}/a_{\mathrm{UO_2}}\right) \tag{9}$$

where $a_{\mathrm{Na_3UO_4}}$ and $a_{\mathrm{UO_2}}$ are the thermodynamic activities of Na_3UO_4 and UO_2 in the respective solid solutions. If $a_{\mathrm{Na_3UO_4}}$ and $a_{\mathrm{UO_2}}$ are identical, then the oxygen potential of the relevant phase field will be the same in both systems. Also, if the solutions were ideal then $a_{\mathrm{Na_3UO_4}} = 1 - x_2$ and $a_{\mathrm{UO_2}} = 1 - x_1$, and if there were no segregation of uranium and plutonium cations in the two solid solutions, then the oxygen potential for the quaternary system would be identical with that for the ternary uranium or plutonium systems. If, however, the solid solutions deviated from ideality then $a_i = \gamma_i x_i$ where a_i, γ_i and x_i are the activity, activity coefficient and mole fraction of component i of the solid solution. Earlier we considered the solid solutions to be regular, and thus $RT \ln \gamma_i = E_i(1-x_i)^2$ where E_i is the interaction parameter, and

$$\begin{aligned}&\bar{G}^{\mathrm{eq}}_{O_2}(\text{quaternary system})\\ &\quad= \bar{G}^{\mathrm{eq}}_{O_2}(\text{ternary system}) - E_1x_1^2 + E_2x_2^2 + RT\ \ln[(1-x_2)/(1-x_1)]\end{aligned} \tag{10}$$

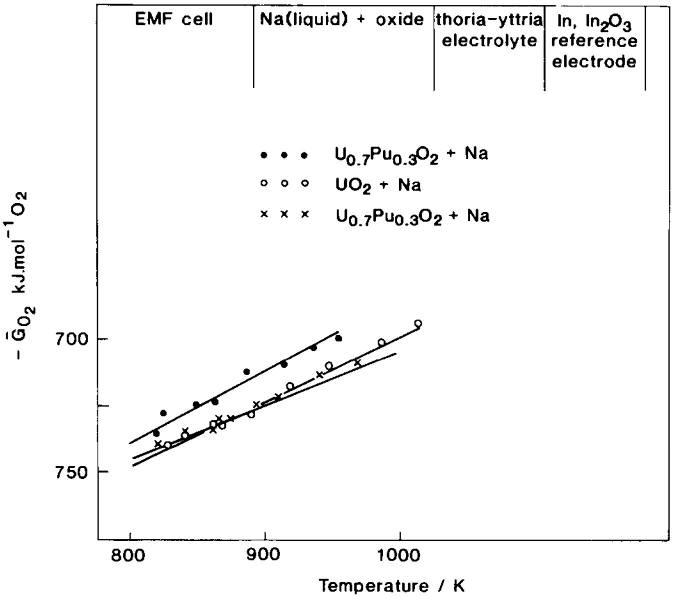

Fig. 4. The experimentally determined variation in $\bar{G}_{O_2}$ with temperature for sodium–urania and sodium–urania–plutonia.

where E_1 and E_2 are regular solution interaction parameters for the U–Pu oxide and the Na uranoplutonate solid solutions. Earlier we examined the influence of the variation of the uranium and plutonium concentrations and of the values of the interaction parameters on the calculated values of $\bar{G}_{O_2}^{eq}$. It was noted that the effects of these variations gave values for $\bar{G}_{O_2}^{eq}$ which were generally within the estimated uncertainties in the values of $\bar{G}_{O_2}^{eq}$ for the uranium system: ±4.2 kJ (mol O_2)$^{-1}$. Only if the interaction parameter for the oxide solid solution (E_1) were less than −17 kJ, or if Pu were greatly segregated into the sodium uranoplutonate, would the values of $\bar{G}_{O_2}^{eq}$ lie outside the band of values for the uranium system.

The measurements which have been made of the variation of $\bar{G}_{O_2}^{eq}$ with temperature for the three-phase fields using e.m.f. cells with thoria–yttria electrolytes are shown in Fig. 4. The data of Adamson et al. [3] for a solution with Pu/(U + Pu) = 0.25 in the temperature range 1073–1273 K, are in good agreement with the measured values of $\bar{G}_{O_2}^{eq}$ for the urania system. Our measurements are for the solid solutions with Pu/(U + Pu) ratios of 0.3 and 0.7, respectively. The values of $\bar{G}_{O_2}^{eq}$ for the solution with Pu/(U + Pu) = 0.3 are close to the values for the urania system (approximately 5 kJ (mol O_2)$^{-1}$ more positive). For the solution with Pu/(U + Pu) = 0.7 the values of $\bar{G}_{O_2}^{eq}$ were approximately 5 kJ (mol O_2)$^{-1}$ more negative than those for the urania system. There were also some small differences in the slope or partial entropy ($\bar{S}_{O_2}^{eq}$) of the system; these differences, however, are not pronounced.

The determinations of $\bar{G}_{O_2}^{eq}$ by Martin and McIver [10] for the solid solutions of urania–plutonia with Pu/(U + Pu) = 0.11, 0.15 and 0.30 using an e.m.f. cell in the temperature range 1023–1323 K indicated that the oxygen potential of these solid solutions at a given temperature was determined solely by the average valency of the plutonium cations and was not dependent on the plutonium concentration. These conclusions were supported by subsequent studies of Woodley [8]. They used mainly thermogravimetric techniques, but also some measurements with e.m.f. cells, for solid solutions with Pu/(U + Pu) = 0.10, 0.25 and 0.40 in the temperature range 1273–1473 K. However the absolute values of $\bar{G}_{O_2}^{eq}$ are very different.

We should find that the threshold Pu valency for the appropriate three-phase field of the quaternary system Na–U–Pu–O should be constant at least in the range of plutonium concentrations with Pu/(U + Pu) ratios between 0.1 and 0.4. We have seen that the data for $\bar{G}_{O_2}^{eq}$ for the quaternary system could deviate from those for $\bar{G}_{O_2}^{eq}$ of the ternary Na–U–O system if there were marked departures from ideality in the oxide solid solution. The analysis of the data carried out by Woodley [8] and by Rand and Markin [11] suggest that deviations from ideality are not large; for example at 1273 K with an average Pu valency of 3.60, $\gamma_{PuO_{1.8}}$ was estimated to be 1.087 [8], and at 1150 K, $\gamma_{PuO_{1.5}}$ was 1.26 [11]. The magnitude of these deviations is such that the values of $\bar{G}_{O_2}^{eq}$ for the quaternary system should not deviate from those of the ternary system.

We have found that this relationship is not appropriate to the pure plutonia system for which the threshold valency of plutonium is 3.0 compared with the values estimated here which are considerably greater than 3.0.

Our recent assessment [12] of the measurements of the lattice parameter of the oxide solid solution phase in equilibrium with liquid sodium and sodium uranoplutonate, and of measurements of the swelling of dense pellets of the mixed oxide solid solution, have indicated the following.

(i) The threshold plutonium valency decreases with an increase in temperature in the range 673–1073 K.

(ii) The threshold plutonium valency most probably decreases for a given temperature with an increase in the plutonia concentration of the solid solution.

(iii) The values of the threshold valency derived from measurements of the swelling of dense pellets of urania–plutonia solid solutions on reaction with liquid sodium, and those derived from lattice parameters of the remaining oxide phase, were in acceptable agreement. Similar trends were observed although there is considerable scatter in the derived values of the plutonium valency.

(iv) The values of the threshold plutonium valency derived from lattice parameters of the remaining oxide phase depend upon the relationship employed between lattice parameter and composition of the solid solution.

The values of the lattice parameter for the solid solution obtained using a uranium–plutonium alloy or carbon to reduce the oxide are different from those of the solution prepared by reduction in hydrogen. This difference was explained [13] in terms of different concentrations of uranium and plutonium in the metal or carbide phases from that of the "fully reduced" oxide with which they are in equilibrium. Because of the effects of segregation in the oxides containing a second metal or carbide phase, we have chosen to use the lattice parameter data of the oxide reduced in hydrogen for the determination of the threshold plutonium valency. The relationship which we have used to determine this threshold plutonium valency (V_{Pu}) in $U_{1-x}Pu_xO_{2-z}$, from a given value of lattice parameter (a, nm) is

$$V_{Pu} = 4.0 + (72.993/x)[(1-x)0.54707 + 0.5396x - a] \qquad (11)$$

When comparing data on the threshold plutonium valency obtained from the determination of the lattice parameters of the residual oxide phase, it is essential that the same relationship between composition and lattice parameter is employed, otherwise marked discrepancies will appear. There is clearly a need for more detailed experimental determinations of the variation in the lattice parameters of the solid solutions with composition.

We now return to the measurements of $\bar{G}_{O_2}^{eq}$ and, in order to obtain values of the threshold plutonium valency from these measurements, we require the relationship between oxygen potential and O/(U + Pu) ratio of the solid solution for different plutonia concentration at the appropriate temperatures. There is disagreement in the data for this relationship which leads to considerable uncertainty in the values of the threshold Pu valency. This is illustrated in Fig. 5, in which the variations in $\bar{G}_{O_2}$ for the oxide solid solution obtained by Woodley [8], Woodley and Adamson [14] and Martin and McIver [10] are given. The data of Woodley and Adamson have been extrapolated below 1273 K, and those of Martin and McIver were measured over the range 1023–1323 K. The disagreement in these data is unsatisfactory and further experimental measurements would be helpful for obtaining consistency. With a solid solution containing 30 mol% plutonia at 1096 K, the derived values of threshold Pu valency can be either 3.3 ± 0.1 [10] or 3.7 ± 0.1 [8] compared with a value of 3.44 ± 0.04 obtained from our assessment of the data on swelling of pellets of the oxide solid solution on reaction with liquid sodium [12]. The assessment tends to give some support to the measurements of Martin and McIver [10].

From Fig. 5 it can be seen that the data of Martin and McIver [10] do not support the observation that the threshold plutonium valency decreases with increasing temperature; this observation is, however, supported by the extrapolated data of Woodley and Adamson [14].

Measurements of $\bar{G}_{O_2}$ for hypostoichiometric urania–plutonia solid solutions with Pu/(U + Pu) = 0.2 have been reported by Mari et al. [15] and Ewart et al. [16]. Measurements were made using an e.m.f. cell technique on

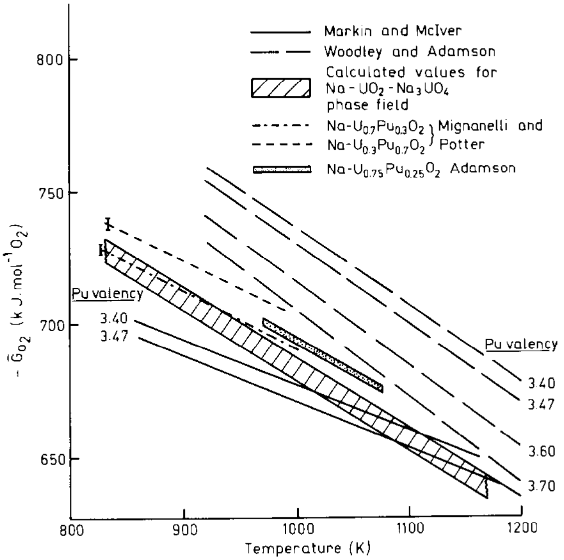

Fig. 5. A comparison of oxygen potentials for the sodium–urania and sodium–urania–plutonia systems with those for the urania–plutonia system.

solutions with oxygen to (U + Pu) ratios of 1.995, 1.985 and 1.964 in the temperature range 800–1300 K. The solutions were prepared by coprecipitation and the desired O: (U + Pu) ratio was obtained by reduction at 1473, 1573 and 1673 K for 6 h. Coprecipitation was the method used by Martin and McIver, but Woodley obtained the solution using both coprecipitation and mechanical blending of the powders. The data of Mari et al. [15] support the measurements of Woodley; subsequent studies by Ewart et al. [16] indicated, however, that the temperature dependence of $\bar{G}_{O_2}$ may be influenced by the method of preparation. For example, Ewart et al. found that at 1350 K, successive temperature cycling of the specimen resulted in a lowering of the oxygen potential $\bar{G}_{O_2}$ and an increase in the entropy ($\bar{S}_{O_2}$).

Finally in this section on the phase equilibria of this quaternary system it should be noted that we require further information on the threshold Pu valency for solid solutions with concentrations Pu/(U + Pu) > 0.4. We wish to determine why the threshold Pu valency decreases with increasing Pu concentration. It should be noted that in solid solutions of urania and ceria, at a given temperature, $\bar{G}_{O_2}$ is not solely determined by the Ce valency, but also by the Ce concentration [17]. In these solutions with Ce/(U + Ce) ratios of up to 0.5, at a given value of $\bar{G}_{O_2}$, the valency of Ce decreases as the Ce concentration increases. If this were a feature of the urania–plutonia solid solutions, then for solutions with Pu/(U + Pu) ratios greater than 0.4, we might expect to find a decrease in the threshold Pu valency for reaction with liquid sodium with an increase in Pu concentration; we know that for the pure Pu system, the threshold valency is 3.0. There is still a discrepancy for solutions with plutonia concentrations of up to 40 mol%, since $\bar{G}_{O_2}$ of the solid solution is only dependent on the Pu valency and thus the threshold Pu valency for the reaction of liquid sodium with the oxide solid solution should not vary with the composition of the solution. We found, however, that the threshold Pu valency obtained from measurements of the swelling of pellets and the lattice parameter of residual oxide gave an indication that the threshold Pu valency decreases with increasing Pu concentration.

The influence of dissolved fission product cations on the reaction of liquid sodium with fuel oxides

We have discussed the conditions under which liquid sodium would react with urania, plutonia and urania–plutonia solutions. We have considered our understanding of the thermodynamic aspects of such reactions. Such knowledge is essential for describing the consequences of failure of fuel which has only been in the core of the reactor for a comparatively very short time. We have also to consider the consequences of burn-up and, with the desirability of obtaining significantly greater than 10% burn-up of the actinide atoms, we have to examine the effects of the presence of considerable quantities of fission products on the reactions of fuel with sodium. In this section we shall briefly describe some of our preliminary experimental studies on the effects of the presence of additional cations in the urania–plutonia lattice on the reactions with liquid sodium.

We have studied experimentally the reactions between liquid sodium and urania–ceria solid solutions [18]. We have found that the reaction between sintered pellets of stoichiometric urania–ceria solid solution, with ceria contents between 20 and 80 mol%, at 750 °C for 50 h could be interpreted as complete reduction of the cerium cations to the trivalent state. The interaction of liquid sodium with sintered pellets of cerium oxides in the temperature range 400 to 800 °C resulted in the formation of the ternary compound $NaCeO_2$; the remaining oxide phase was $CeO_{1.5}$ [19].

For the solid solutions containing 3–20 mol% ceria, it was found that the extent of reaction was determined by the amount of ceria present and the average valency of the cerium cations. The effect of the addition of 4-valent cerium cations to urania is to raise the thermodynamic potential of oxygen and hence exceed the threshold value for reaction with sodium. A pellet of stoichiometric urania–ceria containing 15 mol% ceria reacts destructively with sodium; the reaction took place at 400 °C in less than 1 h, although no reaction was observed at 200 °C. The presence of 3 mol% ceria also provided sufficient oxygen to the system for reaction, which was confined to the periphery of the pellet. The complete reduction of the solid solution in hydrogen prevented any reaction with sodium.

From the evidence of X-ray powder photographs, the additional phase present was a quaternary compound. The values of the lattice parameters for the reduced ceria–urania solid solution indicate that the ceria content of this solution is the same as that of the oxide. This quaternary compound has a tetragonal structure, and in the composition range 20–80 mol% ceria, the reaction could be expressed by

$$(1+x/2)U_{1-x}Ce_xO_{2.00}\xrightarrow{\text{excess Na}}(x/2)Na_{2x+1}U_{1-x}Ce_xO_3+U_{1-x}Ce_xO_{2-x/2} \tag{12}$$

These results possibly indicate that the presence of cerium as a fission product cation in urania or urania–plutonia could result in additional reaction with sodium.

We have also reacted some spheres of sintered doped urania–plutonia with liquid sodium; the spheres were of 800 μm diameter and 98% theoretical density. Their composition was $U_{0.63}Pu_{0.27}Fp_{0.10}O_2$ with $0.1Fp = Ba_{0.010}La_{0.009}Ce_{0.020}Pr_{0.008}Nd_{0.023}Zr_{0.003}$. After reaction with sodium at 850 °C for 48 h, the spheres remained intact and a volume swelling of approximately 13% occurred. X-ray powder photographs showed only the presence of the reduced oxide phase with a face-centred cubic structure and lattice parameter $a_0 = 0.54464 \pm 0.0004$ nm; the lattice parameter of the unreacted oxide was $a_o = 0.54371 \pm 0.0002$ nm. The presence of the cations had caused an additional volume swelling of about 4%.

If the increase in swelling were a result of the further reduction of the oxide, this is not reflected in the increase in the lattice parameter of the oxide product phase relative to the pure oxide system (0.5437 nm to 0.5446 nm for the doped oxide, and 0.5450 nm to 0.5470 nm for the pure oxide).

When the reaction was carried out at 450 °C for 170 h, a volume swelling of approximately 8.3% was obtained. It would appear, therefore, that the rate of reaction is also influenced by the presence of these additional cations in the oxide lattice, since negligible swelling was observed with urania–plutonia solid solutions at this temperature.

The results from these studies on the reactions of liquid sodium with urania–plutonia containing fission product cations show that the inclusion of these cations can cause an increase in reaction rate, increased swelling and break-up of pellets. Our results in terms of swelling and temperature are less pronounced than those of Housseau et al. [5].

Some measurements of the oxygen potential ($\bar{G}_{O_2}$) of the phase field with liquid sodium and the doped spheres were made using the same e.m.f. technique as described earlier. The spheres were crushed before placing into the e.m.f. cell with liquid sodium. The variation in the measured values of $\bar{G}_{O_2}$ with temperature are shown in Fig. 6. It should be noted that there is considerable scatter in these data. Problems were encountered in obtaining a constant value with time for the e.m.f. of the cell at each temperature; it seems likely, therefore, that the values which are presented may not be true equilibrium values of $\bar{G}_{O_2}$. At the higher temperatures, the effect of this drift was to approach values of $\bar{G}_{O_2}$ for the urania–plutonia system.

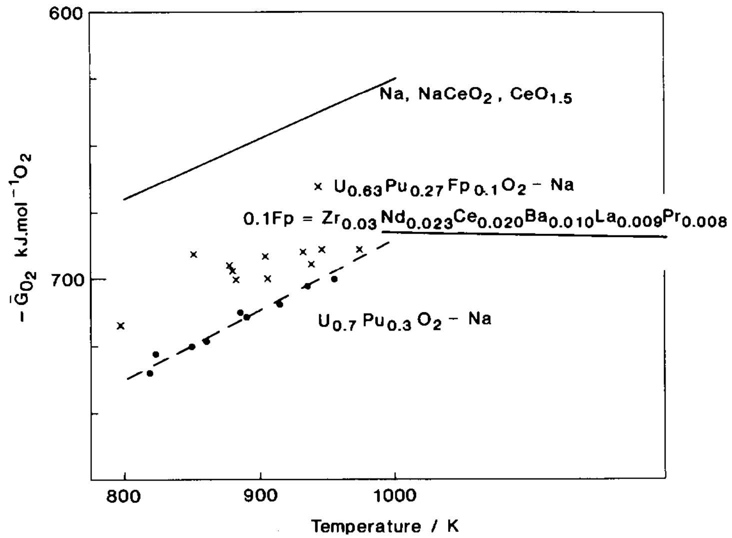

Fig. 6. $\bar{G}_{O_2}$ for sodium–ceria, sodium–urania–plutonia and sodium–urania–plutonia with the addition of fission product cations (Fp).

The variation in $\bar{G}^{eq}_{O_2}$ with temperature for the phase field, Na(l), Ce_2O_3(s), $NaCeO_2$(s), has been determined [20] using the same e.m.f. cell method as described earlier, and this variation can be expressed by

$$\bar{G}^{eq}_{O_2}\left(\mathrm{J}\ (\mathrm{mol}\ \mathrm{O}_2)^{-1}\right) = -848070 + 223.4\,T \tag{13}$$

These data are also shown in Fig. 6, and are considerably more positive than those for the Na(l), UO_2(s) and Na_3UO_4(s) phase field.

When urania–ceria solid solutions react with liquid sodium, it seems likely that the first phase to form will be Na_3UO_4; there may be some solubility of Ce cations in this phase. With the addition of oxygen, the solid solution would be oxidised until the four-phase field, Na(liquid), urania–ceria solid solution, Na_3UO_4 and $NaCeO_2$, at an oxygen potential close to that for the formation of $NaCeO_2$ from liquid sodium and ceria, is reached. Further oxidation would result in the oxidation of the solid solution and the formation of other ternary or quaternary compounds.

THE REACTIONS OF LIQUID SODIUM WITH IRRADIATED FUEL

The possible chemical state of the fission product elements in irradiated fuel is shown in Table 1. Oxygen will migrate to the colder regions of the fuel and the more volatile fission product elements or species will be found in the fuel clad gap or plenum of the pin. In addition to the rare gases krypton and xenon, appreciable quantities, of the elements rubidium and

TABLE 1

The chemical state of fission products in irradiated urania breeder and urania–plutonia solid solution fuel

Fission product elements	Likely chemical state
Kr, Xe	Elemental state
Y, La–Eu and actinides	Oxides which dissolve in host matrix
Ba, Sr	Oxides which can dissolve to a limited extent in the fuel and also form separate phases $Ba_{1-x}Sr_x[Zr_{1-w-y-z}Mo_wU_yPu_z]O_3$
Br, I	Single-phase halide solution $Cs_{1-x}Rb_xBr_{1-y}I_y$
Rb, Cs	$Cs_{1-x}Rb_xBr_{1-y}I_y$ and compounds analogous to Cs_2UO_4 and $Cs_2UO_{3.56}$ e.g. $(Cs_{1-x}Rb_x)_2(U_{1-y}Pu_y)O_4$
Se, Te	Single-phase chalcogenide solution $(Cs_{1-x}Rb_x)_2Se_{1-y}Te_y$
Zr, Nb	Some dissolution in host matrix, see also Ba, Sr group.
Mo, Tc, Ru, Rh, Pd	Usually single-phase alloy, sometimes two phase. Some Mo can oxidise to MoO_2 and also form a compound analogous to Cs_2MoO_4—$(Cs_{1-x}Rb_x)MoO_4$
Ag, Cd, In, Sn, Sb	Fission yields low; alloyed.

caesium, bromine and iodine, selenium and tellurium and possibly molybdenum will be found in the fuel clad gap. We shall only consider the reactions of the fission products with significant yields (namely, caesium, iodine and tellurium) within the fuel clad gap. In addition to the reactions of the fission product elements with the fuel we have to consider their reaction with the components of the cladding.

The dissolution of the cations of the fission product elements in the urania–plutonia solid solution (particularly the lanthanides for which the predominant valency is 3) would result in an increase in oxygen potential at a given anion : cation ratio. So that charge neutrality is maintained, uranium cations would be oxidised to the 5-valent state. Woodley [21] has carried out some determinations of the effects of the cations of Y, Ce, Pr, Nd and Ce dissolved in $U_{0.75}Pu_{0.25}$ oxide on $\overline{G}_{O_2}$. Concentration levels up to those which simulate irradiation of up to 10% burn-up of the heavy atoms, for temperatures 1173, 1273 and 1373 K, were examined. Woodley's conclusions were the following. For a given hypostoichiometry, $\overline{G}_{O_2}$ increases linearly with simulated burn-up, and the rate of increase increases with initial stoichiometry. At 1173 K, $\bar{G}_{O_2}$ increases more rapidly with added cation concentration, than at 1273 and 1373 K, for which the rates of increase for a given stoichiometry are essentially identical.

In addition to this effect of irradiation, the presence of other fission product elements will influence the change in $\bar{G}_{O_2}$ with burn-up, as will the steep temperature gradients within the operating fuel. The centre temperature of the fuel will be > 2000 °C and that of the fuel surface approximately 800 °C. The temperature gradients will result in transport of both oxygen, the actinide elements and the fission product elements along the gradients. The amounts of the fission product elements which would be found in the fuel clad gap and in the plenum will be very dependent on the operating conditions of the fuel, for example, the rating, the power history, and the burn-up. Such aspects of fission products release were considered by Feuerstein et al. [22] in their review.

We are modelling the chemical constitution of the fission product elements in the fuel clad gap. The physical parameters of the operating fuel pin are obtained using the TRAFIC Code [23] and with these parameters the changes in chemical constitution with burn-up are modelled using the code SOLGASMIX [24]. SOLGASMIX calculates the position of chemical equilibrium by minimising the total Gibbs energy of the system, and some preliminary calculations of the constitution of a fast reactor fuel have been presented previously [25].

With a knowledge of the chemical state of the fission product elements in the fuel, we can then consider the likely effects of a breach of the cladding and the reactions of irradiated fuel with liquid sodium. The value of $\bar{G}_{O_2}$ in the gap will determine the compounds which are formed, or alternatively, we can consider that the formation of some compounds will determine the value of $\bar{G}_{O_2}$ and act effectively as a buffer against a rise in $\bar{G}_{O_2}$ with burn-up of the heavy atoms.

We have examined the conditions of $\bar{G}_{O_2}$ under which the groups of compounds could be formed. These have been plotted as Ellingham diagrams in Figs. 7 and 8.

We shall now consider the effects of sodium ingress on the compounds in the fuel clad gap. Of the phases given in Table 1 those that would be found in the gap are as follows: $Cs_2UO_{3.5}$, Cs_2UO_4, Cs_2Te, Cs_2MoO_4, Te and I. Additionally the phases Cs_4CrO_4, Cs_3CrO_4 and Cs_2CrO_4 could be found. The exact constitution would depend on $\bar{G}_{O_2}$ and temperature.

We have seen that the stabilities of these phases, with respect to excess sodium in Figs. 7 and 8, would result in the decomposition of the Cs uranates and chromates to form Na_3UO_4 or $NaCrO_2$. Na and Cs are completely miscible in the liquid state [26,27]. At the temperatures of the coolant (between 450 and 650 °C) it is most probable that Cs_2Te would dissolve in liquid sodium; there is considerable solubility of Te in Cs (> 10

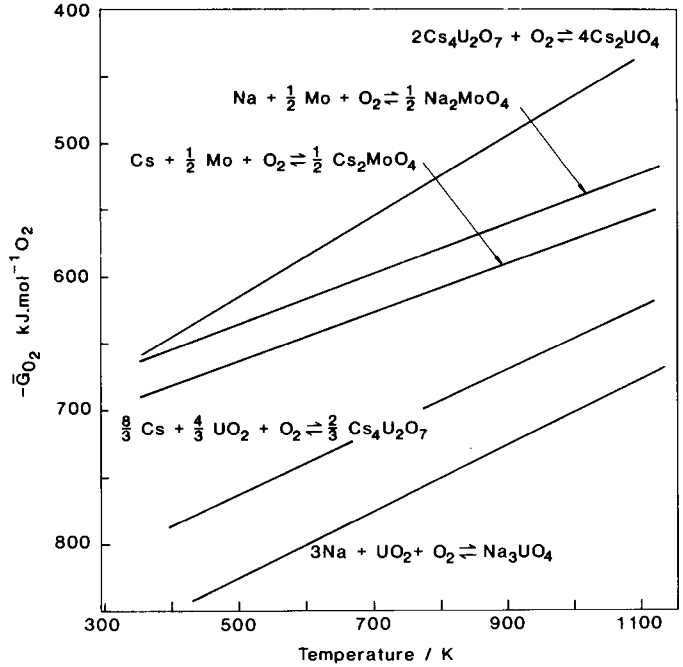

Fig. 7. Stabilities of caesium and sodium uranates and molybdates.

at% at 300 °C) [28]. The phase diagram of the Na–Te system suggests that there could be up to 15 at% Te solubility at 650 °C [29], although the subsequent measurements of Walker [30] give a much lower solubility: 0.23 at% Te at 650 °C.

Recent determination of the thermodynamic parameters of Cs_2Te [31,32] have shown that this compound is very stable, and before other tellurides could be formed with, for example, the cladding, the thermodynamic activity of tellurium would have to increase. This could be achieved by an increase in the oxygen potential. Relatively high tellurium potentials are required for the formation of tellurides of the fission product element Pd [33,34] and for the formation of tellurides of the main components of the cladding and structural materials, chromium, iron and nickel [35–40]. CsI will also dissolve in liquid sodium. The available data on the solubility of halogens in the alkali metals has been reviewed by Barker [41]. At 833 K, the solubility of NaI in Na is approximately 0.2 mol%, and for CsI in Cs is about 25 mol%.

Any Cs chromates formed by reaction of Cs with the cladding would not be stable in the presence of liquid sodium and would result in the release of Cs to the liquid sodium.

We also note, however, that any molybdenum in the form of Cs_2MoO_4 would be stable with respect to sodium, provided that the thermodynamic data assessed for Na_2MoO_4 are reliable [42].

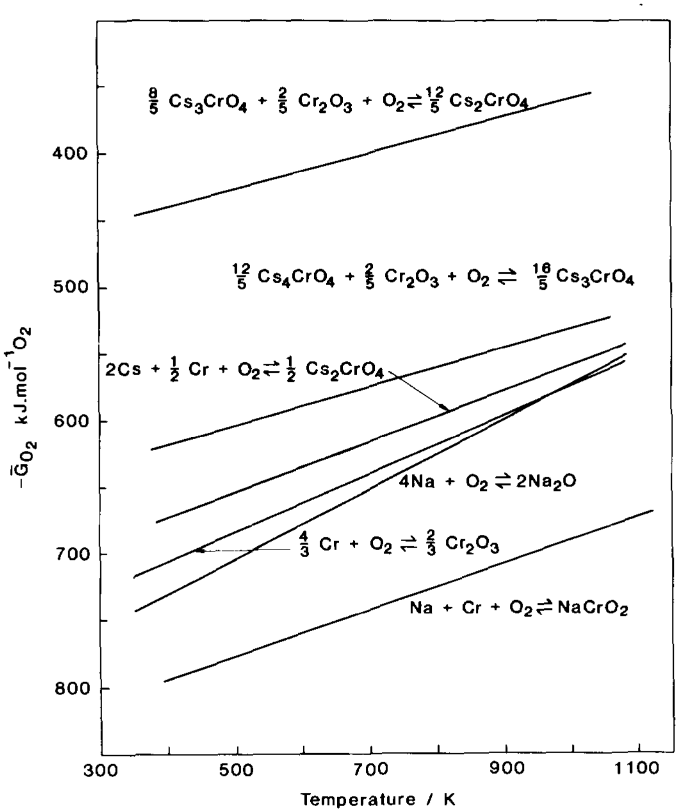

Fig. 8. Stabilities of caesium and sodium chromates.

We have already considered the effects of the ingress of sodium on the changes of the chemical constitution of the fission product species in the fuel clad gap. The outer region fuel matrix will also react with sodium to form essentially a sodium uranoplutonate. These reactions will result in contamination of the primary coolant by dissolved fission product elements and by particulate materials. Some of the dissolved and particulate materials will be found on the surfaces of the primary circuit.

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