

MATERIALS FOR NUCLEAR ENERGY

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Abstract - The paper reviews the state of some current areas of interest in reactor materials, with particular reference to reactor fuels and to the release of fission products from a degrading core and their subsequent containment.

The following topics are discussed.

1. The properties of urania at high temperatures.

An analysis of the various theoretical contributions to the heat capacity of urania (following Hyland) accounts satisfactorily for the enthalpy increment up to 2500-2600K. Above this temperature an additional contribution to the enthalpy is required - the data suggest that the heat capacity of UO_2 is essentially constant (at $\sim 19.5R$) from 2600K to 3120K, the melting point. This phenomenon is presumably related to the increasing Frenkel disorder found in UO_2 (and other compounds with the fluorite structure) at temperatures above c. 0.8 times their melting points.

The methods used to extrapolate the oxygen potential of UO_{2-x} through the solidus-liquidus are discussed, with emphasis on the difference in slope of the G_{O_2} vs. T curve in the two regions.

2. The interaction of fission products released from a degrading LWR core with steam-hydrogen mixtures, with special emphasis on barium, strontium and tellurium.

3. The importance of gaseous iodine compounds other than $I_2(g)$ over iodine solutions (for containment studies).

INTRODUCTION

In a nuclear reactor fuel, more than thirty elements are formed as fission products and a wide range of other materials (zirconium alloys, steels, graphite, high temperature water) are used as casing, structural, moderating and cooling agents. The term 'nuclear energy material' thus covers a broad part of the science of materials. The nuclear energy industry has always been in the forefront in the application of thermodynamics for the interpretation of the behaviour of materials at high temperatures, partly because of the chemical complexity of an irradiated nuclear fuel, and partly because the industry developed strongly at a time when measurement techniques in chemical thermodynamics were reaching some precision. The recent development of efficient computer programs and data bases for the industrial application of thermodynamics has ensured that this trend has continued.

In this paper, some current aspects of work in reactor materials are reviewed, with particular reference to fuels for both light-water and fast reactors, and the possible release (from a degrading core) and containment of fission products.

THE PROPERTIES OF URANIA AT HIGH TEMPERATURES

The thermophysical properties of both UO_2 and $(U,Pu)O_2$ from ambient temperature to about 5000K and pressures up to 10 MPa (in particular the heat capacity and total vapour pressure) are of interest in safety assessments, particularly for fast reactors. Two recent developments in our background knowledge of the properties of urania at high temperature are discussed.

Heat capacity contributions, including defect behaviour

The internal energy of urania and (U,Pu)O₂ is of course of direct relevance in determining the temperatures and pressures likely to be reached in a degrading fast reactor core. There are a number of measurements of the enthalpy increment H(T)-H(298.15) for UO₂, both in the solid up to the melting point (3120K) and a short range of the liquid (up to 3520K).

The heat capacity of UO₂ increases quite sharply above ~ 2000K, and a lively discussion has developed concerning the origin of this increase.

Bredig (1,2), followed by Szwarc (3), were the first to suggest that the high-temperature enthalpy data, particularly those of Hein and Flagella (4), indicate a second-order transition in UO₂ around 2600K. Subsequently, a number of attempts have been made to fit the enthalpy data, with or without a transition, by including a term of the form which represents a contribution from the defects, which were first suggested to be of the Frenkel type (3). However MacInnes and Catlow (5) and Walker and Catlow (6) suggested that in stoichiometric UO₂ electronic defects due to the equilibrium



were the dominant defect. Recently Browning *et al.* (7) have pointed out that the various contributions to the heat capacity could now be calculated relatively accurately, and showed that there was excellent agreement up to 2500K between the experimental enthalpy data and the values derived from the following five contributions:

- harmonic phonon term (modelled by a combination of Einstein and Debye functions)
- an anharmonic term (Hyland and Stoneham (8))
- a Schottky term, representing the contribution from the crystal field component (based on the energy levels reported by Thorn *et al.* (9))
- an electronic defect contribution, from the $2 \text{U}^{4+} = \text{U}^{3+} + \text{U}^{5+}$ reaction (Hyland and Ralph (10))
- a dilation contribution, based on temperature dependent values of the expansion coefficient, density and compressibility given by Fink *et al.* (11).

The relative contributions of these terms are given at three typical temperatures in Table 1, and the overall fit to the enthalpy data is shown in Fig. 1. These would indicate that up to ~ 2500K, there is a small electronic contribution to C_p, but the contribution from any Frenkel defects must be small. Around 2500K, however, the enthalpy increment data indicate that the heat capacity changes relatively suddenly, but above 2500-2600K remains relatively constant, but at a very high value (~ 19.5 R) - Fig. 2 indicates that there is certainly no evidence for a continuous increase (with an exponential component) which might be expected if there were continuously increasing proportion of defects above 2500K.

TABLE 1. Contributions to H(T)-H(298.15) for UO₂ (J.mol.⁻¹K⁻¹)

| T/K | Harmonic | Anharmonic | Schottky | Elect. Defect | Dilation | Experimental - total |
|------|----------|------------|----------|---------------|----------|-------------------------|
| 1174 | 62580 | 664 | 2182 | 27 | 2802 | 1451 |
| 2073 | 129382 | 2166 | 6842 | 1477 | 13707 | - 1863 |
| 3101 | 206098 | 4903 | 14230 | 8339 | 41790 | 23210 |

The enthalpy data therefore support a quite normal behaviour of UO₂ up to ~ 2500K, where a relatively sharp transition to a phase with a quite high heat capacity (close to 20 R) occurs. This behaviour is similar to that recently found by Fischer *et al.* (12) in ThO₂, where the enthalpy data show a distinct discontinuity at 2960K, which is close to 0.81 T_{fus}, as is 2500K for UO₂. Since ThO₂ has no 5f electrons, it seems unlikely that this anomaly can be electronic in origin.

Neutron scattering work by Clausen *et al.* (13) has provided some evidence that defects may be formed in UO₂ at 2673K, and the extension of this work to 2900K (and to ThO₂) which is to be presented at this conference (ref. 14) will be most illuminating with respect to the phenomena discussed in this section.

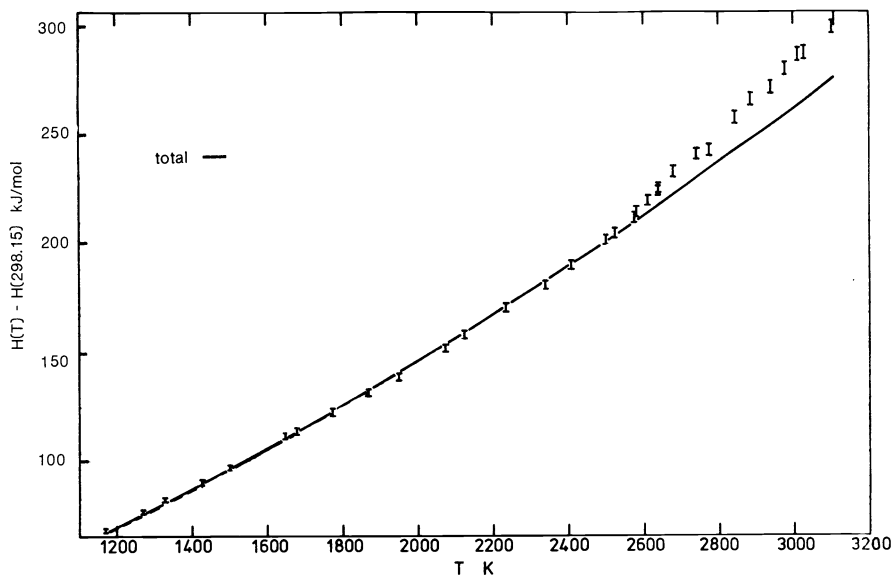


Fig. 1 Comparison of experimental enthalpy values (ref. 4) with the sum of experimentally identified contributions.

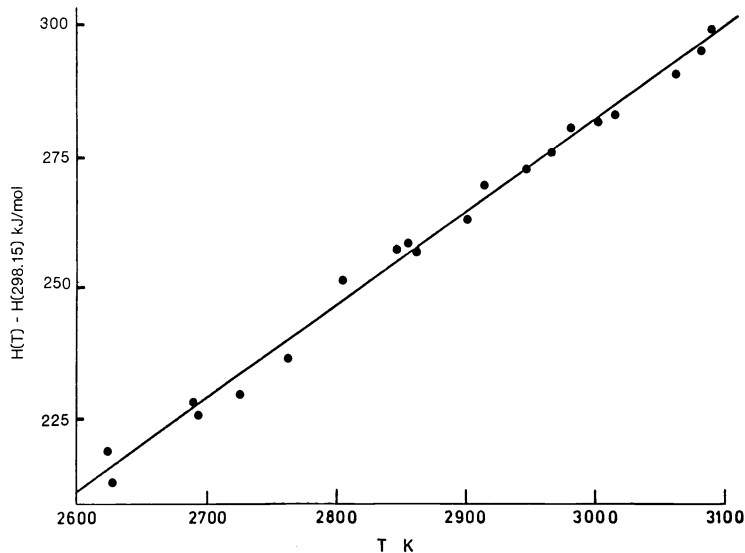


Fig. 2 Enthalpy increment for $\text{UO}_2(\text{s})$ above 2600K.

Oxygen potentials in urania at high temperatures

An important property for safety analyses of fast breeder reactors is the equation of state of an irradiated fuel $\text{U}_y\text{Pu}_{1-y}\text{O}_2$. A knowledge is therefore required of the vapour pressure of this mixed oxide up to $\sim 6000\text{K}$, and considerable effort has been expended world-wide in defining the vapour pressure of $(\text{U,Pu})\text{O}_2$ and UO_2 , both by experimental measurement by laser bombardment (refs. 15-17) and extrapolation by theoretical models (see for example refs. 18 to 20). Breitung (21) has recently given an excellent review of the results of these numerous studies, showing that although the experimental and theoretical results are tolerably consistent with the international consensus (ref. 22), there is still an uncertainty of nearly a factor of 10 in the total vapour pressure over UO_2 at 5000K.

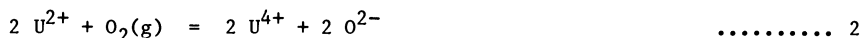
Since UO_2 and $(\text{U,Pu})\text{O}_2$ do not vaporise congruently, an important quantity in all the theoretical calculations is the oxygen potential over UO_{2-x} and $(\text{U,Pu})\text{O}_{2-x}$, as this determines the relative proportions of gaseous uranium and plutonium oxides, and of course of diatomic and monatomic oxygen (which may be the predominant gaseous species above 5000K). In this section we discuss the problem of extrapolating oxygen potentials predicted by models through the solidus-liquidus, and mention an interesting new analysis by Hyland of the oxygen potential data very close to UO_2 which draws attention to the existence of systematic 'errors' in measured compositions due to the different criteria for defining the stoichiometric UO_2 composition used by different authors.

There have been a considerable number of models for both UO_{2-x} and $(\text{U,Pu})\text{O}_{2-x}$ (for a recent review see ref. 23). To discuss the extension into the liquid, we shall concentrate on one of the simpler models, that proposed for UO_2 by Blackburn (24).

Blackburn's model assumes that the oxygen excess or deficit is accommodated by the formation of U^{6+} and interstitial O^{2-} ions and U^{2+} and oxygen vacancies, respectively; the oxygen ions on interstitial sites are not differentiated from those on normal lattice sites. By straightforward algebra, the oxygen pressures over UO_{2-x} are then given by

$$\ln p(O_2) = 2 \ln [(2-x)(U^{4+})/U^{2+}] - \ln K_2$$

where (U^{4+}) and (U^{2+}) , the concentrations of the relevant ions, are simple functions of K_1 and K_2 , the equilibrium constants for the reactions



These equilibrium constants were evaluated from the oxygen potentials at the lower and upper phase boundaries of urania; these constants (expressed as $\ln K_i = A_i + B_i/T$) have recently been revised (ref. 25) by Blackburn to include later data. Despite a number of criticisms which can be levelled at the model (particularly the assumption of U^{2+} and U^{6+} as the ions formed, when theoretical calculations using the HADES computer program, and other observations, suggest strongly that the formation of U^{3+} and U^{5+} would be considerably more favourable), it predicts reasonably accurately the oxygen potentials of both hypo- and hyperstoichiometric solid urania over an extensive range of composition and temperature. This, combined with the simplicity of its expressions, even when extended to $(U,Pu)O_{2+x}$, has made it an attractive model for reactor safety assessments.

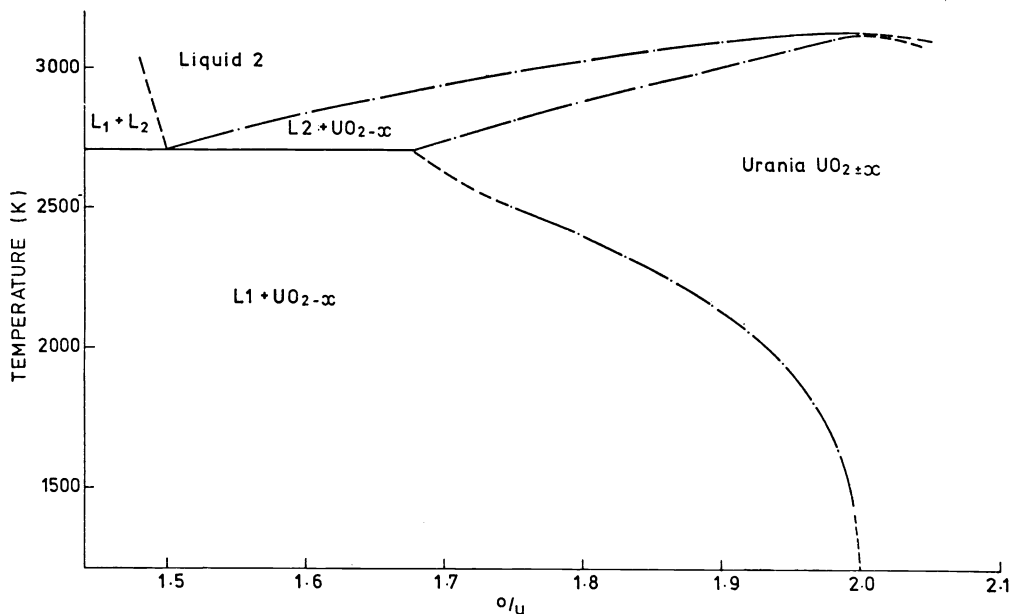
How can a model such as this be extrapolated into the liquid region? In particular, can we predict how the partial molar entropy and enthalpy of solution of oxygen change on passing into the liquid? Figure 3 from the review by Rand et al. (26) shows the relevant part of the phase diagram of urania.

Formally we may write

$$\text{for solid } UO_{2-x} : \bar{S}_U^s + \frac{(2-x)}{2} \bar{S}_{O_2}^s = \Delta_f S(UO_{2-x}(s))$$

$$\text{liquid } UO_{2-x} : \bar{S}_U^l + \frac{(2-x)}{2} \bar{S}_{O_2}^l = \Delta_f S(UO_{2-x}(l))$$

where \bar{S}_i^s and \bar{S}_i^l are the partial molar entropy of solution of i ($= U$ or O_2) in the solid and liquid, for a given composition UO_{2-x} , and subscripts f and fus (used below) refer to formation and fusion respectively.



PHASE DIAGRAM OF HYPOSTOICHIOMETRIC URANIA

Fig. 3 Phase diagram for hypostoichiometric urania.

So by difference

$$\Delta_{\text{fus}} [(\bar{S}_U) + \frac{(2-x)}{2} (\bar{S}_{O_2})] = \Delta_{\text{fus}} (UO_{2-x})$$

where $\Delta_{\text{fus}} (\bar{S}_{O_2}) = \bar{S}_{O_2}^{\text{L}} - \bar{S}_{O_2}^{\text{S}}$ etc.

$\Delta_{\text{fus}} (UO_{2-x})$ can be measured only for $x = 0$, the congruently melting composition, but could be derived for other compositions from realistic models for solid and liquid urania. The problem is thus to apportion the entropy (and enthalpy) of fusion of urania between the partial molar quantities for uranium and oxygen.

Green and Leibowitz (25) have achieved this by an ingenious extension of Blackburn's model. Equilibria 1 and 2 are still assumed to occur, but with different equilibrium constants in the liquid phase. They write the equilibrium constants for the solid as K_1^{S} instead of K_1 , and put

$$\ln K_1^{\text{S}} = A_1^{\text{S}} + B_1^{\text{S}}/T \quad \text{in } UO_{2-x}(\text{s})$$

and $\ln K_1^{\text{L}} = A_1^{\text{L}} + B_1^{\text{L}}/T \quad \text{in } UO_{2-x}(\text{l})$

As noted the values of A_1^{S} and B_1^{S} are derived from (very few) oxygen potential measurements at or near the lower phase boundary of urania. Unfortunately no oxygen potential data exist for $UO_{2-x}(\text{l})$, so Green and Leibowitz have estimated A_1^{L} and B_1^{L} by making the following assumptions:

- (i) $A_1^{\text{L}} = A_1^{\text{S}}$ (the entropy of reaction 1 is the same in liquid and solid urania).
 - (ii) $\Delta S_2 = \Delta S$ for the reaction $2 UO + O_2(g) = 2 UO_2$ for both solid and liquid oxides.
Hence, $(A_2^{\text{L}} - A_2^{\text{S}}) = 2 (\Delta_{\text{fus}} UO_2 - \Delta_{\text{fus}} UO)/R$
 - (iii) $\Delta_{\text{fus}} S(MO_n) = 1.4 (1+n).R$ (the entropy of fusion of an oxide is 1.4R per atom).
- Hence $(A_2^{\text{L}} - A_2^{\text{S}}) = 2.8$

B_1^{L} and B_2^{L} are then calculated from the compositions of the coexisting solid and liquid at two temperatures (2700 and 3120K).

The oxygen potentials predicted for solid and liquid urania by their model are shown in Fig. 4 where the curved heavy line gives the potential of the diphasic (solid + liquid) region. It is also of interest to calculate the change in the entropy of solution of oxygen on fusion, which is not readily apparent from the above analysis - see Table 2.

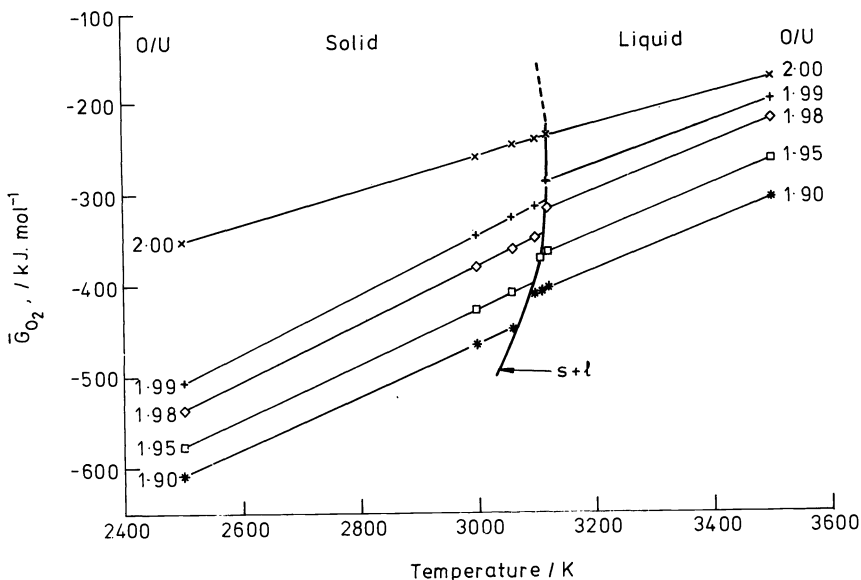


Fig. 4 Gibbs energy of solution of oxygen in UO_{2-x} solid and liquid (Blackburn/Green model).

TABLE 2. Change of the partial molar entropy of solution of oxygen in UO_{2-x} upon fusion (Blackburn/Green model).

| x | $\Delta_{fus} \bar{S}_{O_2}/R$ |
|------|--------------------------------|
| 0 | 2.9 |
| 0.01 | 7.2 |
| 0.02 | 4.6 |
| 0.05 | 3.2 |
| 0.10 | 2.9 |

Thus on this model, the change in the partial molar entropy of solution of oxygen in hypostoichiometric UO_{2-x} on fusion is always greater (sometimes substantially so) than the entropy of fusion of UO_2 (2.88 R).

However, it should be remembered that the change of \bar{S}_{O_2} on fusion may be markedly dependent on the particular defect. For example, there is evidence that the entropy of solution of oxygen in liquid $Fe_{1-x}O$ ($0.06 < x < 0.14$) is actually more negative than in solid wüstite (ref. 27), possibly because the predominant defects are iron vacancies rather than any imperfections in the oxygen lattice.

We conclude this section by mentioning a new analysis of the data for UO_{2+x} with $|x| < 0.005$ by Hyland (28). This assumes, as have other models, that the predominant defects in this region are U^{3+} , U^{5+} , oxygen interstitials and vacancies. The equilibria between the defects are written in a very rigorous manner, (differentiating for example between interstitial and lattice oxygen ions), leading to somewhat different final expressions for $\ln p(O_2)$ from other authors. However the major novelty in the treatment is to emphasise that in the intrinsic region, where the equilibrium concentrations of U^{3+} and U^{5+} and/or interstitials and vacancies (Frenkel defects) exceed those resulting from the non-stoichiometry, it is essential to correct the experimental compositions reported by the authors. These compositions are never absolute, but are obtained by difference from another oxide whose composition is assumed known - frequently ' UO_2 ' under given conditions (e.g. a defined CO/CO_2 ratio at a given temperature) or U_3O_8 heated to air in given conditions. However there is considerable disagreement in the values of \bar{G}_{O_2} for $UO_{2.000}$ taken or derived by various authors, as shown in Fig. 5. By analysing the only two sets of data which extend each of side of $O/U = 2$ in terms of his model, Hyland was able to rationalise these differences and calculate the offset in composition of each author's defined zero (= UO_2) and the true zero. In addition values were derived for the equilibrium constants (at 1073 and 1970K) for the reactions

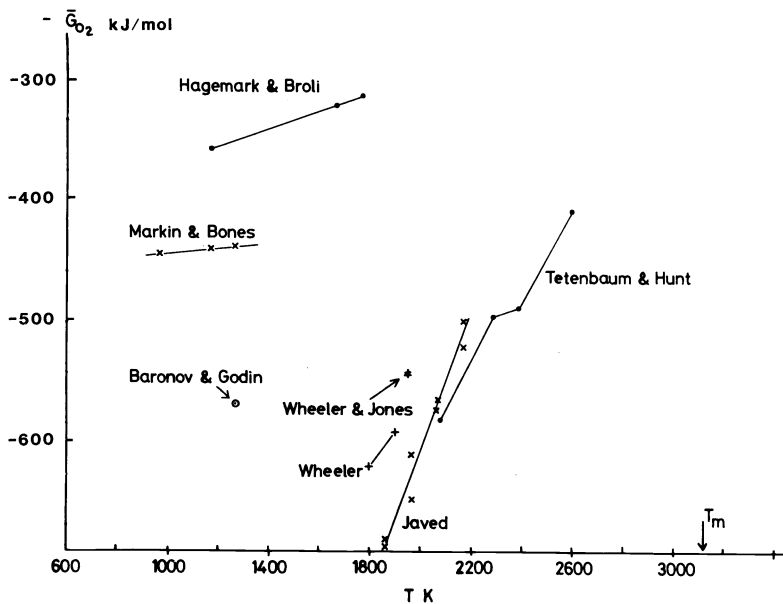
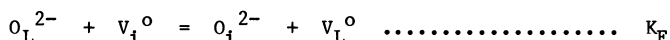


Fig. 5. Experimental values for \bar{G}_{O_2} over stoichiometric UO_2 (ref. 28).

and the Frenkel defect equilibrium



where V = vacancy, and the subscripts i and L refer to interstitial and lattice positions.

The value of K_e obtained overlaps, within the combined uncertainties with values obtained from transport measurements, but that for K_F is much smaller than that determined from anion diffusion data. This is the only inconsistent feature of this interesting new model.

FISSION PRODUCT RELEASE FROM A DEGRADED WATER REACTOR CORE

In recent years there has been a major effort in the nuclear industry to try to understand more fully and thus predict the rate of release of various fission products from a over-heating core of a pressurised water reactor, and their subsequent behaviour inside the containment which minimizes their release to the environment. We shall here deal with the predictions, essentially from equilibrium thermodynamic considerations, of the chemical behaviour of some fission products in irradiated UO_2 . It must be emphasised that there are several barriers (fuel can, reactor pressure vessel, primary and secondary containments) which would have to be breached before any release of fission products to the environment could occur.

The probable chemical state of the major fission products in the fuel element is shown in Table 3, although during normal operation, when the maximum temperature of fuel may be as low as 1500K, nucleation of many of these phases may not have occurred. If a loss of coolant occurs, the fuel temperature starts to rise rapidly (mainly due to the steam-Zircaloy reaction) leading ultimately to clad failure and exposure of the fission products to a flow of a steam-hydrogen mixture. If a substantial part of the core has melted, a mixture of a Zr-U-(Cr,Fe,Ni) metal phase with a UO_2 - ZrO_2 molten oxide phase will be dripping through the remaining core. The distribution of fission products between these phases is of some importance, since these will provide the main source of heating in the later stages of the accident. Clearly a proper thermo-hydraulic analysis of this situation is so complicated that many simplifying assumptions have to be made in the thermodynamic analysis. However it is clear that we must distinguish between three types of fission products:

- those (such as Kr, Xe, Cs and I) which are completely volatile when the cladding ruptures (~ 2000K)
- those which forms compounds of low volatility in the fuel, but can react with the streaming steam-hydrogen mixture to given appreciable amounts of vapour - e.g. Ba, Sr, Ru.
- those which form compounds of low volatility and no other volatile compounds are formed reaction with $H_2(g)$ or $H_2O(g)$ - e.g. Pd, Zr. The loss of these materials will be governed by the vapour pressure of the appropriate compounds at the relevant temperature.

TABLE 3 Some possible chemical states of fission product elements in irradiated UO_2 .

| Element | Chemical State |
|---------------------------------|--|
| Kr, Xe | elements |
| Y, La-Eu Actinides Zr, Nb | oxides which dissolve in the urania matrix |
| Br, I | $Cs_{1-x}Rb_xBr_{1-y}I_y$ |
| Rb, Cs | $Cs_2UO_{3.56}$, $Cs_2UO_4^*$ |
| Se, Te | $(Cs_{1-x}Rb_x)_2 Se_{1-y}Te_y$ |
| Sr, Ba | oxides which can dissolve in urania to a limited extent and form separate phases, $Sr_{1-x}Ba_xO$ and $Ba_{1-x}Sr_x(Zr_{1-y-z}U_yPu_z)O_3$ |
| Mo, Tc, Ru, Rh, Pd | alloy phase some Mo could be present as MoO_2 or Cs_2MoO_4 |
| Ag, Cd, In, Sn, Sh | fission yields low, alloyed |

* Rb would be present in these compounds; and other cations may substitute for those of U in the uranates.

We shall discuss in a little more detail the example of Ba and Sr, in the more interesting second class. These elements have appreciable fission yields and are likely to dissolve in the UO_2 matrix, either as a mixed oxide or zirconate (Zr is also a fission product, with $Zr/(Ba + Sr) \approx 2$). Although in principle Zircaloy would partially reduce the oxides, the inside of the Zircaloy can be covered by a relatively impermeable layer of ZrO_2 during normal operation and heat-up before melting, and reduction would be slow.

We have therefore calculated (ref. 29) the vaporisation of barium and strontium in typical flows of hydrogen-steam mixtures at 2250K, given in Table 4, for the more probable case of zirconate formation. All similar barium and strontium species are assumed to form ideal solutions. The results are shown in Fig. 6. The pressures of fission products are not negligible; if realistic flows of $H_2(g)$ and $H_2O(g)$ can be defined from thermohydraulic calculations, these results enable the rate of release of Ba and Sr into the containment to be defined. Since the barium compounds are more volatile than the strontium species, the condensed phases remaining can become enriched in Sr.

TABLE 4. Conditions for vaporisation of barium and strontium from an oxide core.

Temperature = 2250K; Total pressure = 3 bar.
Ba = 7.35 mol; Sr = 8.11 mol.

$H_2 + H_2O = 1200$ mol; $0.1 < H_2/H_2O < 10$

Condensed phases $(Ba,Sr)ZrO_3(s) + ZrO_2(s)$

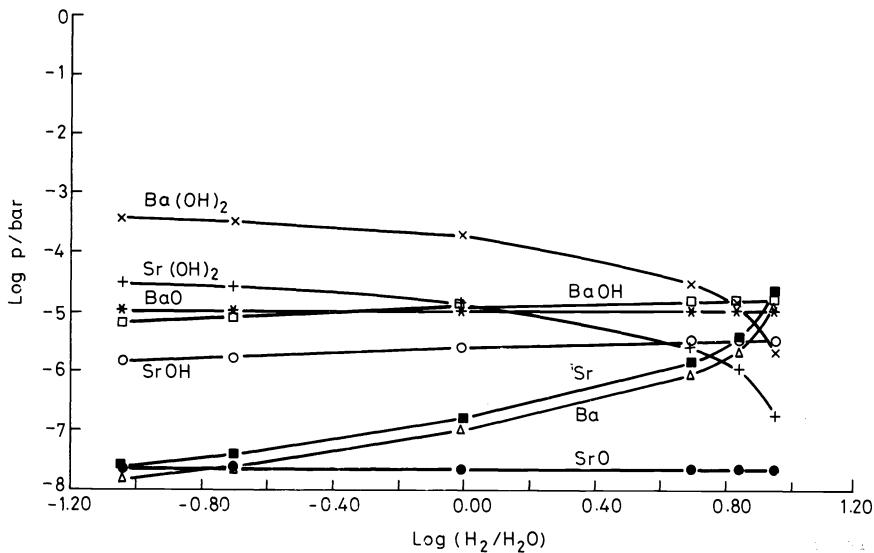
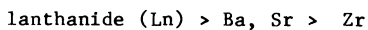


Fig. 6. Vapour species in equilibrium with $(Ba,Sr)ZrO_3 + ZrO_2$ and H_2/H_2O mixtures.

In the more reducing conditions ($H_2/H_2O > 1$), the pressures of the dihydroxide gases decrease, these compounds giving way to the lower-valent species (metal and monohydroxide). However calculations made for lower temperatures in the reactor pressure vessel, away from the degrading core, show that these lower-valent species, as well as the gaseous oxides, react to form the condensed dihydroxides. Thus under all conditions the barium and strontium are likely to be present in the reactor pressure vessel as solid particulates which would be retained by subsequent barriers.

The behaviour of tellurium in a degrading core is also of considerable interest, since it is one of the precursors, albeit a minor one, of iodine. Rather little is known of stability, or even the phase relationships of most of the relevant tellurides. Blackburn and Johnson (30) have suggested that the tellurides become less stable in the order



However, as noted previously, the Ln, Ba, and Sr fission products will preferentially form oxides and the Zircaloy may be deactivated by a ZrO_2 film; hence the suggestion in Table 3 that tellurium is likely to be present in combination with Cs. Adamson and Leighty (31) have

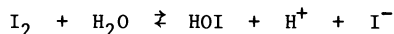
recently published a tentative Cs-Te phase diagram, which shows Cs₂Te to melt congruently at about 1083K. With the estimated stability of Cs₂Te (ref. 32), this would completely vaporise before clad melting, giving predominantly Te₂ and Te in the gas phase, with some H₂Te(g) under reducing conditions. There is strong evidence from work at Sandia National Laboratory (ref. 33) that Te rapidly plates out on steel surfaces, where it is held rather firmly as tellurides of Cr, Fe and Ni. Experimental release fractions of Te from the core are usually somewhat less than unity, perhaps suggesting some reaction within the fuel element with Zr. The enthalpy of formation of zirconium ditelluride has just been determined at Argonne National Laboratory (ref. 34). However a considerable amount of experimental work is still required to improve our knowledge of the stability and phase relationships of tellurium compounds.

The section gives a typical example of the use of computer programs (in this case SOLGASMIX) to study the behaviour of fission products during an accident involving loss of coolant in a PWR type reactor. Clearly the conditions of temperature, pressure and oxygen potential, in particular, must be well-defined so that the important chemical species for any given accident sequence can be determined. In practice, calculations are usually made for a range of these variables covering all the likely conditions for the postulated accident.

VAPORIZATION OF IODINE FROM AQUEOUS SOLUTIONS

Since iodine (particularly I¹³¹) is one of the most important contributors to the possible environmental hazard in a reactor accident, there has been a considerable effort recently to understand more fully the complex aqueous chemistry of iodine. As noted above, iodine is likely to be released from a degrading core as CsI, which will finally find itself as a very dilute aqueous solution [$\sim 1 \times 10^{-6}$ molar] in the containment at temperatures less than 425K. However the main hazard from radioactive iodine arises from airborne species, so that partition coefficient (aqueous \rightleftharpoons gas) of all the neutral species present are important parameters for accident analysis.

It is extremely unlikely that the iodide concentration will be sufficiently high to control the oxidation potential of the system, which will be fixed by some oxide-aqueous ion buffer (perhaps involving iron) which will vary according to the postulated accident. Partition coefficients are therefore required to be known over a considerable range of pH and oxygen potential and to a smaller extent, temperature, suggesting that a thermodynamic approach would be valuable. Lemire *et al.* (35) and Davies and Barry (36) have calculated the concentrations of the numerous aqueous iodine species under a range of conditions. The only two neutral species which would also be volatile are I₂ and HOI - the latter is always assumed to be the formula of the (rapid) disproportionation of iodine in water



although unambiguous identification of this molecule is still lacking. The partition coefficient of I₂ between the aqueous and gas phases is well known, with good agreement between experimental determinations and values calculated from thermodynamic data. However the stability of HOI(g) is still under considerable discussion. Lin (37) has re-analysed partition coefficient data at 294 and 345K. These seem to indicate that in very dilute solutions, the total iodine volatility is greater than that which can be accounted for by I₂(g) alone. However the enhanced volatility appeared only at concentrations below 10^{-2} mg (I)/l, that is $\sim 10^{-7}$ molar, and there was no identification of HOI in the gas phase. Since these low iodine concentrations are likely to be less than those of many impurities (e.g. organic compounds with which HOI(aq) is known to react rapidly), the derived partition coefficient of HOI and hence stability of HOI(g) must be subject to considerable uncertainty.

Paquette *et al.* (38) have recently reported attempts to identify HOI as a gaseous species directly in a mass-spectrometer, without success. HOI⁺ ions were observed, but only when I₂(g) was also present, indicating that it was formed by an ion-molecule reaction. Their conclusion is that HOI(g) is probably at least a factor of ten less volatile than predicted from Lin's analysis.

CONCLUSIONS

In this paper we have attempted to highlight some of the recent developments in the application of thermodynamics to aid our understanding of a number of current aspects in nuclear energy technology, emphasizing the wide range of temperature (up to 6000K) and pressures (up to 10 MPa) and materials that are involved. It is clearly important to continue to develop models which enable us to extrapolate meaningfully to these conditions.

However, our discussion has also made clear that our knowledge of the thermodynamic properties of many compounds, which could be measured with existing experimental techniques, is often still the limiting factor in the successful application of thermodynamical reasoning to nuclear technology.

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