

Conf-8106164--4

CONF-8106164--4

DE83 007935

THERMOPHYSICAL PROPERTIES OF REACTOR FUELS

by

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To be contributed to the Eighth Symposium on Thermophysical Properties, June 15-19, 1981, National Bureau of Standards, Gaithersburg, Maryland.

Work performed under the auspices of the U.S. Department of Energy.

ABSTRACT

Reactor safety analysis involves, in part, the use of large computer codes to follow the course and consequences of hypothetical reactor accidents. As part of the input to these codes, knowledge of the thermophysical properties of reactor materials to very high temperature is required. In many cases, the data needed are neither available in the literature nor readily determinable by conventional experimental means. As a result, long extrapolations, estimates, and theoretical calculations are being used to supply the needed information. Among the more important of the properties needed are vapor pressure and heat capacity of reactor fuel. In this paper, a review is presented of the literature on the enthalpy of uranium, thorium, and plutonium oxide and an approach is described for calculating the vapor pressure and gaseous composition of reactor fuel. In these calculations, thermodynamic functions of gas phase molecular species (obtained from matrix-isolation spectroscopy) are employed in conjunction with condensed phase thermodynamics. A summary is presented of the status of this work.

INTRODUCTION

One of the first studies of fast reactor disassembly accidents was given in a now classic report by Bethe and Tait in 1956 [1], in which an estimate was made of the energy release resulting from the collapse of the core of a uranium-fueled fast reactor. It was assumed that all the coolant had disappeared and that the core melted due to fission product heating. In that report, estimates were made of density, heat capacity, and vapor pressure for uranium up to 6600°C. Since that time, there has been a considerable increase in the complexity of reactor safety analysis, as

well as in the increased need for high-temperature thermophysical property data for reactor materials, particularly vapor pressure and heat capacity.

In general, accident analysis schemes follow, by means of large computer codes, a sequence of events such as is shown in Fig. 1.[2] In such an analysis, some hypothetical initiating event (such as loss of coolant flow) is postulated, the core behavior followed, and the consequences evaluated. Eventually, an assessment of the hazard incurred from such events is made. These analyses, as Bethe and Tait pointed out, do not include an assessment of the probability of occurrence of the events, which is quite a separate issue. At every stage of these computations, property data for the relevant materials are needed; however, for much of the region of interest, conventional experimental methods are inadequate since some extreme, accident calculations predict peak temperatures as high as 6000 K. In order to permit rational use of available resources, considerable effort has been expended on studying the sensitivity of accident analysis schemes to the thermophysical property data input, [3,4,5,6], and such work is continuing. Because of the complexity of the events being modeled and because the sensitivity of results to property data varies with the accident being modeled, it is difficult to generalize broadly about such sensitivity studies.

The two properties which, however, have continually been shown to have the greatest impact on fast-reactor safety studies are the heat capacity and vapor pressure of the reactor fuel. In the following, a review is presented of available data on enthalpy and heat capacity of uranium, thorium, and plutonium oxides. An outline is also given of an approach to the calculation of vapor pressure and gaseous composition for oxide fuel,

which is based on thermodynamic properties of vapor species (obtained spectroscopically) and the condensed oxide; some results of application of this approach are presented.

ENTHALPY

Uranium Dioxide

Enthalpy measurements have been performed on urania up to about 3500 K and reasonably good agreement has been obtained among the various investigators involved.[7,12,15-18] It would be expected that heat capacity would have the form:[7,12,46]

$$C_p = C_v + \frac{\alpha_p^2 V}{\beta_T} T + C_a \quad (1)$$

where C_p and C_v are heat capacities at constant pressure and volume, V , is the molar volume, α_p is the thermal expansion coefficient, β_T is the isothermal compressibility, and T is the temperature. The first two terms are the classical thermodynamic contributions. For UO_2 , it has been found [7,12] that an additional, so-called anomalous contribution C_a was required to be included in Eq. (1) at high temperatures. In the solid region for urania (up to 3120 K), the enthalpy data have generally been correlated using such a three term equation for which the third term had been previously attributed to the formation of Frenkel defects.[7,8] More recently, however, various investigators have found [9,10,11] that it is more reasonable to include an electronic rather than a defect contribution to the heat capacity. In recent reviews of enthalpy and heat capacity data for UO_2 , [12,13] it was found that this recommendation appeared to be correct and the enthalpy data were fitted to an integrated form of the following heat capacity equation:

$$C_p = C_1 \frac{\theta^2 e^{\theta/T}}{T^2 (e^{\theta/T} - 1)^2} + 2C_2 T + C_3 k e^{-E_a/kT} \left(1 + \frac{(T-T^*)E_a}{kT^2} \right) \quad (2)$$

where the constants have the following values:

$$C_1 = 78.212 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_2 = 3.8616 \times 10^{-3} \text{ J mol}^{-1} \text{ K}^{-2}$$

$$C_3 = 3.3993 \times 10^8 \text{ J mol}^{-1} \text{ eV}^{-1}$$

$$E_a = 1.8815 \text{ eV}$$

$$\theta = 516.11 \text{ K}$$

$$T^* = 298.15 \text{ K}$$

and k (the Boltzmann constant) = $8.614 \times 10^{-5} \text{ eV K}^{-1}$. Recent reviews of the available data [7,12,13] for the urania solid region have concluded that a phase transition occurs at about 2670 K as was discussed by Bredig.[14] Work on thorium (q.v.) has given additional support to the existence of both an electronic contribution and a phase transition for the urania solid.

In Fig. 2 is shown a plot of the experimental enthalpy data for urania [15,16,17] up to the melting point (3120 K). Up to the transition temperature, 2670 K, these data are well described by Eq. (2).[12] It would be expected that the constant C_1 would be approximately $9 R$ or about $75 \text{ J mol}^{-1} \text{ K}^{-1}$, which, with the value of about 78, is roughly correct. Examination of available thermal expansion and compressibility data for UO_2 [12] also indicate reasonable consistency with the value found for C_2 from enthalpy measurements. The value found for E_a , however, which would

be expected to be about 1 eV [9,10], was actually found to be nearly 2 eV. The reason for this difference is not understood at present.

From 2670 to the melting point, 3120 K, enthalpy is a linear function of temperature with a constant heat capacity of about $167 \text{ J mol}^{-1} \text{ K}^{-1}$. Any contribution from the third term in Eq. (1) appears to be roughly constant over this temperature range. Thus, for solid UO_2 enthalpy, reliable data and reasonable understanding exist.

For the liquid, however, the situation is quite different in that data are only available to about 3500 K [15,18], far below the 6000 K maximum which would be needed in calculation of the most extreme cases. These liquid UO_2 enthalpy data are shown in Fig. 3. Over this limited temperature range, the enthalpy is a linear function of temperature with a constant heat capacity of about $131 \text{ J mol}^{-1} \text{ K}^{-1}$. Again, any contribution from the third term of Eq. (1) appears to be constant over this temperature range (3120 to 3500 K).

In performing extrapolations to higher temperatures, it is often assumed that the liquid heat capacity continues to be constant even up to the highest temperatures considered.[12] Critical temperature considerations aside (see Conclusions), even though Eq. (1) is expected to apply to the liquid, the sparseness of available data and the uncertainties in the other property values required make extrapolation uncertain. There are experimental values for liquid UO_2 density, thermal expansion coefficient and adiabatic compressibility (from speed of sound measurements), and these may be used to estimate the liquid heat capacity using Eq. (1).

We use the following values from Ref. [12]:

$$\rho = 8.7 \times 10^3 \text{ kg m}^{-3}$$

$$\alpha_p = 10.5 \times 10^{-5} \text{ K}^{-1}$$

$$\beta_S = 33 \times 10^{-6} \text{ MPa}^{-1}$$

where ρ is the density and β_S the adiabatic compressibility. Since

$$\beta_T = \frac{C_p}{C_v} \beta_S \text{ and assuming that } C_v = 75, \text{ we find } \frac{\alpha_p^2 C_v}{\beta_T} = 6 \times 10^{-3} \text{ J mol}^{-1} \text{ K}^{-2}.$$

The estimated temperature coefficient of heat capacity for the liquid calculated from the second term in Eq. (1) is, thus, fairly small. At the melting point, we have $C_p = C_v + (6 \times 10^{-3}) \times 3120 = 94$. The first two terms would be expected to account for roughly 3/4 of the observed heat capacity of $131 \text{ J mol}^{-1} \text{ K}^{-1}$. The estimated temperature coefficient predicts only a few percent change in heat capacity over the experimental temperature range which would not be seen experimentally. Uncertainties in the third term in Eq. (1) make extrapolation of the liquid data difficult, although relatively large errors in that term will not introduce correspondingly large errors in the total heat capacity, unless that term becomes unexpectedly dominant.

There has been considerable discussion in the literature of how this extrapolation should be made [9,10,11]; as yet, no clear consensus has emerged. These discussions, which have proceeded in the absence of essential data, have centered chiefly on what electronic effects would be expected.

The importance for reactor safety analysis of uncertainties in the heat capacity of uranium lies in the sensitivity of estimated accident consequences to the data uncertainties. The effects of data uncertainties have been examined by several workers.[3-6] Buttery [5] has examined in some detail

the effect of variations in heat capacity of uranium dioxide on the energy yield from a hypothetical core disruptive accident in a liquid metal cooled fast breeder reactor. Based in part on arguments of MacInnes [4], Buttery selected several possible (somewhat arbitrary) linear and exponential variations in heat capacity and calculated the consequences in terms of energy yield in a hypothetical accident. Although the uncertainties chosen for heat capacity appear to be quite large, the results of his calculations show that there is a rough proportionality between uncertainty in heat capacity and in energy yield. A similar conclusion was also reached by Nicholson and Jackson [3], who calculated that the available energy yield was also approximately proportional to the fuel heat capacity and the uncertainty in energy release was proportional to the uncertainty in heat capacity.

There are, however, considerable uncertainties introduced in these calculations due simply to limited understanding of the accident process itself. Indeed, reactor safety analysts widely believe that modeling uncertainties far exceed uncertainties introduced by thermophysical property extrapolations.[19] The sensitivity of reactor accident simulations to thermophysical property values depends on the particular accident events being examined. In some cases, nevertheless, data uncertainties have already been shown to be significant [4], and as accident models improve, these cases will increase in importance.

In terms of lowering the uncertainty in accident energy yield, improved data for high-temperature heat capacity is one of the most promising areas. Since conventional techniques are not suitable for such measurements, new measurement techniques are being developed

although application to reactor fuels will not be simple. These include experimentation in the microgravity environment of space [20] and micro-second-resolution pulse heating experiments.[21] The development of levitation calorimetry by Margrave and coworkers [22] has added a new dimension to high temperature calorimetry; unfortunately, this technique is not readily applicable to reactor fuels whose relatively low electrical conductivity (compared to metals) makes it unlikely that suitable measurements can be performed with existing systems. In a low gravity environment, however, such measurements may be possible [23,24], and studies are being made of the feasibility of such work.

The pulse heating techniques of Cezairliyan and coworkers [21], while not yet yielding enthalpy data on uranium dioxide, have been tested on that material and may provide valuable high temperature data in the future.

Thorium Dioxide

High temperature enthalpy data on thoria are quite limited and only recently has information close to the melting point (3643 K) become available. The highest temperature measurements on thorium dioxide have been performed by Fischer [27] to 3400 K. High temperature data are also available from Springer, et al. [25] from 273 to 2270 K, and by Hoch and Johnson [26] from 1456 to 2753 K. Data at moderate temperatures have also been reported by Southard.[28] A comparison of the experimental values is shown in Fig. 4. Quite good agreement is seen, and striking evidence for a phase transition at 2950 K is also apparent. The data were fit by Fink and coworkers [31] using a scheme similar to that used by Fink, et al. [12] for UO_2 . It was found that, in contrast to uranium dioxide, an electronic term was not needed to fit the thorium dioxide enthalpy data;

this finding is in agreement with the arguments of Young [9] and MacInnes and Catlow [10] on the electronic structures of uranium, thorium, and plutonium dioxides. The fitting parameters [31] for Eq. (1) for thorium dioxide show reasonable consistency with the uranium dioxide values. Above the transition temperature of 2950 K, a linear equation with a constant heat capacity of about $142 \text{ J mol}^{-1} \text{ K}^{-1}$ is suitable which is also reasonable compared with the UO_2 value.

It will be extremely difficult to obtain data on liquid thoria because of its high melting point. Conventional techniques of drop calorimetry are not suited to such work and the low electrical conductivity of thoria makes success unlikely for techniques involving levitation or direct electrical heating. Thoria-urania has been proposed as a reactor fuel, and data above the liquidus temperature may be obtained for some mixed-oxide compositions of interest. Fischer and coworkers [27] have performed measurements on several thoria-urania compositions in the solid region, which generally show consistency with the results on the pure compounds. Further work on these materials would be very valuable.

Plutonium Dioxide

Relatively few high temperature enthalpy data are available for plutonium dioxide. The measurements of Kruger and Savage [29] to 1406 K and those of Ogard [30] to 2715 K represent the published data. These results are plotted in Fig. 5. Also shown in Fig. 5 is the fit by Fink [31] to these data. The five highest temperature points obtained by Ogard [30] appear to have been made on substoichiometric material in a two-phase region, most likely a consequence of reaction between plutonium dioxide and the tungsten container. Ogard did not include those points in his own fit to the data, and this appears to have been a reasonable decision. The data in this case are too scanty

to make any positive decision on the existence of a phase transition. On the basis of the ratios of transition temperature to melting point for uranium and thorium oxides, however, such a transition might be expected in the neighborhood of 2200 K. The data appear to be reasonably well fit by Eq. (1) without inclusion of electronic contributions, again in accord with the suggestions of Young [9] and of MacInnes and Catlow.[10] The fitting parameters [31] here, too, seem consistent with what would be expected from Eq. (1). There appears to be an inconsistency between the data of Ogard [30] for plutonium dioxide and the data available for mixed uranium-plutonium oxide in that a mole average of UO_2 and PuO_2 does not well fit the mixed oxide measurements in contrast to the case of mixed uranium-thorium dioxide.[31] Further study and additional measurements on this material would be of great value in providing a better basis for comparison with the data available for uranium and thorium oxides.

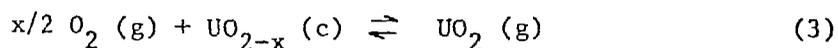
In summary, enthalpy data for the three oxides being considered, which are presented together in Fig. 8, show good consistency for the solid phase. The fitting parameters, with the exception of E_a for UO_2 , as was discussed, are consistent with what is known about these materials. For the enthalpy of the liquids, however, considerable uncertainties exist and improved understanding will be difficult without additional experimental data. The most pressing uncertainty at present is the electronic contribution to the heat capacity of liquid actinides.

Vapor Pressure of Uranium Dioxide

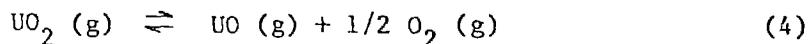
Considerable attention has been devoted to vapor pressure of fast reactor fuels for many years. Data for solid UO_2 have been recently reviewed [32] and reasonably good agreement has been found among the

measurements that have been performed. For liquid UO_2 , however, despite a great many studies using a variety of experimental and theoretical approaches, considerable uncertainty remains in the vapor pressure up to 6000 K. Measurements have been made on liquid UO_2 by transpiration [33] and by pulse techniques [34-37]. Calculations have also been performed using a variety of theories including corresponding states [38,39], significant structures [39], and oxygen potential models [40]. At Argonne, a different approach has been adopted which is outlined schematically in Fig. 9 [41]. The procedure entails determination of thermodynamic functions for the condensed phase as well as for individual gaseous species. The equilibrium vapor composition and total pressure may then be calculated from conventional thermodynamic relations as outlined in Fig. 9. The procedure for performing these calculations is summarized below [41].

The vapor in equilibrium with UO_{2-x} is a complex mixture containing O , O_2 , U , UO , UO_2 , and UO_3 molecules. Thermodynamic functions for O and O_2 are readily available. Thermodynamic functions for the gaseous species UO , UO_2 , and UO_3 are obtained from spectroscopic data [42,43]. Condensed phase functions are calculated from recommendations of Fink et al.[12]. Since all the gaseous species are in equilibrium with each other and with the same condensed phase, there are many possible choices of equilibria to consider. Two examples from the set chosen in Ref. [41] are:



and



If the oxygen pressure is obtained from the oxygen potential, then the partial pressures of UO_2 and UO can be calculated from the thermodynamic functions available by using relations such as:

$$\ln p(UO_2) = x/2 \ln p(O_2) + [\Delta G_f^\circ (UO_{2-x},c) - \Delta G_f^\circ (UO_2,g)]/RT \quad (5)$$

The free energy of formation for UO_{2-x} may be found from that for UO_2 by means of the Gibbs-Duhem equation which leads to:

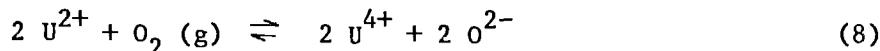
$$\Delta G_f^\circ (UO_2,c) - \Delta G_f^\circ (UO_{2-x},c) = RT/2 \int_0^x \ln p(O_2) dz \quad (6)$$

In this manner, partial pressures for all the vapor species, O , O_2 , U , UO , UO_2 , and UO_3 , may be calculated if the oxygen potential is available.

An oxygen potential model developed and revised by Blackburn [44] has been adapted for these calculations. In this model, it is assumed that the following equilibria exist in solid UO_{2-x} :



and



In addition, uranium conservation and charge balance require that:

$$(U^{6+}) + (U^{4+}) + (U^{2+}) = 1 \quad (9)$$

and

$$3 (U^{6+}) + 2 (U^{4+}) + (U^{2+}) = 2 - x \quad (10)$$

Blackburn has found the equilibrium constants for reactions (7) and (8) from conditions at various phase boundaries in the hypostoichiometric region.

With these constants (assumed to be of the form $\ln K = A + B/T$) and the two

conservation equations, oxygen pressures can be calculated as a function of temperature and composition. The assumed form for the equilibrium constants allows the association of the A's with $\Delta S^\circ/R$ for the corresponding reaction. Blackburn's original calculated results have been found to agree well with experimental values [44]. For extension to the liquid, it is assumed [41,44] that the same model applies and that only new A's and B's need be found. These new constants have been found, in part, from the O-U phase diagram [7] by equating the oxygen pressures for the solid and liquid phases at 3120 K for $UO_{2.00}$ and at 2700 K (the monotectic temperature) for $UO_{1.67}$ (s) and $UO_{1.5}$ (l). The remaining conditions needed to find equilibrium constants were found from considerations of the entropy change for reactions (7) and (8). From an examination of analogous cases [41], it was found that the change due to melting on $\Delta S^\circ/R = A$ for Eqs. (7) and (8) was quite small, and have been estimated as about 0 and 2.8, respectively. Attempts to calculate the new equilibrium constants solely from the phase diagram were not successful although in principle this should be possible. It should be possible to select four points along the solidus and equate the oxygen potential with the liquidus composition at the same temperature. These four points should allow for calculation of the four new constants required. This was found not to be possible since the oxygen pressures are insensitive to the value of the equilibrium constant for Eq. (7).

Some of the results of the above described calculations are presented in Fig. 8 [41], where the gaseous phase percentage composition is shown as a function of temperature for condensed phase $UO_{1.96}$. The figure clearly shows that the vapor at high temperatures is not well approximated by the composition $UO_{2.00}$; in fact, at 6000 K, the vapor is mostly oxygen.

Fig. 9 presents a comparison of pressures calculated using this scheme with those recommended by an international advisory group [45]. As can be seen from the figure, agreement is quite good between the calculated [41] and recommended [45] values, thereby demonstrating that reasonably good agreement exists on the total vapor pressure for UO_2 in the temperature range of interest to reactor safety analysts. Since the vapor-composition calculations depend on an oxygen potential model, experimental support for that model in the liquid phase would be very valuable. For mixed uranium-plutonium oxide, considerable effort will be required to bring our understanding of vapor pressure to the same level as exists for UO_2 .

CONCLUSIONS

While considerable work has been done on the heat capacity and vapor pressure of uranium, plutonium, and thorium oxides, significant areas of uncertainty still remain. For all three materials (and for the technologically important mixed oxides as well), extrapolation of heat capacity for the liquid state to the high temperatures needed in reactor safety analysis is subject to considerable uncertainty. Measurements of heat capacity or electrical conductivity, as well as improved theoretical understanding of the three reactor materials, particularly regarding the electronic effects in the liquid, would help considerably. For vapor pressure, considerably more confidence exists for the extrapolations but a difficulty remains in that, as the temperature increases, liquid and vapor compositions grow increasingly further apart [41], a situation which cannot continue up to the critical temperature. Estimates of the critical temperature of uranium dioxide have ranged from roughly 6000 to 9000 K, with little consideration

generally being given to the differences in vapor and liquid composition. Indeed, the vapor is usually considered to consist solely of UO_2 molecules which is not the case. Theoretical understanding of the critical behavior of these actinide oxides would be of considerable importance in improving confidence in extrapolations for both heat capacity and vapor pressure.

ACKNOWLEDGMENT

The author is grateful to Dr. D. W. Green and Dr. J. K. Fink for many valuable discussions and for their permission to cite work unpublished and in progress. He is also grateful to D. F. Fischer for providing data on thorium oxide enthalpies and to Dr. D. W. Deitrich for helpful comments on the accident analysis portions of this paper.

REFERENCES

1. Bethe, H. A. and Tait, J. H., "An Estimate of the Order of Magnitude of the Explosion when the Core of a Fast Reactor Collapses," RHM(56)/113 Atomic Energy Research Establishment, Harwell, Berks, England (1956).
2. Jackson, J. F., "Proceedings of the Third Post-Accident Heat Removal Information Exchange," L. Baker, Jr. and J. D. Bingle, eds., ANL-78-10, Argonne National Laboratory, Argonne, IL (1977) p. 5.
3. Nicholson, R. B. and Jackson, J. F., "A Sensitivity Study for Fast Reactor Disassembly Calculations," ANL-7952, Argonne National Laboratory, Argonne, IL (1974).
4. MacInnes, D. A., Martin, D., and Vaughan, G. J., "The Effect of Uncertainties of UO₂ and Sodium on MFCI's," SRD R 159, United Kingdom Atomic Energy Authority, Wighshaw Lane, Culcheth Warrington (1979).
5. Buttery, N. E., "The Sensitivity of Excursion Yields to UO₂ Equation of State Uncertainties," RD/B/N4623 Berkeley Nuclear Laboratory (1980).
6. Ostensen, R. W., Trans ANS 28, 485 (1978).
7. Rand, M. H., Ackermann, R. J., Grønvoid, F., Oetting, F. L., and Pattoret, A., Int. Rev. Hautes Temp. et Refract. 15, 355 (1978).
8. Kerrisk, J. F. and Clifton, D. G. Nucl. Technol. 16, 531 (1972).
9. Young, R. A., J. Nucl. Mater. 87, 283 (1979).
10. MacInnes, D. A. and Catlow, C. R. A., J. Nucl. Mater. 89, 354 (1980).
11. Harding, J. H. Masri, P., and Stoneham, A. M., J. Nucl. Mater. 92, 73 (1980).
12. Fink, J. K., Chasanov, M. G., and Leibowitz, L., "Thermodynamic Properties of Uranium Dioxide," ANL-CEN-RSD-80-3, Argonne National Laboratory, Argonne, IL (1981).
13. Fink, J. K. Chasanov, M. G., and Leibowitz, L., Proc. 8th Symposium on Thermophysical Properties, J. V. Sengers, Ed., American Society of Mechanical Engineers, New York, 1981, p. 000.
14. Bredig, M. A., Coll. Int. sur l'etudes des transformations cristalline a hautes temperature, Odeillo, p. 183 (1971).
15. Hein, R. A. and Flagella, P. N., "Enthalpy Measurements of UO₂ and Tungsten to 3260 K," General Electric Corp Report GEMP-578 (1968).

16. Leibowitz, L., Mishler, L. W., and Chasanov, M. G., J. Nucl. Mater. 29, 356 (1969).
17. Fredrickson D. R. and Chasanov., M. G., J. Chem. Thermodynamics 2, 263 (1970).
18. Leibowitz, L., Chasanov, M. G., Mishler, L. W., and Fischer, D. F., J. Nucl. Mater. 39, 115 (1971).
19. Deitrich, L. W., Argonne National Laboratory, private communication.
20. Wouch, G., Gray, E. L., Frost, R. T., Lord, Jr., A. E., High Temp. Sci. 10, 241 (1978).
21. Cezairliyan, A. Morse, M. S., and Foley, G. M., Proc. 8th Symposium on Thermophysical Properties, J. V. Sengers, Ed., American Society of Mechanical Engineers, New York, 1981, p. 000.
22. Margrave, J. L., Proc. 8th Symposium on Thermophysical Properties J. V. Sengers, Ed., American Society of Mechanical Engineers, New York 1981, p. 000.
23. Margrave, J. L. and Weingarten, J., "Thermodynamic Property Determination in Low Gravity," Final Report, NASA contract NAS8-32030 (1977).
24. Frost, R. T., General Electric Corporation, private communication.
25. Springer, J. R., Eldridge, E. A. Goodyear, M. U., Wright, T. R., and Lagedrost, J. F., "Fabrication, Characterization, and Thermal-Property Measurements of ThO₂-UO₂ Fuel Materials," BMI-X-10210 Battelle Memorial Institute (1967).
26. Hoch, M. and Johnson, H. L., J. Phys. Chem. 65, 1184 (1961).
27. Fischer, D., Argonne National Laboratory, private communication.
28. Southard, J. C., J. Amer. Chem. Soc. 63, 3142 (1941).
29. Kruger, O. L. and Savage H., J. Chem. Phys. 49, 4540 (1968).
30. Ogard, A. E., "Plutonium 1970 and Other Actinides," W. N. Miner, Ed., Met. Soc. AIME, New York, (1970) p. 78.
31. Fink, J. K., Argonne National Laboratory, private communication.
32. Ackermann, R. J., Rauh, E. G., and Rand, M. H., J. Nucl. Mater. (in press).
33. Reedy, G. T. and Chasanov, M. G., J. Nucl. Mater. 42, 341 (1972).

34. Ohse, R. W. Berrie, P. G., Bogensberger, H. G., and Fischer, E. A. "Thermodynamics of Nuclear Materials 1974," Vol. I, International Atomic Energy Agency, Vienna (1975), p. 307.
35. Bober, M., Karov, H. V., and Schretzmann, K., Nucl. Technol. 26, 237 (1975).
36. Benson, D. A., "Application of Pulsed Electron Beam Vaporization to Studies of UO_2 ," SAND-77-0429 Sandia Laboratories, Albuquerque, NM (1977).
37. Reil, K. O., Breitung, W. M., and Murata, K. K., Proc. 8th Symposium on Thermophysical Properties, J. V. Sengers, Ed., American Society of Mechanical Engineers, New York, 1981, p. 000.
38. Menzies, D. C., "Equation of State of Uranium Dioxide at High Temperatures and Pressures," TRG report 1119(D), Nuclear Design and Construction Ltd., Whetstone (1966).
39. Browning, P., Gillan, M. J., and Potter, P. E., "The Equation of State of Uranium Dioxide: A Comparison of the Corresponding State and Significant Structures Theories," AERE-R 8129 Atomic Energy Research Authority, Harwell (1977).
40. Breitung, W., "Calculation of Vapor Pressure of Oxide Fuels up to 5000 K in Equilibrium and Non-Equilibrium Evaporation," KFK 2091 Nuclear Research Center, Karlsruhe (1975).
41. Green, D. W. and Leibowitz, L., "Vapor Pressure and Compositions in Equilibrium with Hypostoichiometric Uranium Dioxide at High Temperatures," ANL-CEN-RSD-81-1, Argonne National Laboratory, Argonne, IL (1981); Green, D. W. and Leibowitz, L., J. Nucl. Mater. submitted for publication.
42. Green, D. W., "Tables of Thermodynamic Functions for Gaseous Thorium, Uranium, and Plutonium Oxides," ANL-CEN-RSD-80-1, Argonne National Laboratory, Argonne, IL (1980).
43. Green, D. W., "Calculation of the Thermodynamic Properties of Fuel-Vapor Species from Spectroscopic Data," ANL-CEN-RSD-80-2, Argonne National Laboratory, Argonne, IL (1980).
44. Blackburn, P. E., J. Nucl. Mater., 46, 244 (1973) and private communications.
45. Specialists' Meeting on "Equations of State of Materials of Relevance to the Analysis of Hypothetical Fast Breeder Reactor Accidents," A.E.R.E. Harwell, United Kingdom, 19-23, June 1978, IWGFR/26 International Atomic Energy Agency, Vienna, p. 137.
46. Rowlinson, J. S., "Liquids and Liquid Mixtures," Second Edition, Butterworth, London (1969).

Figure Captions

1. Mechanistic accident analysis scheme [2].
2. Enthalpy of solid uranium dioxide
 $H^\circ(T) - H^\circ(298)$ as a function of temperature.
3. Enthalpy of liquid uranium dioxide
 $H^\circ(T) - H^\circ(298)$ as a function of temperature.
4. Enthalpy of thorium dioxide
 $H^\circ(T) - H^\circ(298)$ as a function of temperature.
5. Enthalpy of plutonium dioxide
 $H^\circ(T) - H^\circ(298)$ as a function of temperature.
6. Enthalpy of actinide oxides
 $H^\circ(T) - H^\circ(298)$ as a function of temperature.
7. Scheme for vapor pressure calculation.
8. Vapor composition in equilibrium with $UO_{1.96}$.
9. Comparison of calculated total pressure with recommended values.

