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CDAP-TR-053

for U.S. Nuclear Regulatory Commission

CODE DEVELOPMENT AND ANALYSIS PROGRAM

FUEL VAPOR PRESSURE (FVAPRS)

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APRIL 1979

EG&G Idaho, Inc.

IDAHO NATIONAL ENGINEERING LABORATORY

DEPARTMENT OF ENERGY

IDAHO OPERATIONS OFFICE UNDER CONTRACT EY-76-C-07-1570

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FORM EG&G-398
(Rev. 12-78)

INTERIM REPORT

Accession No. _____

Report No. CDAP-TR-053

Contract Program or Project Title: Fuel Behavior Analysis Verification

Subject of this Document: Fuel Vapor Pressure (FVAPRS)

Type of Document: Status Report

Author(s): R. E. Mason

Date of Document: April 1979

Responsible NRC Individual and NRC Office or Division: G. P. Marino, Reactor Safety Research

This document was prepared primarily for preliminary or internal use. It has not received full review and approval. Since there may be substantive changes, this document should not be considered final.

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Prepared for the
U.S. Nuclear Regulatory Commission
and the U.S. Department of Energy
Idaho Operations Office
Under contract No. EY-76-C-07-1570
NRC FIN No.
A6046

INTERIM REPORT

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14. FUEL VAPOR PRESSURE (FVAPRS)

(R. E. Mason)

Evaporating reactor fuel, urania or plutonia-uranium mixtures (mixed oxides) can create pressures, during very high temperature excursions, which equal or exceed plenum gas or fission gas pressures in the fuel rod. This pressure will influence the failure mechanism of the cladding and may cause the melted portion of the fuel to froth and swell. Significant volume changes of the fuel may also result from phase changes due to noncongruent evaporation (composition of the vapor phase different than that of the fuel). There are a number of compounds present in the vapor above reactor fuels which are discussed throughout this report. These are actinide and actinide oxide vapors (UO_2 , UO_3 , UO_4 , U, PuO_2 , PuO , Pu) and oxygen vapors (O and O_2). The total pressure of all the actinides and actinide oxides is considered.

The vapor pressure equations described in this report are to be used in transient fuel codes, mechanistic gas release codes or restructuring codes which require vapor pressures or calculate bubble migration by evaporation-condensation.

14.1 Summary

The FVAPRS subcode determines the saturated actinide vapor and oxygen vapor pressures over urania, plutonia, and mixed oxides as a function of fuel oxygen to metal ratio and temperature. Semi-empirical equations based on the Clausius-Clapeyron equation are used. The standard error of estimate (SEOE) with respect to the log of the data base is given for each equation.

For urania:

$$\log_{10} P = -11191/T + 9.9932 \ln T - 0.00039T - 69.174 \quad (\text{A-14.1})$$

$$\text{and } \text{SEOE} (\log_{10} P) = \pm 0.206$$

For plutonia:

$$\log_{10} P = (-5404.1 + 6854.6x)/T + 18.166 \ln T - 0.000389T - 130.65 \quad (\text{A-14.2})$$

$$\text{and SEOE } (\log_{10} P) = \pm 0.559$$

where

P = vapor pressure (Pa)

x = deviation from stoichiometry (fraction of oxygen to metal ratio greater than or less than 2.0)

T = temperature (K).

Equation (A-14.1) is used to calculate the vapor pressure of urania at all stoichiometries. Plutonia vapor pressures are calculated in the FVAPRS code for hypostoichiometric fuel using Equation (A-14.2). Although it is improbable that plutonia or mixed oxides will be hyperstoichiometric the FVAPRS code uses a default input of 2.0 for all oxygen to metal ratios greater than 2.0. Mixed oxide vapor pressures are obtained by multiplying the plutonia and urania equations by the weight fraction of each material and adding the two resulting calculated pressures.

Similar equations are used for the oxygen vapor pressure (P_{O_2} or P_O). These are:

For oxygen to metal ratios greater than 2.004

$$\log_{10} P_{O_2} = -14638.2/T + 21.7752x + 6.2006 \quad (\text{A-14.3})$$

$$\text{and SEOE } (\log_{10} P_{O_2}) = \pm 0.545$$

For oxygen to metal ratios less than 1.999

$$\log_{10} P_o = -(49534.9 + 1418.1 \ln x)/T + 15.181 \quad (\text{A-14.4})$$

$$\text{and SEOE } (\log_{10} P_o) = \pm 0.801$$

For oxygen to metal ratios less than 2.004 but greater than 1.999

$$\log_{10} P'_{o_2} = -14638.2/T - 1.80386 \ln x + 6.29331 \quad (\text{A-14.5})$$

$$\text{and SEOE } (\log_{10} P'_{o_2}) = \pm 9.0$$

The rapid decrease of the pressure predicted by Equation (A-14.5) as stoichiometry is approached is limited by imposing the following restrictions.

$$\text{if } 0.5 \log P'_{o_2} - 13384.57/T + 3.52 \geq \log_{10} P_o$$

$$\log_{10} P_{o_2} = \log_{10} P'_{o_2} \quad (\text{A-14.6})$$

$$\text{if } 0.5 \log P'_{o_2} - 13384.57/T + 3.52 < \log_{10} P_o$$

$$\log_{10} P_{o_2} = 2 \log_{10} P_o^\circ + 26769.14/T + 7.14 \quad (\text{A-14.7})$$

where P_o° is the monatomic gas pressure at an oxygen to metal ratio of 1.999.

The following sections contain a more detailed discussion of the information and techniques used to develop Equations (A-14.1 through A-14.7). Section 14.2 is a discussion of data described in the literature and methods used to obtain that data. Section 14.3 is a discussion of vapor pressure theory, FVAPRS subcode development and comparisons of the FVAPRS subcode with literature data. Section 14.4 is the listing of the

subcode, Section 14.5 contains the report references and Section 14.6 contains a bibliography of references studied but not used to develop the FVAPRS subcode.

14.2 Vapor Pressure Data

Vapor pressure data of urania, plutonia, and mixed oxides are obtained using a number of different experimental techniques such as transpiration, effusion, Knudsen effusion, laser heating, electron beam heating, free evaporation, static testing, boiling point pressures etc. Of these techniques transpiration, Knudsen effusion, static testing, and laser heating have been the most widely used. The vapor pressures reported are generally determined indirectly. That is, measurements of sample weight loss, sample momentum, weight of deposit on a target, or analysis of the ions in a gas stream with a spectograph are observed and vapor pressures are calculated from these measurements. For those data for which the oxygen to metal ratio of the samples was measured, the usual measurement technique was to oxidize the sample to U_3O_8 , use a coulometric technique, or use x-ray analysis. These measurement techniques are discussed in enough detail to indicate advantages or disadvantages of these techniques.

The transpiration or entrainment technique is one of the more common techniques used. It is one of the few measurement techniques that can be used to measure pressure of a vapor in the presence of large concentrations of other gases. This technique is most accurate for temperatures at which the confining material does not contribute significantly to the measured vapor pressure and is not limited by the pressure of the gas being measured. With this technique the sample is heated in a chamber while gases pass over the sample. The flowing gas carries sample vapor from the high temperature region to a cold trap where the vapor condenses. The weight of the condensed vapor is used to

determine the vapor pressure of the sample. A distinct advantage of this technique is that the carrier gas can be used to control the composition of the sample and vapor for bivariant evaporating materials such as nuclear fuels. The vapor pressure is determined from measurements of sample weight loss, weight of vapor condensed in the cold trap or by monitoring molecular species in the carrier gas. A disadvantage of the technique is that vapor pressure is independent of the carrier gas flow rate in only a narrow band of flow rates which depend on other experimental conditions.

The Knudsen effusion technique is a good measurement method for pressures below 13Pa^[A-14.1]. This technique uses a thin edged orifice through which the vapor passes and condenses on a target above the orifice. The weight of vapor deposited on the target surface or weight loss of the sample is used to calculate the vapor pressure. A similar technique is the Langmuir "free-evaporation technique", which differs from Knudsen effusion technique in that no orifice or target is used. An advantage of the Knudsen technique is that there are generally very small temperature gradients in the sample and its surroundings.

The application of lasers or electron beams to heat the surface of materials which melt at very high temperatures has provided experimental means to study materials at temperatures above those which would melt the retaining crucibles. Vapor pressure data results from intense pulses of laser or electron beams on the surface of the samples. These data are derived from observations of sample weight loss, evaporation depth, recoil momentum, torsion or by time resolving techniques of mass spectrometry ion intensity measurements. These experiments must be analyzed with caution because it may not be the equilibrium vapor pressure that is measured. The evaporating surface may also become depleted due to noncongruent evaporation, since solid state diffusion cannot restore the surface to its original composition as fast as material is vaporized. This difficulty can be partially compensated for by heating the sample to melting prior to testing.

14.2.1 Urania Vapor Pressure. The measurement techniques described above have been used to measure urania vapor pressures discussed in the following paragraphs. Most of this data was digitized for use in coding work.

Szwarc and Latta^[A-14.2] reported total equilibrium vapor pressure of hypostoichiometric urania. They used the transpiration technique to obtain this data. Vapor pressures were investigated at temperatures between 2503 and 2917 K with temperature measurements reported accurate to within ± 10 K. The oxygen potential of the carrier gas was controlled with H_2/H_2O mixtures. Three compositions of urania were considered: $UO_{1.88}$, $UO_{1.92}$, and $UO_{1.94}$. The oxygen to metal ratios of the sample residues were determined by ignition weight loss to U_3O_8 and were reported accurate to within ± 0.003 units. They found the initial oxygen to metal ratios remained stable within ± 0.005 . Their vapor pressure data was determined from weight loss measurements during the experiments. This implies that both actinide vapors and oxygen vapors are included in the total vapor pressure calculation but as will be discussed in later sections the oxygen vapor pressures are orders of magnitude smaller and will therefore contribute little to the total measured vapor pressure. They indicate that the vapor pressure changes an order of magnitude as the oxygen to metal ratio varies between 1.88 to 1.94.

Bober et al^[A-14.3] measured urania vapor pressure at temperatures between 4100 and 4400 K and found the vapor pressures to be between 0.608 and 1.01 MPa. They used the laser heating technique to produce these high temperatures. Each test lasted approximately 1 ms so that evaporation occurred in a stationary, thermally constant and congruently evaporating molten surface layer but one not in thermodynamic equilibrium.

Reedy and Chasanov^[A-14.4] used the transpiration technique to obtain total vapor pressure data. The oxygen to metal ratio of the remaining residues were determined and they found the final sample

oxygen to metal ratios to be strongly dependent on the testing temperatures. Their data showed an average deviation of $\pm 10\%$. Each datum reported represents the mean of four to six measurements except that at 3175 K which is a single measurement.

Ackermann et al^[A-14.5] determined the vapor pressure of hypostoichiometric urania between 1580 to 2400 K. An "effective" vapor pressure was calculated from effusion rate measurements assuming the vapor to be UO . They used mass spectrometric measurements on the system and found UO vapor to be about 10 times greater than UO_2 and U vapor pressures. The oxygen to metal ratio of this data was not given.

Tetenbaum and Hunt^[A-14.6] measured total vapor pressure of hypostoichiometric urania and nearly stoichiometric urania. They used the transpiration technique to obtain their data. The oxygen to metal ratio of their samples increased as the temperature increased and the fuel vapor pressure increased as the oxygen to metal ratio of the fuel approached the hypostoichiometric phase boundary. Their vapor pressure data is in very good agreement with those of Szwarc and Latta for $\text{UO}_{1.88}$ but is approximately 1.5 to 2 times that of the Szwarc and Latta pressures for $\text{UO}_{1.92}$ and $\text{UO}_{1.94}$. They also observed an order of magnitude pressure change as the oxygen to metal ratio of the samples changed.

Benezech et al^[A-14.7] used the transpiration technique to obtain urania vapor pressure data at temperatures between 2200 and 2600 K with oxygen to metal ratios varying between 2.0 and 2.15. A solar furnace was used to heat their samples. They report large temperature gradients in the crucible but no mention was made of the temperature profile within the samples. They also found the dominant vapor specie (UO_2 or UO) to depend on the composition of the carrier gas.

Ohse et al^[A-14.8,A-14.9] reported vapor pressures of urania at temperatures up to 4710 K. A laser was used to heat the urania samples. These data are important because they are at temperatures above melting

and indicate that vapor pressure at very high temperatures increases with increasing temperature at a much slower rate than it does at the melting temperature or lower.

Alexander et al^[A-14.10] measured the total vapor pressure and oxygen dissociation pressures of urania, thoria, zirconia and combinations of the three using the transpiration technique. Vapor pressure measurements of stoichiometric urania were obtained at temperatures between 2000 and 3000 K. They observed vapor pressures of thoria-uranium mixtures to be an order of magnitude less than urania vapor pressures. Oxygen dissociation pressures of urania and thoria were obtained for compositions between 1.97 and 2.03 at 2360 K.

Ackermann et al^[A-14.11,A-14.12] measured vapor pressures of urania at temperatures between 1600 and 2800 K using the Knudsen effusion technique. These data were later revised and some new data added^[A-14.13]. They concluded that the urania vapor pressure is invariant to 2700 K. This is in conflict with the results of previous data sets. They report that their samples appeared to melt at approximately 2678 K. This is 457 K lower than the presently accepted melting point (3133 K) implying that the UO_2 samples contained impurities which lowered the melting point by about 400 K. Sample composition probably varies from pure urania which may affect observed vapor pressures. It should be noted, however, that the slope of the data and the magnitude are within the data scatter bands of other investigators' data.

Chapman and Meadows^[A-14.14,A-14.15] investigated nonstoichiometric urania of compositions between $UO_{2.02}$ and $UO_{2.63}$ in the UO_{2+x} and U_3O_8-y phase regions at temperatures between 1273 and 1873 K. They used a thermogravimetric technique to obtain the vapor pressure data--a sample was heated in a vacuum furnace and the weight loss per unit time was recorded. They reported evidence of UO_4 vapor instead of UO or UO_2 as reported by many authors. Chapman and Meadows report that the

equilibrium oxygen to metal ratio above 1973 K in vacuum is less than the ratio 2.0 obtained by other investigators.

Ohse^[A-14.16] measured urania vapor in an effusion cell at temperatures between 2278 and 2768 K. Ohse observed urania vapor pressures between 1×10^{-6} and 3.4×10^{-4} MPa.

Benson^[A-14.17] investigated vapor pressures of urania using an electron beam to heat the samples. Data were obtained at temperatures between 4500 and 7200 K.

Babelot et al^[A-14.18] reported urania vapor pressure data obtained from laser heated samples. They measured urania vapor pressures at temperatures between 3300 and 4700 K. The slope and magnitude of their data agrees very well with that observed by Benson.

The literature data discussed in this section generally indicate that urania evaporates bivariantly. A composition change from stoichiometry can, at temperatures less than 2500 K, cause the vapor pressure to increase 10 times or more as the urania becomes more hypostoichiometric. There are not sufficient data to determine how much effect deviation from stoichiometry has on vapor pressures in the hyperstoichiometric region. Tetenbaum and Hunt observed little effect of urania stoichiometry on the vapor pressure at temperatures near melting with hypostoichiometric fuel. Data at temperatures above melting and not having oxygen to metal ratios reported can therefore be used. There is little or no observed discontinuity of the vapor pressure at the urania melting temperature although the temperature dependence does begin to decrease. The early data of Ackermann et al^[A-14.12] is considered in error by its author^[A-14.5] and is therefore not useful for code development. The scatter of the Chapman and Meadows data is large, probably due to oxygen to metal ratios much greater than 2.0 but not reported for each data point. Because of this scatter and because all the oxygen to metal ratios are not reported this data is not applicable to code development. All the rest of the data discussed is amenable to code development

although there is some scatter between data sets. Data discussed in this section are displayed in three graphs, Figure A-14.1 through A-14.3. The urania vapor pressure as a function of temperature can be seen in each figure. The decreasing rate of change at temperatures above 3000 K can also be seen.

14.2.2 Plutonia Vapor Pressure. Plutonia (PuO_2) is very similar to urania in many of its materials properties. The plutonia vapor pressure data presently available in the literature are briefly discussed in the following paragraphs.

Ohse and Ciani^[A-14.19] reported vapor pressures of urania at 1800, 2000, and 2200 K based on effusion cell measurements. Vapor pressure of plutonia with oxygen to metal ratios between 1.51 and 1.61 were investigated. They found it very difficult to obtain good data of samples with oxygen to metal ratios greater than 1.94. Ohse and Ciani suggest that pressure measurements at these compositions (1.94 to 2.0) are difficult due to rapid change of fuel oxygen to metal ratios and/or vapor oxygen to metal ratios.

Ackermann et al^[A-14.20] measured plutonia vapor pressures of substoichiometric plutonia in effusion cells. They investigated the effects of both temperature and composition on the total vapor pressures. Successive tests of approximately 10 minutes were used. The authors found the evaporation rate to decrease over 30% from the initial rate after 48 successive tests (~8h) and found the composition to change with time. Chemical and x-ray analysis were used to determine the oxygen to metal ratios. X-ray analysis indicated that oxygen to metal ratios were between 1.90 and 1.93. Chemical analysis showed them to be between 1.923 and 1.916.

Phipps et al^[A-14.21] used the Knudsen effusion method to measure vapor pressures between 1589 and 2060 K. These vapor pressure data points were derived from radiochemical analysis of the deposit on the

Fig. A-14.1 Urania vapor pressure data.

Fig. A-14.2 Urania vapor pressure data.

Fig. A-14.3 Urania vapor pressure data.

effusion target. Two different cell designs were used in these experiments and oxygen gas was included in another. Phipps et al report that the oxygen reacted with the vapor flow and therefore had to be accounted for in the calculations. The oxygen to metal ratio of the plutonia was not reported.

Pardue and Keller^[A-14.22] measured the vapor pressure of plutonia in three atmospheres of air, argon and oxygen at temperatures between 1723 and 2048 K. They used the transpiration technique to obtain their data.

Mulford and Lamar^[A-14.23] reported plutonia vapor pressure data measured at temperatures between 2000 and 2400 K using the Knudsen effusion technique. The oxygen to metal ratios of the samples were not determined. Their vapor pressures were significantly different than those observed by Phipps et al and they propose that the vapor pressure data of Phipps et al apply to reductive processes making the vapor pressures invalid because of vaporization of both reactants and products.

The plutonia data reviewed above include vapor pressures of plutonia between 1600 and 2500 K. These data are shown in Figure A-14.4. Oxygen to metal ratios varied between 1.5 and 2.0. Vapor pressures of plutonia decrease as the hypostoichiometric phase boundary is approached. Vapor pressures were observed between 10^{-6} Pa and 10 Pa. As can be seen in Figure A-14.4, there is large scatter in the data. This is at least partially a result of oxygen to metal ratio effects not recorded by many of the investigators. Therefore only the data of Ackermann et al^[A-14.20] and Ohse and Ciani^[A-14.19] should be used for code development.

14.2.3 Mixed Oxide Vapor Pressure. Some mixed oxide data have appeared in the literature. These are discussed briefly.

Tetenbaum^[A-14.24] reported the results of an investigation of total pressure of actinide-bearing species over the U-Pu-O system. He

Fig. A-14.4 Plutonia vapor pressure data.

used the transpiration technique to obtain this data. The data indicate that mixed oxides of composition $(U_{0.8} Pu_{0.2}) O_{2-x}$ have vapor pressures between 0.1 and 1 Pa at temperatures between 2150 and 2450 K. Analysis of this data shows that the urania vapor pressure is approximately 0.85 of the total vapor pressure and plutonia is approximately 0.15 of the total vapor pressure.

Ohse and Olson^[A-14.25] reported the vapor pressures of coprecipitated mixed oxide with a composition of $(U_{0.85} Pu_{0.15}) O_{2-x}$. Vapor pressures were obtained in an electron beam heated tungsten effusion cell. Compositions varied between 2.0 and 1.94 and measurements were taken at temperatures between 1800 and 2350 K. Ohse and Olson observed urania vapor pressures to be about 10 times greater than any of the other oxides present.

Battles et al^[A-14.26] reported vapor pressures of mechanically mixed urania and plutonia $(U_{0.8} Pu_{0.2}) O_{2-x}$. The oxygen to metal ratio was varied between 1.92 and 2.01 and the temperature was approximately 2240 K. They used the Knudsen effusion technique with a mass spectrometer to determine the vapor pressure. They also reported the urania vapor pressure to be much the largest.

Ohse et al^[A-14.8,A-14.9] reported mixed oxide data measured at very high temperatures (4000 to 7000 K) using the laser heating technique. These test samples were melted before the test was started.

The four data sets just reviewed all show the vapor pressure of urania to be on the order of 10 times the pressure of other chemical species present. Fuel compositions between 1.91 and 2.00 were investigated and at temperatures between 2100 and 2500 K. Vapor pressures are found to range from approximately 0.01 Pa at 2150 K to approximately 12 MPa at 7000 K. Figure A-14.5 shows the mixed oxide data just discussed. The high temperature data shows a significant decrease in the

Fig. A-14.5 Mixed oxide data.

rate of vapor pressure increase. The data also shows scatter bands of about an order of magnitude at temperatures below 3000 K.

14.2.4 Oxygen Vapor Pressure

Although actinide oxide vapors constitute the most prominent vapors evolving from reactor fuels, oxygen vapors (O and O_2) do evaporate and thereby change the chemical composition of the fuel. A number of investigators have found metallic uranium in otherwise pure urania after heating above 2073 K in a vacuum. For example Aitkens et al^[A-14.27] found the stoichiometry of urania, both hypo and hyperstoichiometric urania, to change with time and temperature until an oxygen to metal ratio of 1.88 was reached. Vaporization of oxygen from the fuel not only changes the composition of the fuel but is directly related to the oxidation of the internal surfaces of the cladding. Oxygen vapor pressures have been determined for urania up to approximately 2900 K. Most of this oxygen data is derived from measurement of moisture content of carrier gases or sample weight or composition changes. Only one set of oxygen vapor pressure data for plutonia^[A-14.28] has been found. This data set is at low temperatures (less than 1323 K) and, is not considered useful until more data are available. Coding of plutonia oxygen pressures was therefore not attempted. Data reported for oxygen pressures over urania are described in the following paragraphs.

Tetenbaum and Hunt^[A-14.29] used the transpiration technique to measure oxygen partial pressure of hypostoichiometric urania. Monatomic oxygen pressures were determined up to 2700 K. Vapor pressure measurements were determined for compositions ranging from $UO_{2.0}$ to approximately $UO_{1.86}$. Their data show oxygen vapor pressure to increase sharply near stoichiometry at the lower temperatures measured. This increase near stoichiometry is not as steep at the higher temperatures.

Markin et al^[A-14.30] used a unique technique to obtain monatomic oxygen vapor pressure data. They obtained data from sample composition

measurements after equilibrium was reached in sealed silica systems. Oxygen to metal ratios are reported accurate to within ± 0.005 . Measurements were obtained for hypostoichiometric urania between 2200 and 2400 K and for hyperstoichiometric urania between 1600 and 1700 K. Their data agrees well with that of Tetenbaum and Hunt.

Wheeler^[A-14.31] measured the monatomic oxygen vapor pressure of urania between 1800 and 2000 K. He used a technique of equilibrating UO_{2-x} in an oxygen atmosphere controlled by the equilibrium reaction:

Data was obtained of urania at compositions between 2.0 and 1.986. This data agrees well with both data sets just described.

Javed^[A-14.32] reported diatomic oxygen vapor pressure data of urania using the transpiration technique. He measured vapor pressures at temperatures between 1873 and 2173 K. Oxygen to metal ratios were obtained from chemical, x-ray and metallographic techniques. These oxygen vapor pressure data tend to be higher than that just discussed.

Aitken et al^[A-14.27] used free evaporation and flowing gas transpiration techniques to obtain the oxygen pressure of urania between 2023 and 2223 K. These data were reported as diatomic oxygen pressures. Aitken et al observed the oxygen to metal ratio of the urania to approach 1.88 for both hypo and hyperstoichiometric urania when the samples were heated above 2000 K. The oxygen vapor pressure implied by these data is approximately two to ten times that of the Tetenbaum-Hunt data. Tetenbaum and Hunt suggest the discrepancy is a result of the Aitken et al data not having reached equilibrium.

Roberts and Walter^[A-14.33] investigated diatomic oxygen equilibrium vapor pressure of urania with compositions between $\text{UO}_{2.00}$ and $\text{UO}_{2.3}$ and

at temperatures between 1273 and 1723 K. Temperature measurements were obtained using a tensimetric technique (direct measurement of pressure). The technique is crude and there was no control of the sample oxygen to metal ratio. The investigators found deposits of a mixture of U_4O_9 and $UO_{2.61}$ phases in cooler parts of the furnace indicating the oxygen to metal ratio of the samples was changing. The authors also suggest that an equilibrium vapor pressure may not have been obtained. This data should therefore not be used as part of the data base for code development.

Hagemark and Broli^[A-14.34] conducted an extensive investigation of diatomic oxygen pressures of urania of oxygen to metal ratios between 2.0 and 2.25 and at temperatures between 1173 and 1773 K. Oxygen vapor pressure measurements were obtained from thermobalance measurements during testing.

Alexander et al^[A-14.10] used the transpiration technique to determine the oxygen dissociation pressure of urania. They investigated oxygen vapor pressures of urania compositions of $UO_{2.03}$, $UO_{2.0}$, and $UO_{1.97}$ with compositions accurate to ± 0.01 units at temperatures between 1950 and 2720 K.

Blackburn^[A-14.35] used the Knudsen effusion technique to measure the diatomic oxygen vapor pressure of urania. He obtained oxygen vapor pressure data for compositions between 2.1 and 2.6 and at temperatures between 1263 and 1400 K. For purposes of the FVAPRS code and this report only the data of compositions less than 2.2 can be used. This is roughly the boundary of urania-oxygen solid solution at temperatures above 1273 K. This data is in fair agreement with that reported by other investigators.

Aronson and Belle^[A-14.36] used an electrochemical measurement technique (emf measurements on urania half-cells) to measure the diatomic oxygen vapor pressure of urania. Vapor pressures for urania compositions between $UO_{2.0}$ and approximately $UO_{2.5}$ at temperatures

between 1150 and 1350 K were investigated. Only that data of urania at compositions below 2.2 are considered for code development.

Kiukkola [A-14.37] used emf measurements from galvanic cells to obtain diatomic vapor pressures of urania. Vapor pressure measurements of urania at compositions of $UO_{2.01}$ to $UO_{2.67}$ were obtained at temperatures between 1073 and 1473 K. Here again, only those data points of urania compositions less than $UO_{2.2}$ were considered.

Markin and Bones [A-14.38] used emf measurements of urania with compositions between 2.00 and 2.003 in a high temperature galvanic cell. Diatomic oxygen pressures of urania between the temperatures of 973 and 1673 K were investigated. Oxygen to metal ratios were controlled and determined by coulometric titration of oxygen ions using NiO as a source of oxygen. The main purpose of their investigations was to obtain thermodynamic functions and not oxygen vapor pressures so there is very little discussion of the vapor pressure data. Their data indicates a steep slope (decrease in vapor pressure) as the composition of the urania approaches stoichiometry. This is consistent with other data in this composition range and was therefore useful in the coding effort.

Aukrust et al [14.39] determined equilibrium oxygen pressures over hyperstoichiometric urania. The oxygen to metal ratios were determined by a thermogravimetric method and oxygen pressures were determined from known CO_2/CO or O_2/Ar gas mixtures and oxygen to metal ratio measurements. Data was obtained at temperatures between 1373 and 1673 K. They report oxygen to metal ratios accurate to within ± 0.0002 and the $\log_{10} P_{O_2}$ accurate to ± 0.02 .

The data discussed in this section must be divided into two groups, hyperstoichiometric and hypostoichiometric. For hypostoichiometric fuel the data of Tetenbaum and Hunt, Markin et al, Wheeler, Alexander et al, represent the best available data. The data of Javed and Atkins et al were probably measured under nonequilibrium conditions and should therefore not be used. For hyperstoichiometric fuel the oxygen pressure data

of Hagemark and Broli are the most extensive and are the best. The rest are within an order of magnitude of this data and can be used.

14.3 Development of the FVAPRS Code

The equations used in FVAPRS are based on thermodynamic equations fitted to the appropriate data. The following section is a discussion of thermodynamic and chemical theory and the technique used to develop the FVAPRS correlations.

14.3.1 Review of Basic Theory. Evaporation is a change in chemical state obeying the law of conservation of mass. Equations can therefore be used to show which elements or compounds could be expected to be present in the vapor phase above a fuel substrate. The possible reactions of urania are^[A-14.12]

where the subscripts β and g denote the material is in the solid or liquid, and gas phase respectively and α is a fraction. These equations apply only in the oxygen solid solution regions of solid and liquid urania. Of these possible compounds one is usually much more prominent

than the others. Analysis of the data indicates that for substrate temperatures below 2000 K the magnitude of the actinide oxide vapors follow the order $P_{\text{UO}} > P_{\text{UO}_2} > P_{\text{U}} > P_{\text{UO}_3}$ where P is the vapor pressure. At about 3000 K the order of partial pressures is $P_{\text{UO}_2} \approx P_{\text{UO}} > P_{\text{UO}_3} \approx P_{\text{U}}$ and at temperatures above 3500 K the partial pressure order is $P_{\text{UO}_2} > P_{\text{UO}_3} > P_{\text{UO}} > P_{\text{U}}$. The oxygen partial pressure at all temperatures is generally much smaller than the combined vapor pressure of the actinide oxides.

For plutonia the chemical reactions are similar to those of urania

It is experimentally determined that PuO is the prominent specie of plutonia up to an oxygen to metal ratio of approximately 1.99 where PuO₂ becomes most prominent.

Evaporation can be described by simple thermodynamic considerations of a first-order phase transition of a pure substance, solid to vapor or liquid to vapor, at constant temperature and pressure. At the phase transition

$$dG_{\beta} = dG_g \quad (\text{A-14.10})$$

where

dG_{β} = change in Gibbs free energy for the solid or liquid.

dG_g = change in Gibbs free energy for the gas

Since the process is reversible for a first-order phase transition at constant temperature and pressure

$$dG_{\beta} = V_{\beta} dp - S_{\beta} dT \quad (A-14.11)$$

$$dG_g = V_g dp - S_g dT \quad (A-14.12)$$

where

V_g = molar volume of gas

V_{β} = molar volume of solid or liquid

p = pressure

S = entropy of gas

S_{β} = entropy of solid or liquid

T = temperature.

Combining Equations (A-14.10 through A-14.12) and rearranging gives

$$(S_g - S_{\beta})dT = (V_g - V_{\beta})dp \quad (A-14.13)$$

Since V_g is generally much greater than V_{β} , Equation (A-14.13) can be reduced to

$$\frac{\Delta S}{V_g} = \frac{dp}{dT} \quad (A-14.14)$$

From the second law of thermodynamics we know that

$$\Delta S = \int_B^G \frac{dQ}{T} \quad (A-14.15)$$

where dQ is the differential of heat for a reversible phase transition proceeding at constant temperature and pressure.

The first law and the definition of system enthalpy can be used to relate dQ to enthalpy. From the first law

$$dU = dQ - pdV \quad (A-14.16)$$

where U is the internal energy and V is the volume. The differential of the system enthalpy for a reversible process is

$$dH = dU + pdV + Vdp \quad (A-14.17)$$

At constant pressure Equations (A-14.16) and (A-14.17) imply

$$dQ = dH \quad (A-14.18)$$

The change of enthalpy can then be written as

$$\Delta S = \int_B^G \frac{dH}{T} \quad (A-14.19)$$

Integrating Equation A-14.6 at constant temperature gives

$$\Delta S = \frac{\Delta H}{T} \quad (A-14.20)$$

where ΔH is the enthalpy change of the phase transition.

Since the enthalpy change of the phase transition is a function of heat capacity which is different for solids and gases at different temperatures, the temperature dependence of ΔH must be taken into account

for the vapor pressure to be evaluated accurately. The temperature dependence of ΔH can be approximated by the second order empirical equation

$$\Delta H = a + f(x) + bT + cT^2 \quad (\text{A-14.21})$$

where

$f(x) =$ a function of composition

$a, b, c =$ constants.

Substituting Equation (A-14.21) into Equation (A-14.20) and the resultant expression into Equation (A-14.14) gives

$$\frac{dp}{dT} = \left\{ \frac{[a + f(x)]}{T} + b + cT \right\} / V_g \quad (\text{A-14.22})$$

If the vapor behaves as an ideal gas

$$V_g = RT/p \quad (\text{A-14.23})$$

where R is the universal gas constant ($\frac{\text{m}^3 \text{Pa}}{\text{mole K}}$). Equation (A-14.22) reduces to

$$\frac{dp}{p} = \left\{ \frac{[a + f(x)]}{T^2} + \frac{b}{T} + c \right\} R \, dT \quad (\text{A-14.24})$$

and integrating gives

$$\ln p = \left\{ -\frac{a + f(x)}{T} + b \ln T + cT + d \right\} R \quad (\text{A-14.25})$$

14.3.2 Evaluation of Constants. Constants used in Equations (A-14.1) were obtained from fitting of Equation (A-14.25) to literature data. Hyperstoichiometric and hypostoichiometric data were fit separately where possible and appropriate.

The urania subcode is based on the data discussed in Section A-14.2.1 except for that of Chapman and Meadows^[A-14.14] and Ackermann^[A-14.12] for the reasons discussed in that section. The data of Tetenbaum and Hunt indicate the urania total pressure to be dependent on the urania oxygen to metal ratio but this dependence diminishes near the melting temperature. Since many of the data have been obtained at temperatures where the oxygen to metal ratio seems to have little effect and most of the data do not include the oxygen to metal ratio, the FVAPRS urania correlation was developed assuming no dependence on oxygen to metal ratio. The low temperature data of Ackermann et al^[A-14.5], Alexander et al^[A-14.10], and Benezech et al^[A-14.7] were used assuming that their test samples did not deviate greatly from stoichiometry. The best-fit correlations prediction (solid line) is shown in Figure A-14.6 compared to the urania data in Section A-14.2.1. The standard error of estimate of the FVAPRS equation and log of the data is ± 0.206 .

Material constants of Equation (A-14.1) for hypostoichiometric plutonia were obtained by fitting the vapor pressure data of Ackermann et al^[A-14.20] and Ohse and Ciani^[A-14.19]. The data of Mulford and Lamar^[A-14.23], Phipps et al^[A-14.21], and Pardue and Keller^[A-14.22] were not used because this data did not include oxygen to metal ratios. As a result of the vapor pressure studies of mixed oxides at temperatures between 4000 and 7000 K (which indicate maximum pressures of 100 MPa, the data of Ohse et al^[A-14.8] were modified and used to find the plutonia constants for temperatures above 4000 K. The data of Ohse et al was modified by multiplying it by the weight fraction of plutonia in the samples. This modification of observed vapor pressure approximates the ratios of urania and plutonia vapor pressures over mixed oxides observed in the Tetenbaum^[A-14.24] data. The fitting method followed this sequence: Data in a narrow oxygen to ratio band near stoichiometry was used to determine a normalization curve. The resulting equation was then used with all applicable data to normalize the data with respect to temperature while a best fit slope as a function of deviation from stoichiometry was determined. This stoichiometric dependent function was then used to determine the final equation as a function of temperature and oxygen to metal ratio. Figure A-14.7 shows FVAPRS plutonia subcode predictions

Fig. A-14.6 FVAPRS calculations (solid line) compared to urania data.

Fig. A-14.7 Plutonia vapor pressure data compared with corresponding FVAPRS calculations (solid line).

using oxygen and metal ratios of 2.0 (bottom curve) and 1.5 (top curve). The data with oxygen to metal ratio's between 1.5 and 2.0 are seen to lie between the two calculations.

The FVAPRS correlation for mixed oxide vapor pressure was obtained by combining the equation calculations of urania and plutonia. This is accomplished by multiplying the weight fraction of urania and plutonia times the calculated vapor pressure of urania and plutonia respectively. This approach was used rather than modeling the mixed oxide directly because mixed oxide data at typical mixture ratios (<10%) have not been investigated and Tetenbaum's^[A-14.24] plutonia pressures are roughly the same fraction of the total pressure as the weight fraction. For comparison, Equation (A-14.1) was fitted to the mixed oxide data available and then compared with the FVAPRS calculation. Data and FVAPRS subcode comparison result in a standard error of estimate of 0.422 and a comparison of the fitted equation to the data give a standard error of estimate of 0.286. A comparison of the FVAPRS mixed oxide predictions (VAPMIX) is shown in Figure A-14.8. The fit is good at temperatures below 5000 K but becomes too large by about an order of magnitude at 6000 K well above the temperatures for which this subcode will usually be used.

FVAPRS oxygen vapor pressure calculations for hypostoichiometric urania are of monatomic oxygen up to oxygen to metal ratio's of 1.999. Because of the scatter in the data a simplified form of Equation (A-14.24) was used. The resultant expressions are equations (A-14.3 through A-14.7). The constants of the equations were obtained by a simple least squares fitting technique. A log function of the deviation from stoichiometry is reported to describe the oxygen vapor pressure for hypostoichiometric fuel. This was used in Equation (A-14.4) with good results. The fitting procedure was to determine a composition normalization factor from a narrow range of temperature (1300 to 1400 K). This was then used to normalize all the data as the temperature dependent function was obtained. The data of Tetenbaum and Hunt^[A-14.28], Markin et al^[A-14.30], Wheeler^[A-14.31], and Alexander^[A-14.10] was used to develop the equation constants.

Fig. A-14.8 Mixed oxide data compared to FVAPRS calculations. An oxygen to metal ratio of 2.0 was used in the FVAPRS calculations.

R = universal gas constant ($\frac{\text{J}}{\text{K}}$)

T = temperature (K)

P_O = monatomic vapor pressure (Pa)

P_{O₂} = diatomic vapor pressure (Pa)

Since $\Delta G_{O_2}^\circ$ is defined as zero, combining Equations (A-14.26 through A-14.28) and solving for $\log P_O$ gives

$$\frac{1}{2} \log P_{O_2} - \frac{\Delta G_{O_2}^\circ}{2.303RT} = \log P_O \quad (\text{A-14.30})$$

The heat of formation or $\Delta G_{O_2}^\circ$ of Equation (A-14.29) has been reported by Markin et al [A-14.30] and Breitung [A-19.40] among others. For the FVAPRS code the value Markin et al was used

$$\Delta G_{O_2}^\circ = 61250 - 16.1T \quad (\text{A-14.30})$$

which gives the following expression when substituted into Equation (A-14.28)

$$\log P_O = 0.5 \log P_{O_2} - 13384.57/T + 3.52 \quad (\text{A-14.31})$$

Equation (A-14.31) is used with Equation (A-14.4) to find the monatomic pressure and limits the calculation of Equation (A-14.4) to the maximum calculated by Equation (A-14.3) at an oxygen to metal ratio of 1.999. The reader should be cautioned that Equation (A-14.31) does not always produce reasonable results (especially at low temperatures) when using it to compare different data sets. It should therefore be used with caution except in this case of defining continuity of equations.

Figure A-14.9 shows the FVAPRS hypostoichiometric oxygen vapor pressure correlation (UOXVAP) predictions compared to the literature data. The FVAPRS predictions for oxygen to metal ratios of 1.8 and 2.0 (solid lines) show fair agreement and correlation predictions bound the

FVAPRS oxygen vapor pressure for hyperstoichiometric urania is defined in two composition regions - 1.999 to 2.004 and 2.004 to 2.2. Data, especially that of Hagemark and Broli^[A-14.34] show an approximately linear increase in pressure as the oxygen to metal ratio increases from 2.004 to 2.2 and an exponential increase as oxygen to metal ratio increase from 1.999 to 2.004. Equation A-14.3 and A-14.5 were developed by determining a composition normalization factor using the data of Hagemark and Broli^[A-14.34]. These normalization factors were then used in a least squares fit using the data of Hagemark and Broli, Blackburn^[A-14.35], Aronson and Belle^[A-14.36], and Markin and Bones^[A-14.38], resulting in the final Equations (A-14.3 and A-14.5).

To ensure that no discontinuity exists between the hyperstoichiometric and hypostoichiometric calculations thermodynamic equations must be applied. At equilibrium the reaction $O_2 \rightleftharpoons 2O$ implies that

$$2\mu_O = \mu_{O_2} \quad (A-14.26)$$

where

μ_O = monatomic oxygen chemical potential

μ_{O_2} = diatomic oxygen chemical potential.

For ideal gases at equilibrium the chemical potentials are

$$\mu_O = \Delta G_O^\circ + RT \ln P_O \quad (A-14.27)$$

$$\mu_{O_2} = \Delta G_{O_2}^\circ + RT \ln P_{O_2} \quad (A-14.28)$$

where

ΔG_O° = heat of formation of monatomic oxygen (J)

$\Delta G_{O_2}^\circ$ = heat of formation of diatomic oxygen (J)

Fig. A-14.9 FVAPRS hypostoichiometric vapor pressure calculations (UOXVAP) compared to the data.

vapor pressure data with oxygen to metal ratios between 1.6 and 2.0. Figure A-14.10 compares the FVAPRS hyperstoichiometric oxygen vapor pressure calculations (DIOVAP) at oxygen to metal ratios of 2.004 and 2.2 to the literature data having oxygen to metal ratios greater than 2.004. These calculations are also seen yield pressures in the same range as the data. Because of the large scatter in the data, the standard error of estimate of the log of the data are large, ± 0.545 in the case of hyperstoichiometric oxygen pressures and ± 0.806 for hypostoichiometric oxygen pressures.

Different correlations for urania (UO₂VAP), plutonia (PUOVAP), mixed oxide (VAPMIX) and monatomic oxygen (UOXVAP) are compared in Figure A-14.11. FAVPRS code calculations follow the basic trends discussed in the literature. The urania vapor pressures calculations are much the largest with plutonia vapor pressure calculation about an order of magnitude less and the oxygen vapor pressure calculations (for oxygen to metal ratios less than 2.0) much smaller. Oxygen vapor pressure calculations are probably not accurate above 4000 K (much above the data base temperatures and the plutonia vapor pressure calculations are useful only to about 5500 K where calculated vapor pressures begin to decrease.

Fig. A-14.10 FVAPRS hyperstoichiometric vapor pressure calculations (DIOVAP) compared to the data.

Fig. A-14.11 FVAPRS vapor pressure calculations of plutonia (PUOVAP), urania (UO2VAP), mixed oxides (VAPMIX) and monatomic oxygen over urania (UOXVAP) using an oxygen to metal ratio of 2.0.

14.4 Fuel Vapor Pressure Subcode Listing

The FORTRAN subcode FVAPRS is presented in Table A-14.I.

TABLE A-14.I

LISTING OF THE FVAPRS SUBCODE

SUBROUTINE FVAPRS(FTEMP, FOM, FRPU, UO2VAP, PUO2VAP,
VAPMIX, UOXVAP, DIOVAP)

FTEMP = INPUT FUEL TEMPERATURE(K).
FOM = INPUT FUEL OXYGEN TO METAL RATIO(UNITLESS)
FRPU = INPUT PUO2 IN FUEL(WEIGHT FRACTION).
UO2VAP = OUTPUT TOTAL VAPOR PRESSURE OF URANIA
VAPOR SPECIES(LOG(PA)).
PUO2VAP = OUTPUT TOTAL VAPOR PRESSURE OF PLUTONIA
VAPOR SPECIES(LOG(PA)).
VAPMIX = OUTPUT TOTAL VAPOR PRESSURE OF MIXED OXIDE
VAPOR SPECIES(LOG(PA)).
UOXVAP = OUTPUT VAPOR PRESSURE OF MONATOMIC OXYGEN(LOG(PA)).
DIOVAP = OUTPUT VAPOR PRESSURE OF DIATOMIC OXYGEN(LOG(PA)).

- DATA BASE -

URANIA:

- M. TETENBAUM AND P. D. HUNT, "TOTAL PRESSURE OF URANIA-BEARING SPECIES OVER OXYGEN-DEFICIENT URANIA," JOURNAL OF NUCLEAR MATERIALS, 34 (1970).
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TABLE A-14.I (continued)

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PLUTONIA:

- R. J. ACKERMANN, R. L. FAIRCLOTH, M. H. RAND, "A THERMODYNAMIC STUDY OF THE VAPORATION BEHAVIOR OF THE SUBSTOICHIOMETRIC PLUTONIUM DIOXIDE PHASE," JOURNAL OF PHYSICAL CHEMISTRY, 70 (1966).
- R. W. OHSE AND C. CIANI, "EVAPORATION BEHAVIOR AND HIGH-TEMPERATURE THERMAL ANALYSIS OF SUBSTOICHIOMETRIC PLUTONIUM OXIDE FOR $1.51 < O/Pu < 2.00$," THERMODYNAMICS OF NUCLEAR MATERIALS, IAEA, VIENNA (1968).

OXYGENS:

- C. A. ALEXANDER, J. S. OGDEN, AND G. W. CUNNINGHAM, THERMAL STABILITY OF ZIRCONIA-AND THORIA BASED FUELS, BMI-1789 (1967).
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THE CONSTANTS LISTED IN THE DATA STATEMENTS BELOW ARE FOR THE FOLLOWING MATERIALS IN THIS ORDER :

PuO_2
 UO_2
 O_2

PROGRAM

TABLE A-14.I (continued)

CODED BY R. E. MASON APRIL 1979.
DIMENSION A(7), B(7), C(7), D(7), E(7)

```

      X < 1.99      X > 2.00
DATA A /-0.5404056E+04, 0.1788581E+05,
      -0.1119149E+05, 0.0
      -0.4953488E+05, -0.1463821E+05,
      -0.1463821E+05/

DATA B / 0.1816551E+02, 0.3058922E+02,
      0.9993252E+01, 0.0
      0.0, 0.0
      0.0, 0.0

DATA C /-0.3389145E-02, -0.4706266E-02,
      -0.1318286E-02, 0.0
      0.0, 0.0
      0.0, 0.0

DATA D /-0.1306529E+03, -0.2337348E+03,
      -0.6917448E+02, 0.0
      0.1518089E+02, 0.6206205E+01,
      0.6293306E+01/

DATA E / 0.6854587E+04, 0.0
      0.0, 0.0
      -0.1418138E+04, 0.2177517E+02,
      0.1803860E+01/

```

```

VAPEON(A,B,C,D,E,X,T) = (A + E*X)/T + B*ALOG(T) + C*T + D
IF (FOM .LE. 0.0) FOM = 2.0
X = ABS(FOM - 2.)
IF (FRPU .GE. 1.0) GO TO 20

```

PARTIAL PRESSURE OF OXIDE VAPOR.

- STOP -

PARTIAL PRESSURES OF MONATOMIC OXYGEN ARE CALCULATED UP
TO OXYGEN TO METAL RATIOS OF 2.000 AFTER WHICH DIATOMIC
OXYGEN PRESSURES ARE CALCULATED.

```

IF (FOM .LE. 1.990) GO TO 5
IF (FOM .GE. 2.004) GO TO 6
IF (FOM .LE. 2.000) GO TO 4
GO TO 9
4 CONTINUE
UXVAP = D(5) + (A(5) + E(5) * 6.9078)/FTEMP
DIOVAP = 0.0
GO TO 10

5 CONTINUE
UXVAP = D(5) + (A(5) + E(5) * ALOG(X))/FTEMP
FOR FOM < 1.999 THE UNCERTAINTY IS + OR - 0.801
DIOVAP = 0.0
GO TO 10

6 CONTINUE
DIOVAP = D(6) + A(6)/FTEMP + E(6) * X
FOR FOM < 2.004 THE UNCERTAINTY IS + OR - 0.976
UXVAP = 0.0
GO TO 10

```

TABLE A-14.I (continued)

```

C
C
9  CONTINUE
   O      = D(5) + (A(5) + E(5) * 6.9078)/FTEMP
   CO2     = 2. * (O + 13384.87/FTEMP - 3.52)
   O2      = D(7) + A(7)/FTEMP + E(7) * ALOG(2.004 - FOM)
   IF (CO2 .GE. O2) OIQVAP = CO2
   IF (O2 .LT. O2) OIQVAP = O2
   UOXVAP = 0.0
   THE TOTAL UNCERTAINTY IS + OR - 0.0000.
C
C
C 10  PARTIAL PRESSURE OF URANIA VAPOR SPECIES.
     CONTINUE
     UO2VAP = VAPEQN(A(3),B(3),C(3),D(3),E(3),0.0,FTEMP)
     THE TOTAL UNCERTAINTY IS + OR - 0.206
C 18  IF (FRPU .LE. 0.0) GO TO 100
C
C 20  PARTIAL PRESSURE OVER PLATONIA
     CONTINUE
     IF (FOM .GE. 2.) X = 0.0
C
C
C   M      = 1
   PUOVAP = VAPEQN (A(1),B(1),C(1),D(1),E(1),X,FTEMP)
   UNCERTAINTY IS + OR - 0.559
   IF ( FRPU .GE. 1.0) GO TO 100
C
C 30  CONTINUE
     PARTIAL PRESSURE OF MIXED OXIDES.
     VAPMIX = ALOG10((10.**UO2VAP)*(1.-FRPU)+FRPU*(10.**PUOVAP))
     THE UNCERTAINTY IS + OR - 0.442
     VAPMIX = VAPEQN (A(2),B(2),C(2),D(2),E(2),X,FTEMP)
C 100 CONTINUE
     RETURN
     END

```


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