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AN EQUATION OF STATE FOR MIXED-OXIDE FAST REACTOR FUELS

by

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GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Morris Schwarzblat Katz entitled An Equation of State for Mixed-Oxide Fast Reactor Fuels be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

Rocco A. Fazzolare   Sept 30 1974
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SIGNED: *Om Schwarzblatt*

To Libe and Dan

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ABSTRACT

The analysis of hypothetical accidents that could cause a disruption of a nuclear reactor core requires an accurate knowledge of the thermodynamic behavior of the materials involved. In this paper, a new equation of state for mixed-oxide fast reactor fuels is proposed. The equation is derived for application to both the single- and the mixed-phase regions. The effects of fission products and their oxidation states are included. The equation is presented in a numerical form that is suitable for easy implementation in computer simulation of hypothetical accidents. A generalized expression is presented relating the total pressure as a function of temperature, density, burnup, and fractions of noble gases and non-gaseous fission products retained in the core.

The single-phase, both gaseous and liquid, behavior is predicted with the use of a generalized six-parameter non-dimensional equation of state based on the principle of corresponding states. The six-parameter formulation allows for a more accurate representation of intermolecular interactions than the three-parameter formulation now used. The critical parameters of UO_2, which are reexamined in this work, are used in conjunction with

experimental vapor pressures and the density of molten fuel to obtain the relationships between pressure, temperature, and density.

The mixed-phase information is obtained by applying classical equilibrium thermodynamics to determine the composition and partial pressures of a mixture of fuel species and fission products. Partial pressures of the fuel species, fission products and their oxidation states are computed as a function of temperature, density, and burnup. Improvements over previous calculations were made by incorporating a more realistic expression relating the temperature dependence of the theoretical density of UO_2. This expression can also be used to determine whether the single- or mixed-phase conditions exist for given fuel temperatures and densities, which has the advantage that it is independent on possible errors in the equation of state.

Comparison with currently-used formulations indicate that much larger pressures are predicted with the model proposed here. This would appear to reduce the calculated energy released in a hypothetical accident. Fission products have an important bearing on the pressures developed and must necessarily be considered in a realistic accident evaluation.

CHAPTER 1

INTRODUCTION

In the search for scientific truth, man came across knowledge that he could use for the domination of nature. He had tremendous success. Hopefully, it will not be seen as a victory of man over nature, but rather as a step in man's search for integration with nature. Knowledge implies responsibility. It is the role of scientists and engineers to evaluate the safety of the technology they create, and to inform the public about the risks and benefits it implies. It is up to a rational society to accept or reject new developments in order to plan for the future. Nuclear power is one of the many technological achievements of the last few years. The development of fast breeder reactors brings new hope for extending the world's uranium reserves but, as with many technological advances, presents new potential hazards to the public and environment.

1.1 Safety Considerations in Fast Breeder Reactors

A great deal of attention has been devoted to the evaluation of the safety of proposed fast breeder reactor's designs. This is done to protect both the public safety and the large economic investment required for the construction of such reactors. It is customary to hypothesize a wide variety of equipment malfunctions, human errors, etc., and to study the consequences of such events. The purpose is to design adequate safeguards to prevent the occurrence or to minimize the consequences of accidents that would endanger the public safety or the reactor's integrity. The subject is too extensive to be reviewed here. However, excellent discussions on this topic can be found in the work by Okrent (1969) and Hummel and Okrent (1970).

One of the more spectacular of the hypothetical accidents considered that leads to a disassembly of the reactor internals is briefly described next.

1.2 Reactor Disassembly Accidents and the Equation of State

In accident studies that would result in a partial or complete disassembly of the reactor core, events that could lead to a prompt-critical or uncontrolled super-critical condition must be postulated. In this situation the neutron population and the energy production increases exponentially with very short time periods in the order of microseconds (Hetrick 1971). The energy deposited is far beyond the thermal design capabilities of the reactor. It can be further assumed that no shut-down mechanism intercedes which allows the core to actually disrupt due to the massive energy accumulations. The physical events necessary to permit this eventuality are highly improbable and require an exaggeration of assumptions with regard to initiating events. For example, a typical scenario would assume that a coolant pump failure occurs or that a control rod is ejected combined with a failure of reactor shut-down mechanisms. The fuel elements are assumed to eventually melt and the molten material slumps. It can be supposed that the molten mass reaccumulates into the highly supercritical formation which would yield the uncontrolled power excursion required for the core disassembly. It is the disassembly which finally terminates the chain reaction. The thermodynamic behavior (pressure, density and temperature relationships) of the core material plays an important role in determining the manner and time sequence of the disassembly.

Coupled neutronic-hydrodynamics codes such as MARS (Hirakawa 1967), PAD (Stratton, Peterson and Engle, 1972), and VENUS-II (Jackson and Nicholson 1972) are used to follow the excursion from the time prompt-critical conditions are reached to when the excursion is terminated by the disassembly of the core. In such codes the equation of state (EOS), a relationship between the thermodynamic variables, pressure, temperature (or energy) and volume (or density) (Zemansky 1957), serves as a link between the neutronic and hydrodynamic calculations. The neutronic calculations dictate the energy deposition rate. This leads to a pressure increase (calculated via the EOS) which will cause material movement. Changes in temperature and geometry of the reactor modify the reactivity and thus the energy deposition rate, which will in turn modify the pressure, and so on.

One of the more sophisticated disassembly calculations today is performed at Argonne National Laboratory (Jackson and Nicholson 1972); they use an EOS which will be designated as the ANL equation throughout this work. Pure UO_2 is considered in this model. In the two-phase region, extrapolations of measurements made at very low pressures are used to obtain the vapor-pressure relationships. No measurements have been made at high temperatures to justify the large extrapolations made. In the single-phase region, a fit to data obtained by Menzies (1966) based on the principle of corresponding states is used. As it will be discussed later in this work, the corresponding states formulation used by Menzies (1966) is not the most adequate for the prediction of properties of UO_2. In the ANL equation, the transition point from the two-phase to single-phase conditions is obtained by assuming that the pressure is given by the maximum prediction of either the two-phase or the single-phase pressure at any given temperature and density. This scheme would be adequate provided that the predictions for both phases were accurate. However, large uncertainties are associated with these predictions due to insufficient experimental information.

In addition, the effects of the fission products are ignored in the ANL equation. Recent work has shown, however, that fission products can have a profound effect on the total pressure and reduce the energy released considerably in a hypothetical disassembly accident. Gabelnick and Chasanov (1972) developed a computer code (VAPOR) which predicts the vapor pressures of mixed-oxide fuel species, fission products and their oxidation states. The code is based on chemical equilibrium thermodynamics. Their work is significant since it demonstrated a dramatic increase in the total pressure when fission products are included in the calculations.

It would be desirable to incorporate the VAPOR calculations in a VENUS type code. However, this can not be done directly with ease. During a reactor disassembly computer simulation, more than fifty thousand evaluations of the EOS might be required (Jackson and Nicholson 1972). Therefore, the incorporation of the VAPOR code as a subroutine would be prohibitively time-consuming. A tabular form of the VAPOR code results would also be an inconvenient method of incorporating the data. The VAPOR code computes the vapor pressures at discrete fixed temperatures up to 6000 ^{o}K. Interpolation and extrapolation are required to evaluate intermediate points and at temperatures above

6000 °K. Significant computer memory would be required for the storage of large tables. In addition, the VAPOR code is limited to the two-phase region and it has been shown (Jackson and Nicholson 1972) that unrealistic predictions would be obtained if the single-phase region is not included.

Bogensberger, Fischer and Schmuck (1974) developed a computer code similar to VAPOR and applied the results to a few disassembly calculations. They showed that the total energy released in a hypothetical disassembly accident is indeed reduced considerably if the effects of the fission products are included. However, this work has limitations similar to those expressed previously for routine accident calculations and did not consider the single-phase region.

1.3 Objectives

The purpose of this work is to propose a new EOS for mixed Pu-U oxide fuel. The goals of the new EOS are to model appropriately the single- and two-phase regions, to include the effects of fission products and their oxidation states, and to be in a suitable numerical form for easy use in reactor disassembly simulation codes.

In Chapter 2, the principle of corresponding states is discussed. The application of chemical equilibrium thermodynamics to the determination of mixed-oxide fuel vapor-pressures is reviewed in Chapter 3. The development of an EOS for mixed-oxide fuel is presented in Chapter 4. In Chapter 5, results obtained in this work are analyzed and compared with previous formulations. Conclusions and recommendations for future research are given in Chapter 6.

CHAPTER 2

THE EQUATION OF STATE FOR A SINGLE PHASE

2.1 Introduction

The prediction of unknown properties and behavior of many fluids based on the known behavior of a few fluids has been the concern of engineers for many years, particularly in the chemical processes industry. The most widely used method of predicting thermodynamic properties of gases and liquids is based on the corresponding states principle (CSP). The principle was first formulated by Van der Waals before 1900, and according to a statement by Guggenheim (1945), the CSP "may be safely regarded as the most useful byproduct of the Van der Waals equation of state." The study and empirical development of generalized equations of state continues up to the present day.

2.2 The Simple Corresponding States Principle

Dimensional analysis has been applied with great success in many engineering disciplines, i.e., fluid mechanics and heat transfer. Non-dimensional parameters are used to generalize equations to be applicable to a variety of conditions (size, materials, etc.). The CSP can be derived rigorously applying statistical mechanics in combination with a dimensional analysis formulation of the intermolecular potential (potential energy as a function of separation between two molecules) which dictates the interactions between molecules (Reed and Gubbins 1973). The idea is to obtain a generalized EOS in terms of non-dimensional parameters, applicable to a wide variety of materials.

The molecular requirements that a fluid has to satisfy in order to obey the CSP are as follows (Reed and Gubbins 1973):

1. The canonical ensemble partition function describing the fluid is assumed to be separable into independent translational, rotational, vibrational, and configurational factors. The translational energy states must be independent of the rotational states.
2. Only the configurational partition function is considered density dependent. These conditions are usually fulfilled by monoatomic molecules except at very low temperatures. Molecules which exhibit hydrogen bonding are an exception and do not satisfy this requirement. The above conditions are satisfied reasonably well by polyatomic molecules at high temperatures.

Therefore, they should be satisfied by UO_2 and PuO_2 at the high temperatures of interest in reactor disassembly calculations.

3. The translational and configurational portions of the partition function can be treated classically, and Boltzmann statistics apply.

   This requirement is most often satisfied except for the very light molecules such as H_2, He, and Ne. Therefore, UO_2 and PuO_2 ought to satisfy this requirement.

4. The total potential energy of the system can be expressed as

$$U(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_n) = \epsilon\Phi\left(\frac{r_{12}}{\sigma}, \frac{r_{13}}{\sigma}, \ldots, \frac{r_{23}}{\sigma}, \frac{r_{24}}{\sigma}, \ldots\right) \quad (2.1)$$

   where $\bar{r}_i$ is the position vector of molecule i, r_{ij} is the distance between molecules i and j, and ϵ and σ are energy and distance parameters characteristic of the fluid.

Equation (2.1) implies that the intermolecular potential is spherically symmetric, and no angle orientation is preferred for particle interaction. In such case, ϵ represents the minimum potential energy, and σ is defined as the collision diameter which is the point of zero potential energy. The form of a typical intermolecular potential is shown in Fig. 1.

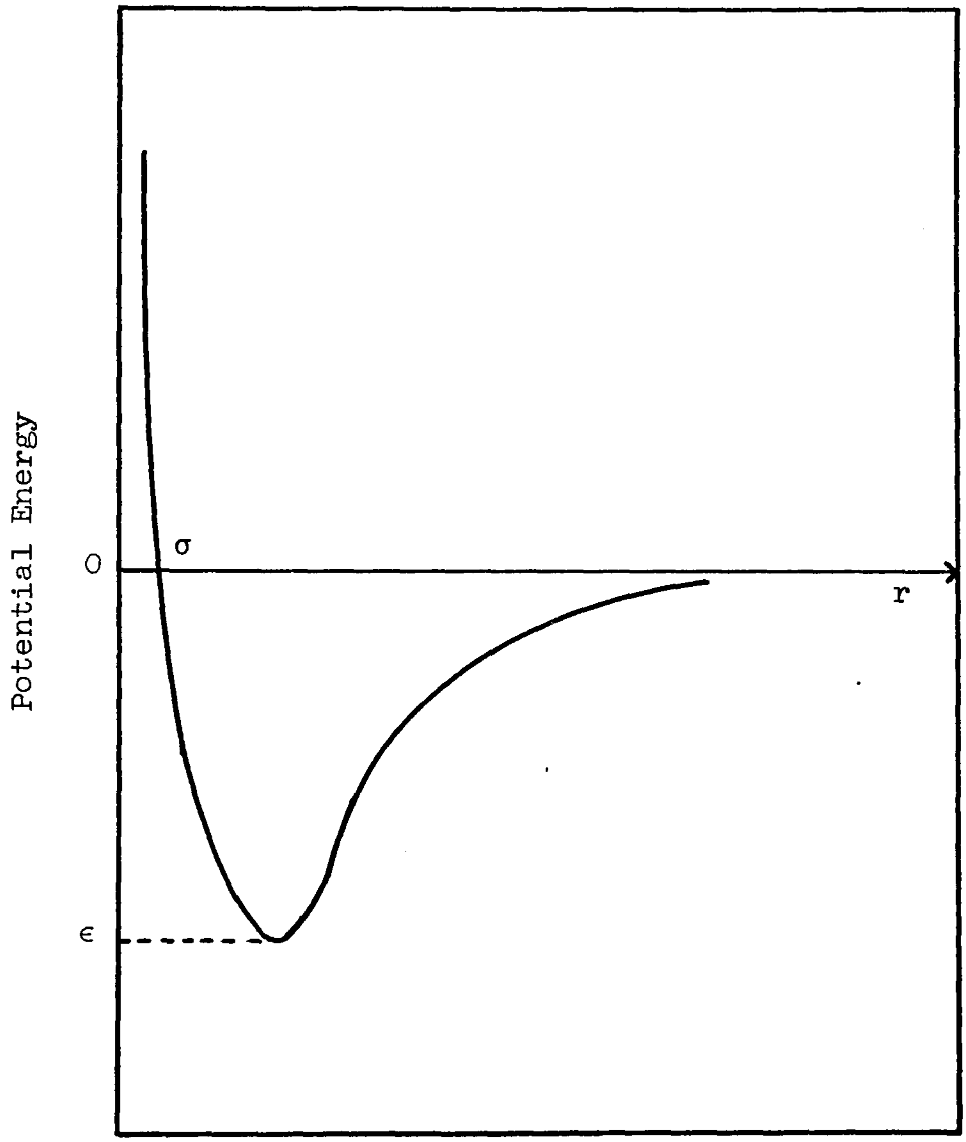

Fig. 1 Typical Intermolecular Potential

Recent spectroscopic evidence (Gabelnick, Reedy, and Chasanov 1973) strongly indicates a linear geometry for UO_2 molecules. Therefore, condition 4 is not expected to be satisfied rigorously by this material. Ways to account for this effect are discussed later in this chapter.

The simple CSP states that the following generalized EOS holds for all substances that satisfy the above requirements.

$$P_r = f(T_r, V_r) \tag{2.2}$$

where P_r, V_r, and T_r are reduced pressure, molal volume, and temperature defined by

$$P_r = \frac{P}{P_c},\ V_r = \frac{V}{V_c},\ T_r = \frac{T}{T_c} \tag{2.3}$$

where subscript c indicates the value at the critical point. The function f is a universal function.

It can be shown (Reed and Gubbins 1973) that the critical parameters are related to ϵ and σ as follows:

$$T_c = c_1\epsilon,\ V_c = c_2\sigma^3,\ P_c = c_3\,\frac{\epsilon}{\sigma^3} \tag{2.4}$$

where c_1, c_2, and c_3 are constants.

The critical compressibility, defined as

$$Z_c = \frac{P_c V_c}{R\ T_c} \tag{2.5}$$

where R is the gas constant, can be used to test the validity of the simple CSP. It is clear that all substances for which Eq. (2.2) applies should have the same critical compressibility. Experiments show that Z_c varies between 0.23 and 0.29 for most substances (Hougen, Watson and Ragatz 1959), indicating a departure from the simple CSP. Actually, only simple molecular substances such as Ar, Kr, and CH_4 obey the simple CSP, since the potential energy of more complex polyatomic molecules can not be simply expressed by Eq. (2.1). In general, the potential energy depends on molecular structure and multipole moments in addition to the parameters ϵ and σ (Hakala 1967). Nevertheless, a generalized CSP can be formulated provided that f in Eq. (2.2) is a function of the same number of parameters required to represent the potential energy of the system.

2.3 Generalized Formulations of the CSP

The first effort to extend the applicability of the simple CSP came with the formulation of a three parameter CSP. Since one of the indications of the failure of the simple CSP is the prediction of a universal critical compressibility for all fluids, a logical first step was to propose an experimental value of Z_c as an empirical third parameter. The use of Z_c as a third parameter was developed extensively by Lydersen, Greenkorn and Hougen (1955);

it is perhaps the most widely used generalized formulation of the CSP. However, the variation in Z_c for most substances is small and is only about 20% for fluids as diverse as argon and water. This means that large deviations from the simple CSP have to be accommodated with a parameter which varies only slightly. The difficulty is compounded since Z_c is often subject to considerable experimental uncertainty. In many cases there are no experimental values for the critical parameters, including Z_c. Thus, only estimations obtained from semi-empirical correlations are available.

In order to circumvent the problems mentioned above, several third parameter formulations have been suggested (Rowlinson 1955, Pitzer et al. 1955, Riedel 1954). All of these formulations use vapor pressure information which is in general easier to obtain experimentally than the critical compressibility. In particular, Riedel (1954) proposed the parameter α, defined as the slope of the vapor pressure with respect to temperature at the critical point, as a third parameter. He also developed an empirical relation for the reduced saturated vapor pressure, P_{vr}, as a function of reduced temperature; namely,

$$\ell n(P_{vr})=\alpha \ell n(T_r)-0.0838(\alpha-3.75)[36/T_r-35-T_r^6+42\ell n(T_r)] \quad (2.6)$$

This relationship is based on the CSP and has been proven to be valid for many substances up to the critical temperature.

With the aid of Eq. (2.6) and knowing P_c and T_c, α can be obtained from vapor pressure measurements below the critical temperature. Riedel (1954) also showed experimentally that Z_c and α are related by

$$\frac{1}{Z_c} = 3.72 + 0.26(\alpha - 7) \tag{2.7}$$

which holds for many, but not all, substances.

From the considerations given in section 2.2, it is clear that a multiparameter CSP formulation can be expected to be valid for a wide spectrum of fluids. The most significant development to date of the multiparameter CSP is the work by Hirschfelder et al. (1958). In dilute and dense gas regions a four-parameter CSP is used in which both Riedel's parameter, α, and the critical compressibility, Z_c,, are introduced as independent parameters. In the compressed liquid region, two additional parameters, c and d, are suggested. The parameters c and d are obtained from the generalized equation for the reduced saturated liquid density, ρ_ℓ,

$$\rho_\ell(T_r) = 1 + c(1-T_r)^{1/3} + d(1-T_r) \tag{2.8}$$

proposed by Guggenheim (1945) and Riedel (1954). This equation has been shown to be accurate to about 1% for most known substances up to the critical temperature. Therefore, experimental data on the density of saturated liquid at two temperatures allow the determination of c and d. The Hirschfelder CSP can be regarded in its most general form as a multiparameter CSP in which

$$P_r = f(T_r, V_r, \alpha, Z_c, c, d) \tag{2.9}$$

This extension permits the inclusion of many more fluids than with any of the previous formulations.

CHAPTER 3

THE MIXED-PHASE REGION

Much attention has been devoted to the development of methods to predict properties and behavior of mixtures. Classical chemical thermodynamics is often applied extensively to the solution of these problems. The subject is too extensive to be examined in detail here, but we will mention some of the basic concepts of chemical equilibrium applicable to the problem of determining the composition of the mixed-phase region. The books by Van Zeggeren and Storey (1970) and Lewis and Randall (1961) are excellent references on the subject.

3.1 Basic Concepts of Chemical Equilibrium Calculations

A fundamental problem in chemical equilibrium theory is the determination of the equilibrium composition of a mixture of different molecular species. Two basic methods can be used to solve this problem.

The first method depends on minimizing the Gibbs free energy of the system. For example, given a single-phase system, the Gibbs free energy, G, depends on the temperature, pressure, and the number of moles of each substance (n_i) in that phase, i.e.,

$$G = f(T,P,n_1,n_2,n_3, \ldots.) \qquad (3.1)$$

It can be shown that G is a minimum at the equilibrium composition (see Van Zeggeren and Storey 1970). Thus, the problem is reduced to finding the values n_1, n_2, n_3, etc. which minimize the total free energy of the system. Optimization techniques are convenient and have been applied to the solution of this type problem. A multi-phase system can be analyzed in a similar fashion.

A second method makes use of classical equilibrium thermodynamics to formulate a set of non-linear equations involving the molar concentrations of all the species present in all phases. In this approach, the set of equations is obtained as follows: Consider a reaction of the type

$$p(\text{Reactants}) \underset{R_r}{\overset{R_f}{\rightleftarrows}} g(\text{Products}) \qquad (3.2)$$

where p and g are the stoichiometry coefficients and R_f and R_r are the reaction constants for the forward and reverse reactions, respectively. The velocities of the forward and reverse reactions, V_f and V_r are

$$V_f = R_f \; [\text{Products}]^g \qquad (3.3a)$$

$$V_r = R_r \; [\text{Reactants}]^p \qquad (3.3b)$$

where the quantities in brackets represent molar concentrations of the respective components. At equilibrium, $V_f = V_r$. Therefore

$$\frac{R_f}{R_r} = K_p = \frac{[\text{Products}]^g}{[\text{Reactants}]^p} \qquad (3.4)$$

where K_p is known as the equilibrium constant. K_p is related to the change in free energy of the products and reactants at the standard condition (1 atm), ΔG^o, by the equation

$$\Delta G^o = - RT \ell n\, K_p \qquad (3.5)$$

Therefore, K_p can be calculated from experimental information on the free energies of formation of the species involved in the reaction.

It can be shown that the chemical potential of each species i, μ_i, which is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \qquad (3.6)$$

has to be equal in all phases at equilibrium, i.e.,

$$\mu_{i\alpha} = \mu_{i\beta} = \ldots\ldots = \mu_{i\Omega} \qquad (3.7)$$

where α, β, ... Ω represent the phases present. The set of non-linear equations is formed by including for each reaction one equation of the type Eq. (3.4) and one of the type Eq. (3.5). In addition, an equation of the type

Eq. (3.7) for each species must be specified. The solution of the set of equations provides the molar concentrations at equilibrium of each species in each phase. The partial pressures of each species in the gaseous phase can be obtained from these concentrations. For example, at low molar concentrations, ideal gas law could be used to calculate the partial pressures.

3.2 Application to Fast Reactor Fuels

Gabelnick and Chasanov (1972) developed an algorithm for the prediction of vapor pressures and oxidation states of fast breeder reactor fuel and fission product elements. They implemented their ideas in a computer code called VAPOR. VAPOR is a simple multi-phase multi-component chemical equilibrium program in which the equilibrium of fuel species, fission products and their oxidation states is calculated. A three-phase closed thermodynamic system is considered (condensed oxide, condensed non-oxide, and vapor), and ideal solution theory is assumed to be valid for both condensed and gaseous phases. Each phase is considered to be a homogeneous mixture at uniform temperature and all vapor species are assumed to have equal access to the free volume, and so a true global thermodynamic equilibrium is achieved. All fission products are assumed to be retained in the system. Compound formation between different fission-product elements is not allowed for.

A brief qualitative description of the algorithm follows and the mathematical formulation is presented in Appendix B. For a given set of parameters (temperature, initial fuel composition, Pu/Pu+U ratio, burnup, and fuel smeared density, defined as the total fuel mass over the total available volume for fuel expansion), a set of simultaneous equations involving molar concentrations of every significant condensed and vapor phase of the metallic or oxide species is established for each fission product and fuel material. These equations are based on mass constraints and equilibrium relationships. The mass constraints are imposed by the initial fuel composition, burnup, and smeared density. The equilibrium relationships are obtained from free energies of formation, obtained from available experimental data and extrapolation of the data to higher temperatures.

In order to solve the equations, a post-burnup oxygen to metal (O/M) ratio is estimated and initial guesses are made for the total number of moles in each of the two condensed phases. The O/M ratio establishes a convergence criterion as discussed later on. The equations are solved for vapor and condensed-phase concentrations for each species. Corrected sums for the total number of moles in each phase are calculated. The corrected sums are then used to develop new sets of equations which are again solved for vapor and condensed-phase concentrations. After three iterations, the amount of oxygen bound to all fission products is calculated. The amount of oxygen available for bonding with the fuel in the condensed phase is estimated, which is used to determine a "calculated" O/M ratio. The initial estimate of the post-burnup O/M ratio is varied, and the entire procedure is repeated until the "calculated" and estimated O/M ratios agree to within a desired tolerance. Molar concentrations of condensed species and vapor pressures of gaseous species are calculated with the final accepted value of the O/M ratio.

Gabelnick and Chasanov point out that the results from the VAPOR code are to be taken as a first approximation due to the assumptions made in the derivation of their algorithm and because of the uncertainties in the free energies of formation of the condensed species at high temperatures. Nevertheless, their work indicates trends related to the various parameters and represents, without any doubt, a significant contribution to the understanding of such a complex problem.

CHAPTER 4

DEVELOPMENT OF AN EQUATION OF STATE FOR MIXED OXIDES

4.1 Critical Parameters

The experimental determination of the critical parameters for UO_2 is a difficult task, if not impossible, at this time. The required experiments can not be easily accomplished since the estimated critical temperature for UO_2 is well above the melting point of all known materials suitable for containment. As a consequence, semi-empirical methods must be used to estimate these parameters. A brief review of the most reliable and accepted estimates of the critical parameters is presented next.

4.1.1 Previous Work

The law of rectilinear diameters (Cailletet and Mathias 1886) is often used to estimate critical parameters. The law states that one-half the sum of the liquid and vapor densities is linear up to the critical point. This empirical rule has been substantiated for many fluids (Grosse 1961). Using experimental data for the density of saturated liquid and estimates of the saturated vapor density from vapor pressure information, the coexistence curves can be estimated, which allows the determination of the critical temperature and density. Once these values are known, the critical pressure is calculated assuming a value for the critical compressibility. Miller (1965) applied this technique to estimate the critical parameters for UO_2. The application of this method has the disadvantage that it requires the extrapolation of vapor pressure behavior far beyond the range of experimental data. In addition, the results are finally contingent on the exactitude of the assumed value of Z_c; however, this consideration is less significant than the potential error introduced by extrapolating the vapor pressure data.

Several investigators have measured the vapor pressure of UO_2 (Ackerman, Gilles and Thorn 1956, Ohse 1964, Dayton and Paprocki 1965). However, the agreement between the different results is not very satisfactory (Miller 1965) which indicates that extreme care is required for such measurements. Menzies (1966) reports that the following equation is a best fit to all the data available at that time:

$$\ell n\ P = -\ 4.34\ \ell n\ T - 76800/T + 56.294 \qquad (4.1)$$

where P is the vapor pressure in atmospheres and T is the temperature in $^{\circ}K$. By comparing Eqs. (4.1) and (2.6) he was able to determine the critical pressure and temperature and the factor α. Using Eq. (2.7), Z_c can be determined and thus the critical density. This method has the advantage that it does not require extrapolation of the vapor pressure beyond the experimental range, but it is sensitive to errors in vapor pressure data. Since Eq. (4.1) represents a fit to several sets of experimental data, some error in the predicted critical parameters must be anticipated.

4.1.2 A New Set of Proposed Critical Parameters

According to Miller (1965), experiments at Argonne and other laboratories tend to confirm Ackerman's results and his low-temperature equation (Ackerman et al. 1956) given by

$$\ell n\ P = -\ 4.026\ \ell n\ T - 76250/T + 52.51 \qquad (4.2)$$

P is the vapor pressure in atmospheres and T the temperature in ^{o}K. This tends to substantiate the use of Eq. (4.2) for the derivation of the critical parameters as was done by Miller. However, instead of applying the law of rectilinear diameters as Miller did with its inherent errors of extrapolation we will apply Riedel's method as did Menzies.

If we now compare Eqs. (4.2) and (2.6) we obtain the following:

$$\alpha' - 0.0838\ (\alpha' - 3.75) \times 42 = -\ 4.026 \qquad (4.3)$$

$$0.0838\ (\alpha-3.75) \times 36\ T_c = 76250 \tag{4.4}$$

$$\ell n\ P_c = \alpha\ \ell n\ T_c + 52.51 - 0.0838\ (\alpha-3.75)(35+42\ \ell n\ T_c + T_r^6) \tag{4.5}$$

From Eq. (4.3) we obtain that $\alpha = 6.8362$; using this value and Eq. (4.4), we can propose that the critical temperature is 8190 ^oK. The term T_r^6 in Eq. (4.5) is negligible for the temperature range in which Eq. (4.2) was obtained (1600-2000 ^oK). Eq. (4.5) yields $P_c = 1315$ atm. Using Eq. (2.6) one obtains $Z_c = 0.272$ and from Eq. (2.4) the critical density is found to be 1.944 gr/cm^3. The results obtained are compared with results by other authors in Table 1.

Table 1. Critical Constants of UO_2

	This work	Miller (1965)	Menzies (1966)
Critical pressure, atm.	1315	1230	2000
Critical temperature, ^oK	8190	9115	8000
Critical density gr/cm^3	1.944	1.588	3
Z_c	0.272	0.27 (assumed)	0.27
α	6.8362	-	6.9373

It can be observed from Table 1 that the predictions by Miller and the ones obtained here are reasonably close to each other. The fact that the predictions were obtained by two different methods but using the same data gives some confidence on the validity of both methods. However, since Riedel's method does not require extrapolation of the data this method should be preferred. Some disagreement is observed when Menzies' predictions are compared with the ones obtained here. The same method was used for both predictions but based on different data. Our predictions are based on a single set of data which is believed to be the most accurate. Figure 2 shows a comparison between a fit to Ackerman's low temperature data [Eq. (4.2)] and predictions obtained by using Riedel's Eq. (2.6) and the sets of critical parameters given in Table 2. The best fit is indeed obtained with the critical parameters proposed here.

4.2 The Single-phase Regions

The EOS for pure UO_2 in the single phase regions was obtained by the use of the generalized multiparameter formulation (Hirschfelder et al. 1958). That was discussed in Chapter 2. The total pressure in this region will be assumed to be the sum of the UO_2 pressure plus the vapor pressure at the departure point from two-phase conditions. This will be discussed in more detail later on.

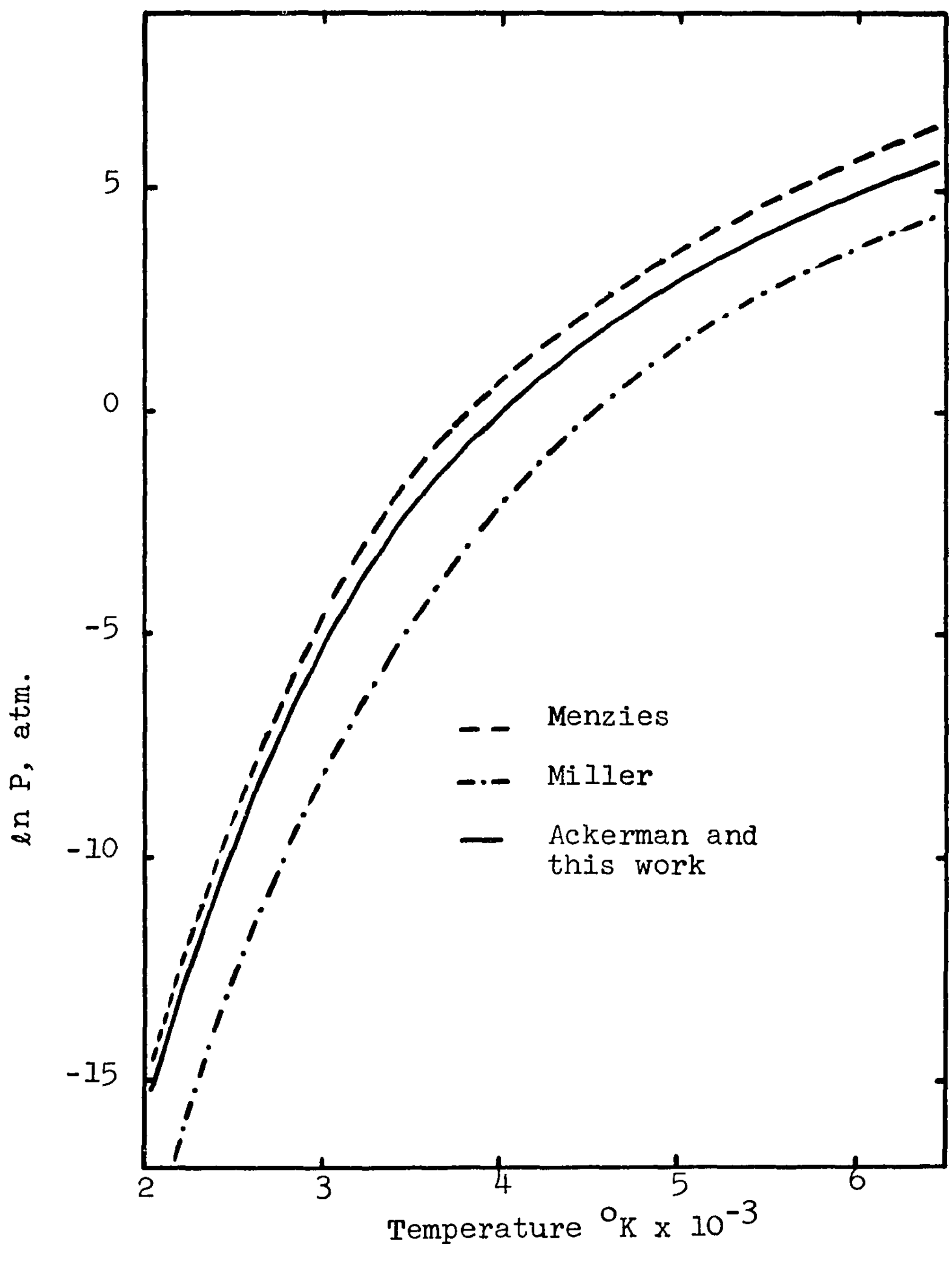

Fig. 2 Comparison of Vapor Pressure Predictions for UO_2

In order to use the generalized formulation, the parameters c and d in Eq. (2.7) are required. Christiansen (1963) determined that the density of molten UO_2 was 8.74 gm/cm^3 at 3074 ^oK, and that the linear expansion coefficient was $3.5 \times 10^{-5}\ ^oK^{-1}$ at that temperature. Assuming that the volumetric expansion coefficient is three times the linear expansion coefficient, the density of molten UO_2 is 8.56 gm/cm^3 at 3274 ^oK. Using these results and Eq. (2.7), we find that c = 1.998 and d = 2.864. The resulting equation for the reduced theoretical density for liquid UO_2 is

$$\rho_{T\ell}(T_r) = 1 + 1.998(1-T_r)^{1/3} + 2.864(1-T_r) \tag{4.6}$$

The Hirshfelder equations were programmed and numerical results for the pressure of UO_2 were generated for temperatures between 3074 and 13000 ^oK and for densities between 3 and 9 gm/cm^3. Analytical expressions were then obtained by least-squares fitting the numerical results. The expressions obtained are

$$P_s = \begin{cases} 1315\{f_1(T_r)[P_g(\rho_r,T_r)-P_g(\rho_{T\ell},T_r)] + f_2(T_r)\} & \text{for } T_r < 1 \\ 1315\ P_g(\rho_r,T_r) \text{ for } T_r \geq 1 & \end{cases} \tag{4.7}$$

where P_s is the single phase pressure for UO_2 in atmospheres [the first expression in Eq. (4.7) represents the liquid region and the second represents the gaseous region],

ρ_f is the reduced fuel smeared density and $\rho_{T\ell}$ is given by Eq. (4.6). The functions f_1, f_2 and P_g are

$$f_1(T_r) = 1.425 - 0.945\ T_r + 0.52\ T_r^{\ 2} \tag{4.8}$$

$$f_2(T_r) = \exp(-43.857 + 130.182\ T_r - 138.575\ T_r^{\ 2} + 52.278\ T_r^{\ 3}) \tag{4.9}$$

$$P_g(\rho, T_r) = A_1(\rho) + A_2(\rho) T_r \tag{4.10}$$

$$\text{where } A_i(\rho) = \sum_{j=o}^{5} a_{ij}\rho^j. \tag{4.11}$$

The coefficients a_{ij} are given in Table 2.

Table 2. Values of the a_{ij} Coefficients

i/j	0	1	2	3	4	5
1	-25.832	44.28	-20.206	-8.164	4.306	-0.26362
2	39.113	-82.112	64.735	-15.702	0.58792	0.2828

All the digits in the coefficients should be retained to avoid large round-off errors due to the high order of the polynomials.

4.3 The Mixed-phase Region

The EOS in the mixed-phase region was obtained with the aid of the VAPOR code developed by Gabelnick and Chasanov (1972) and described in Chapter 3. However, some modifications to the code were made and are discussed next. In order to estimate the void space available for gas expansion, the density of molten UO_2 is calculated in the VAPOR code assuming that the volumetric expansion coefficient obtained by Christiansen (1963) is constant with temperature. This assumption overestimates the density at high temperatures. For example, it predicts a density of 5.685 gm/cm^3 at the value of T_c obtained in section 4.1.2, which is much higher than any of the estimates of the critical density. A more realistic representation is Eq. (4.6) which was used to predict the density of molten UO_2. Figure 3 compares both predictions for the temperature dependence of the theoretical density of UO_2. It can be observed that the relationship proposed here has the correct shape as opposed to the prediction by Gabelnick and Chasanov (1972). The relationship proposed here yields an infinite gradient at the critical temperature and is clearly part of the curve formed by the saturated liquid and saturated vapor lines. This new relationship will be a more accurate representation than that used by Gabelnick and Chasanov. The significance of this modification is discussed in Chapter 5. The VAPOR code calculates the total pressure

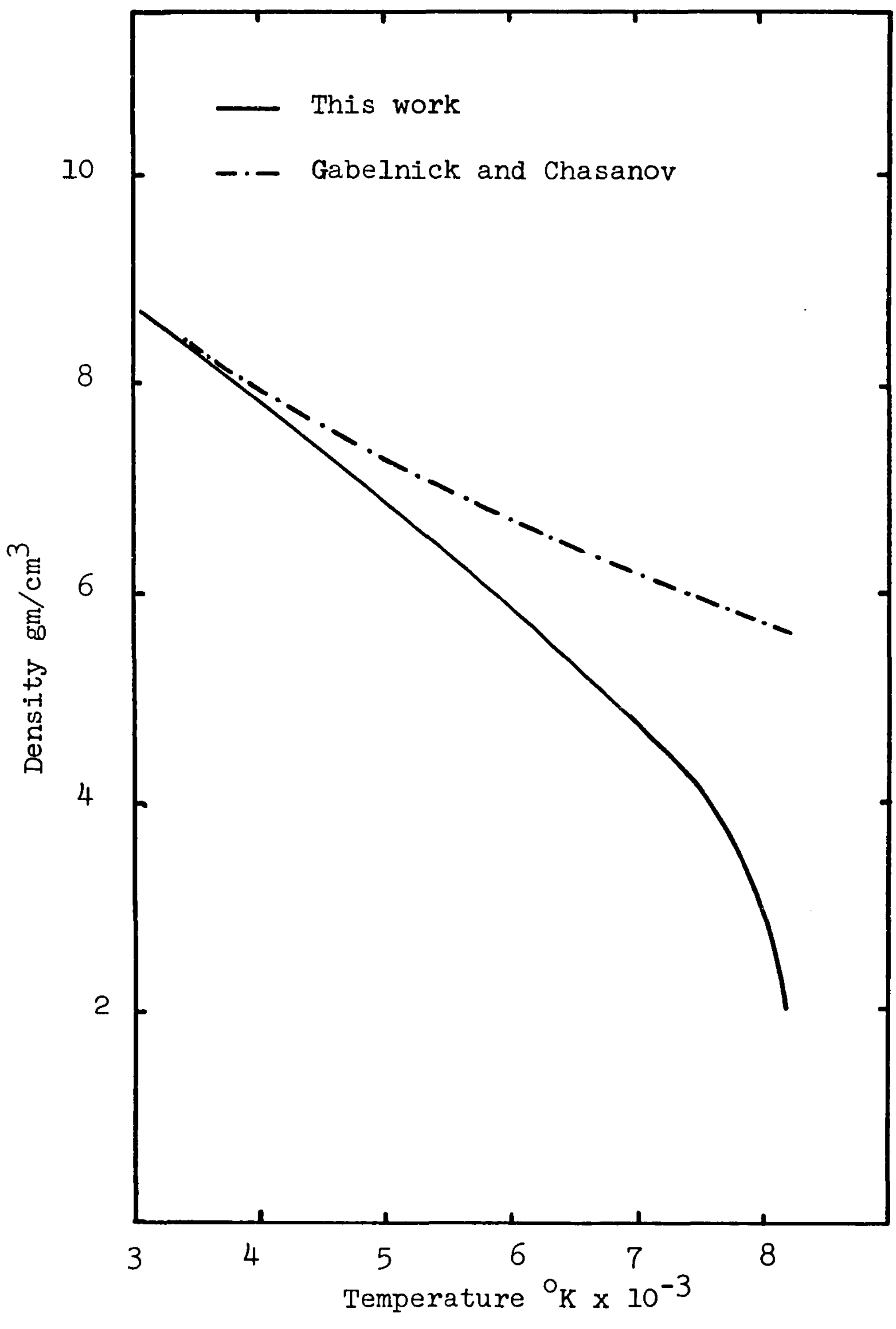

Fig. 3 Temperature Dependence of Saturated Liquid Density of UO_2

assuming 100% retention of the fission products in the core. However, some of the fission products are released during normal operation of the reactor or during a sudden heat-up of the core at the initiation of an accident. Therefore, appropriate retention factors for the different fission products should be introduced in a more realistic approach. Using the modified VAPOR code, vapor pressures were calculated for fuel smeared densities between 3 and 9 gm/cm^3 and burnups between 0 and 10%, for temperatures between 3000 and 6000 ^oK. Next, least-squares fitting techniques were applied to obtain analytical expressions for the partial vapor pressures. The total pressure was separated into three components, namely,

a) the fuel species
b) noble gases
c) the remaining fission products, their oxidation states and oxygen species.

This was done in order to facilitate the incorporation of appropriate retention factors for groups b and c. Care was taken to assure reasonable extrapolations to the partial pressures up to the critical temperature. Vapor pressures are only slightly dependent on oxygen to metal ratios and Pu/Pu + U ratios at the temperatures of interest in disassembly calculations. Our calculations were performed for fuel with a $(U_{0.8}Pu_{0.2})O_{1.98}$ composition. Results are given next.

4.3.1 Fuel Species

The VAPOR code predicts the partial pressures of the different fuel species present (U, UO, UO_2, UO_3, Pu, PuO, PuO_2). The composition varies with burnup and so does the total fuel species pressure. However, the variation is small (of the order of 10% for burnups betwen 0 and 10%) above 4000 ^oK, where the pressure becomes significant. The fuel species vapor pressure turned out to be small compared with the fission products' vapor pressures, and results from the VAPOR code might involve some error due to uncertainties in thermodynamic data for the fuel at high temperatures. In view of this we assumed, for the sake of simplicity, the fuel pressure as independent of burnup and fitted the results obtained at zero burnup. The resultant expression for the fuel species pressure is,

$$P_{fs}(T_r) = \sum_{i=o}^{4} c_i T_r^{\,i} \tag{4.12}$$

where P_{fs} is the pressure in atmospheres and

c_o = - 196.265, c_1 = 1662.841, c_2 = - 4991.148,
c_3 = 5988.812, c_4 = - 2075.691.

4.3.2 Noble Gases

The noble gases' pressure, P_{ng}(atm.) was found to follow a modified ideal-gas expression, namely,

$$P_{ng}(T_r,\rho_f,B) = 11.162\ B\ T_r/V_v \tag{4.13}$$

where B is the burnup percent. V_v is the reduced void space volume defined as

$$V_v = \frac{1}{\rho_f} - \frac{1}{\rho_T} \tag{4.14}$$

where ρ_f is the reduced fuel smeared density. ρ_T is the reduced theoretical fuel density given by

$$\rho_T = \begin{cases} 5.643/(1+9\times10^{-6}\ TT+6\times10^{-9}\ TT^2+3\times10^{-12}\ TT^3) \\ \qquad\qquad \text{if } T_f < 3074\ ^{o}K \\ 1+1.998(1-T_r)^{1/3}+2.864(1-T_r) \\ \qquad\qquad \text{if } T_f \geq 3074\ ^{o}K \end{cases} \tag{4.15}$$

T_f is the fuel temperature in ^{o}K and $TT = T_f - 273$.

4.3.3 Remaining Fission Products and Oxygen Species

Fitting the data for this component of the total pressure was a difficult and time-consuming undertaking. It is not surprising, however, since approximately 30 fission products and their oxidation states plus oxygen species interact in a complex manner to contribute to the total pressure. The composition of this mixture varies with temperature, density and burnup. Although the resulting expressions seem complex, it should be noticed that all the functions that depend on burnup need to be evaluated only once for each disassembly calculation. This greatly simplifies the expression which is ultimately used in the repetitive computations of the accident evolution. The results are presented next, with the burnup functions given at the end. All the digits in the coefficients should be retained to avoid large round-off errors. The pressure due to fission products (not including noble gases), their oxidation states, and oxygen species, P_{fp}(atm.), is given by

$$P_{fp}(T_r,\rho_f,B) = f_3(T_r)\exp\{f_4(T_r)(\rho_f-1.54321)\} + f_5(T_r)/V_v \tag{4.16}$$

where V_v is given by Eq. (4.14),

$$f_3(T_r) = \exp[\sum_{i=o}^{5} f_{3i}T^i] + \sum_{i=o}^{6} d_i(B)T_r{}^i \tag{4.17}$$

where

$$f_{30} = -\ 111.4418,\ f_{31} = 740.1256,\ f_{32} = -\ 2067.3758,$$

$$f_{33} = 3009.8377,\ f_{34} = -\ 2196.084,\ f_{35} = 631.6183$$

$$f_4(T_r) = \sum_{i=o}^{3} e_i(B)T_r{}^i \tag{4.18}$$

$$f_5(T_r) = g_1(B) + g_2(B)T_r \tag{4.19}$$

The burnup functions are,

$$d_i(B) = d_{i1}B + d_{i2}B^2 \tag{4.20}$$

where the coefficients d_{ij} are given in Table 3.

$$e_i(B) = \sum_{j=1}^{6} e_{ij}B^j \tag{4.21}$$

The coefficients e_{ij} are given in Table 4.

$$g_i(B) = -\ 0.1B \tag{4.22}$$

and

$$g_2(B) = 0.819B \tag{4.23}$$

Table 3. Values of the Coefficients d_{ij}

i/j	1	2
0	-9311.6452	1518.5841
1	96842.413	-16240.413
2	-406532.35	70474.085
3	881001.92	-158610.81
4	-1039409.2	195039.7
5	634902.55	-124253.06
6	-157378.73	32068.327

4.3.4 The Total Mixed-phase Pressure

The total pressure in atmospheres in the mixed-phase region, P_{mp}, is the sum of the partial pressures obtained previously, multiplied by appropriate fission product retention factors. The void space available for gas expansion, V_v, tends to zero as ρ_f approaches ρ_T. Since some of the terms in the expressions for P_{ng} and P_{fp} are divided by V_v we assumed that the pressure remains constant for $0.99\ \rho_T \leq \rho_f \leq \rho_T$ in order to avoid indefinite values for the calculated pressures. The total pressure, P_{mp}, is given by

Table 4. Values of the Coefficients e_{ij}

i/j	1	2	3	4	5	6
0	-5.8858576	1.6845398	-0.40740527	7.8078216×10^{-2}	$-7.8358225 \times 10^{-3}$	2.9270459×10^{-4}
1	44.35141	-15.462805	3.9272518	-0.68313157	6.2686068×10^{-2}	$-2.2109669 \times 10^{-3}$
2	-86.955664	26.262285	-5.4657535	0.86371707	$-7.8148052 \times 10^{-2}$	2.7837797×10^{-3}
3	54.860744	-13.7233332	1.9368829	-0.22977183	2.00264×10^{-2}	$-7.5000475 \times 10^{-4}$

$$P_{mp} = \begin{cases} P_f(T_r) + \alpha_{ng}P_{ng}(T_r,\rho_f,B) + \alpha_{fp}P_{fp}(T_r,\rho_f,B) \\ \qquad\qquad\qquad\qquad\qquad \text{if } \rho_f < 0.99\ \rho_T \\ P_f(T_r) + \alpha_{ng}P_{ng}(T_r,0.99\ \rho_T,B) \\ \qquad + \alpha_{fp}P_{fp}(T_r,0.99\ \rho_T,B) \\ \qquad\qquad\qquad\qquad\qquad \text{if } 0.99\ \rho_T \le \rho_f \le \rho_T \end{cases} \tag{4.24}$$

where α_{ng} and α_{fp} are the retention factors for the corresponding elements. These factors would have to be computed or estimated at the assumed burnup time of the disassembly. Since P_{fp} includes the pressure due to oxygen species, the value for α_{fp} has to be included even for calculations at zero burnup.

4.4 Coupling of the Phases

Equation (4.15) provides a rational way to couple the different phases and establishes the phase in which the system is in. If the reduced fuel smeared density, ρ_f, is smaller than the reduced theoretical density, ρ_T, at a given temperature, mixed-phase conditions exist for temperatures below the critical temperature. If ρ_f is larger than ρ_T below the critical temperature, or the temperature is above T_c, then the single-phase condition exists. In the single-phase region, the pressure can be assumed to be the sum of the pressure due to UO_2 in the single-phase conditions plus the pressure of the mixed-phase at the reduced departure temperature, T_d, of two-phase conditions. Equation (4.6) can be used to find T_d since by definition

$\rho_{T\ell}(T) = \rho_f$ at $T = T_d$. Therefore,

$$1 + 1.998(1-T_d)^{1/3} + 2.864(1-T_d) = \rho_f. \tag{4.25}$$

An approximate solution to Eq. (4.25) in the range of interest is,

$$T_d = 0.892 + 0.217\,\rho_f - 0.119\,\rho_f^2 + 9.93 \times 10^{-3}\,\rho_f^3 \tag{4.26}$$

The final expression for the total pressure atmosphere, P_T, is,

$$P_T = \begin{cases} P_{mp}(T_r, \rho_f, B, \alpha_{ng}, \alpha_{fp}) \\ \qquad\qquad \text{if } \rho_f < \rho_T \text{ and } T_r \leq 1 \\ P_s(\rho_f, T_r) + P_{mp}(T_d, 0.99\rho_T(T_d), B, \alpha_{ng}, \alpha_{fp}) \\ \qquad\qquad \text{if } \rho_f \geq \rho_T \text{ and } T_r < 1, \text{ or} \\ \qquad\qquad\quad T_r > 1 \text{ for any } \rho_f \end{cases} \tag{4.27}$$

The equation was derived for temperatures between 3000 and 13000 $^{\circ}$K, densities between 3 and 9 gm/cm^3 and burnups between 0 and 10%. A discussion of the uncertainties involved is presented in Chapter 6.

CHAPTER 5

ANALYSIS OF RESULTS

The results discussed in the last chapter will be analyzed here, and compared with previous EOS formulations. Finally, the implications of the EOS proposed herein on fast reactor disassembly calculations are discussed.

5.1 The Single-phase Region

Some selected predictions for the pressure of pure UO_2 in the single-phase region, P_s, are shown and compared with the ANL EOS in Fig. 4. It can be observed that much higher pressures are predicted with the new formulation as compared with the ANL equation. This is due, in part, to the fact that the critical density in the new formulation is lower than the one used in the ANL equation. Therefore, for any given fuel smeared density and temperature, the UO_2 experiences higher compression by the new equation, and higher pressures are predicted. In addition, it can be observed that the curves differ not only in magnitude but in shape too. While the ANL equation predicts a linear dependence on temperature in the entire region, the new equations are linear only above the critical

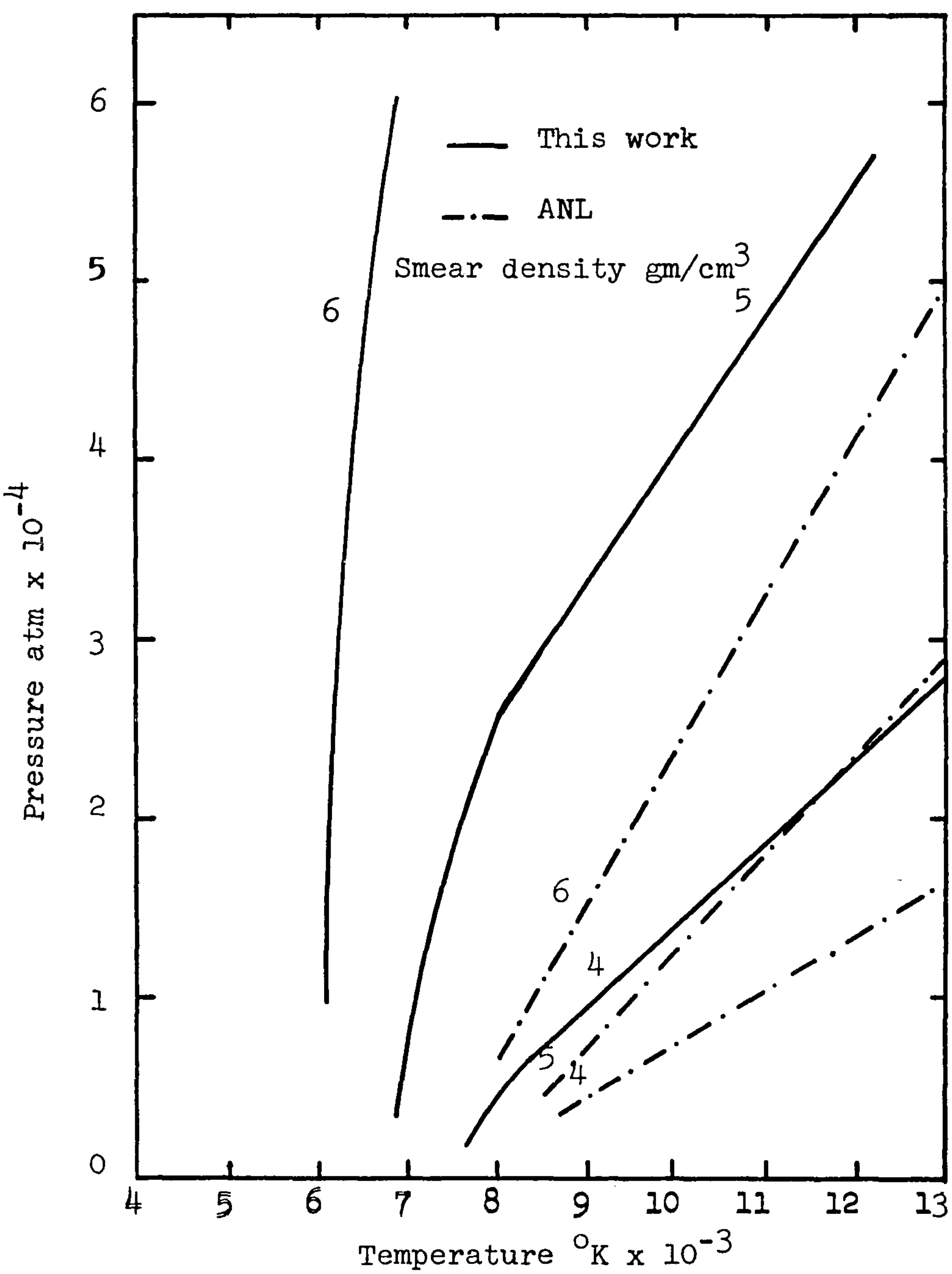

Fig. 4 UO_2 Pressure in the Single-phase Region at Given Fuel Smear Densities temperature. This is due to the fact that the density of saturated liquid as a function of temperature is included explicitly in the new formulation. Since the pressure in the single-phase region according to the new EOS is actually the sum of P_s and the pressure in the mixed-phase at the departure point from two-phase conditions, the difference between the new predictions and the ANL equation are even larger than that shown by Fig. 4.

In the two-phase region, only a small fraction of the fuel is in the vapor form. Since some of the fission products are more volatile than UO_2, they should not be ignored inasmuch as their contribution to the vapor pressure can exceed the fuel species vapor pressure. However, under single-phase conditions, all the fuel molecules present contribute to the pressure buildup. The fission products are only a few percent of the total fuel mass. Therefore, the behavior in the single-phase region is dictated essentially by the UO_2. The effect of the fission products, to a first approximation, is included as a constant term, i.e., the pressure of the mixed phase at the departure temperature from two-phase conditions. The effect of the fission products could be included in a more rigorous form, at least in principle. In the case of mixtures, one can define pseudocritical parameters corresponding to a fictitious single fluid that would have a similar behavior to the mixture (Reed and Gubbins 1973).

The corresponding states principle could be applied to the fictitious fluid in order to predict the properties of the mixture. However, this is not an easy task in our case since the composition of the mixture would depend on many variables.

5.2 The Mixed-phase Region

Selected results in the mixed-phase region are presented in Fig. 5. The relative contributions of the three components to the total pressure for a burnup of 1%, a fuel smeared density of 5 gm/cm^3 and $\alpha_{ng} = \alpha_{fp} = 1$ is given. Below 4000 ^{o}K, the noble gases are the primary contributors to the total pressure. However, as temperature increases, the fission products (without the noble gases) became increasingly important. The contribution of the fuel vapor pressure becomes significant only at high temperatures and low burnups. At high burnups (not shown) the effect of the fuel species on the total vapor pressure is of second order compared to the fission products. Of course, the relative contributions could change depending on the values of α_{ng} and α_{fp}.

The trends shown in Fig. 5 are consistent with those observed by Gabelnick and Chasanov (1972). However, the results differ somewhat since a more realistic expression was introduced for the density of saturated liquid, ρ_{ℓ}, as a function of temperature. The effect of this

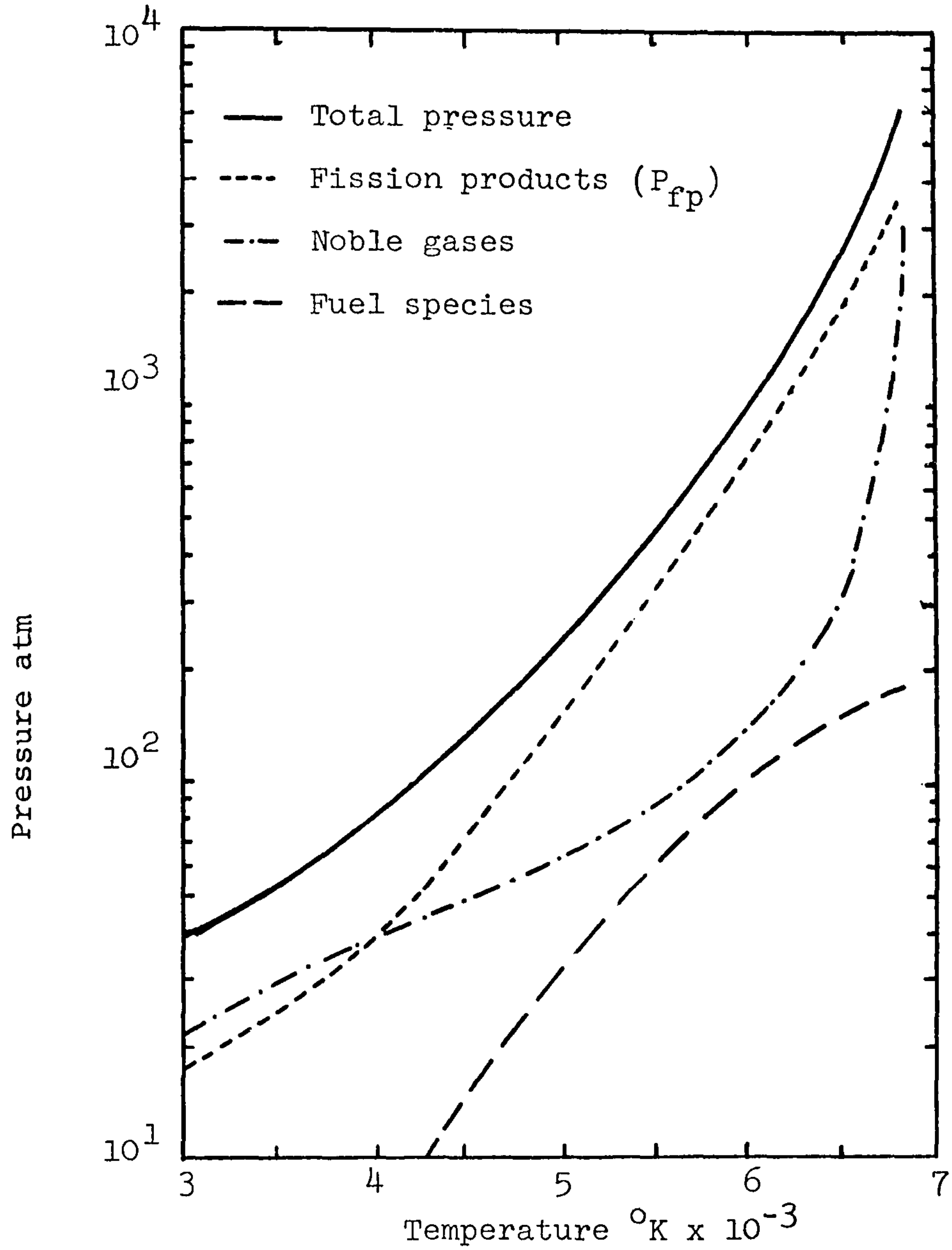

Fig. 5 Relative Contributions of the Total Vapor Pressure

(Burnup = 1%, smear density = 5 gm/cm^3, $\alpha_{ng} = \alpha_{fp} = 1$)

modification is shown in Fig. 6. The total vapor pressure is given as a function of temperature for a fuel smeared density of 6 gm/cm^3, 1% burnup and 100% retention of fission products. The results obtained here are consistent with Gabelnick and Chasanov at low temperatures but differ considerably at higher temperatures. This is due to the fact that ρ_ℓ decreases to a greater extent with temperature than the model they propose, as can be observed in Fig. 3. This reduces the void space available for gas expansion in our calculations, thus yielding higher pressures. The ANL vapor pressure results are also shown but greatly underestimate the pressure since fission products are not considered. The fission product contribution is dramatically demonstrated.

Figure 7 shows the pressure as a function of fuel smeared density for different temperatures at 5% burnup. Again, pressure increases sharply as the fuel density approaches the theoretical density. The sharp rise occurs at a lower density in our calculations for the same reasons discussed in connection with Fig. 6. It should be emphasized that the results obtained here for the two-phase region should be viewed as an approximation because of the assumptions under which the VAPOR code was developed as discussed in Chapter 3.

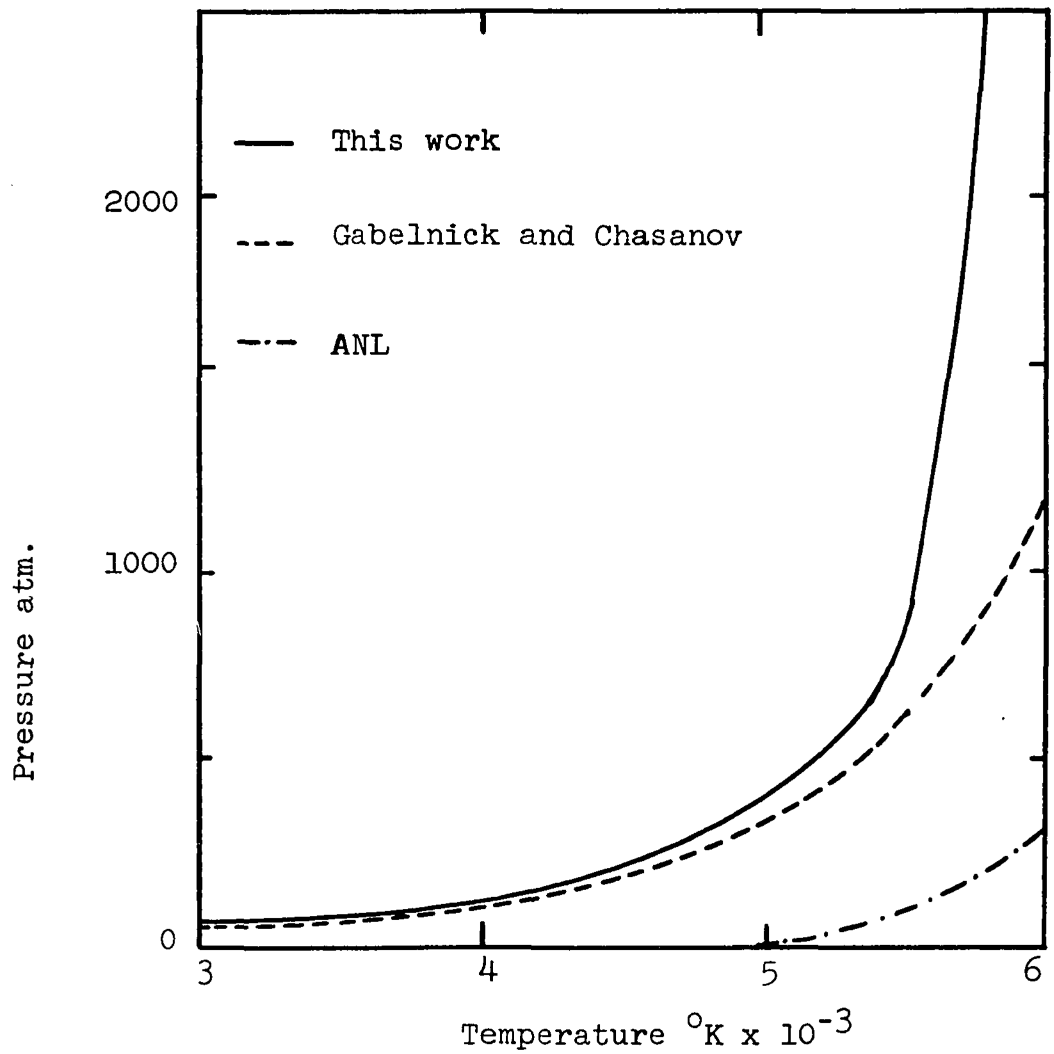

Fig. 6 Vapor Pressure as a Function of Temperature

(Burnup = 1%, smear density = 6 gm/cm^3, $\alpha_{ng} = \alpha_{fp} = 1$)

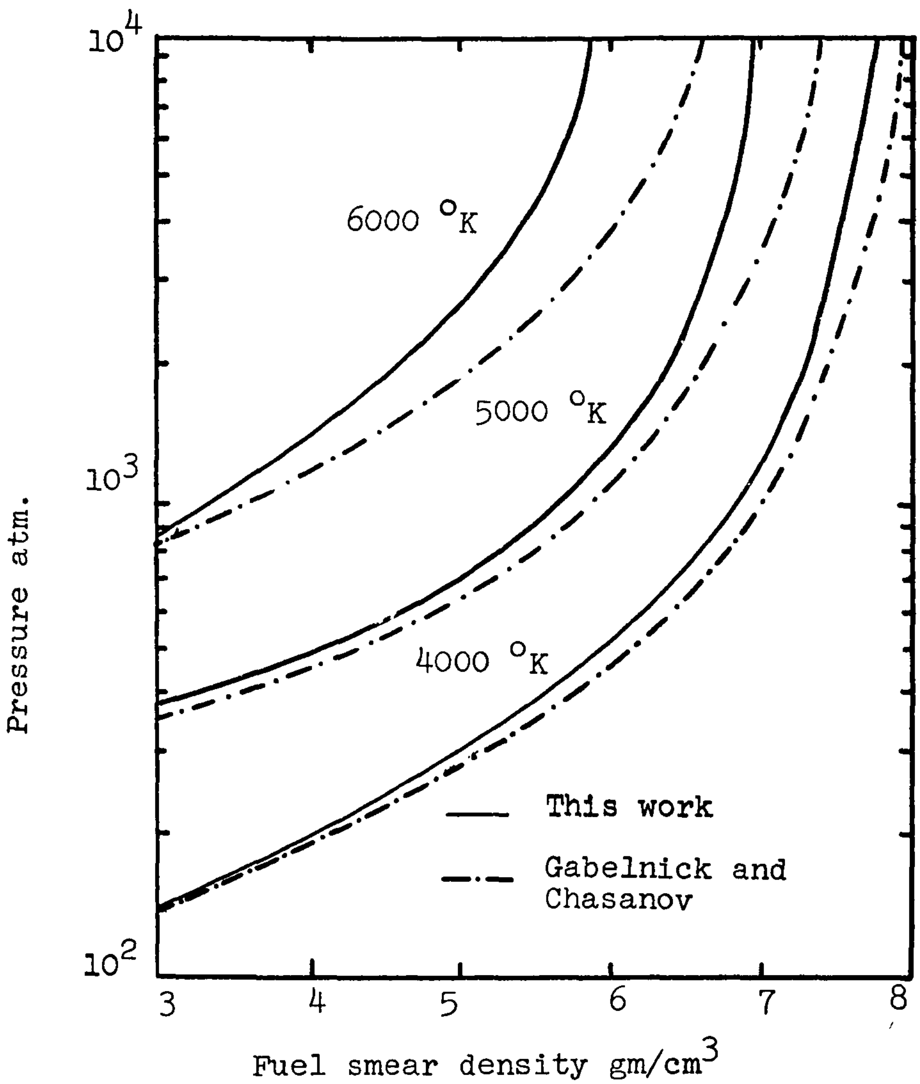

Fig. 7 Density Dependence of the Vapor Pressure at Given Temperatures

(Burnup = 1%, $\alpha_{ng} = \alpha_{fp} = 1$)

5.3 Implications in Disassembly Calculations

The total pressure as a function of temperature is shown in Fig. 8 for a fuel smeared density of 6 gm/cm^3, 1% burnup and assumed values of $\alpha_{ng} = 0.1$ and $\alpha_{fp} = 0.3$. The ANL results for the same fuel smeared density are also shown for comparison. It can be observed that much higher pressures are predicted by our model in all phases even at the low burnup and values of α_{ng} and α_{fp} considered. In addition, transition to single-phase conditions occurs at lower temperatures than the ones predicted by the ANL equation. Since pressure is the driving force for the disassembly of the core, it is expected that the excursion would terminate at an earlier time, if calculations are performed using the new EOS as compared to the ANL EOS. Therefore, the more realistic model presented would appear to reduce the calculated energy released in a hypothetical accident.

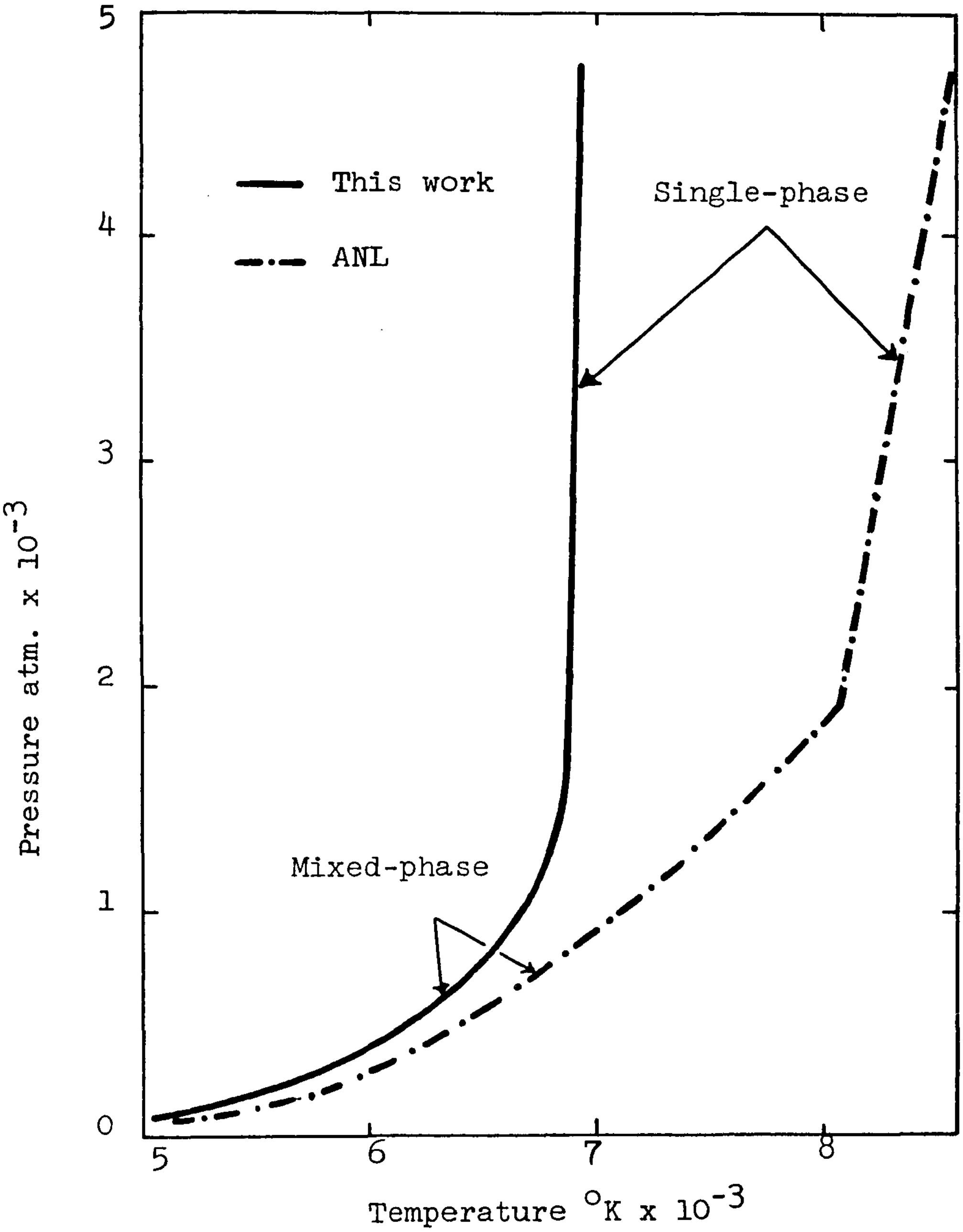

Fig. 8 Equation of State for Mixed Oxide Fuels (smear density = 6 gm/cm^3, burnup = 1%, α_{ng} = 0.1, α_{fp} = 0.3)

CHAPTER 6

DISCUSSION AND CONCLUSIONS

6.1 Summary

A new equation of state for mixed-oxide fast reactor fuels was presented. The equation was derived for application to both the single- and the mixed-phase regions; the effects of fission products and burnup were included. In addition, the equation was presented in a form suitable for easy implementation in nuclear reactor disassembly simulation codes. A rationale for determining whether the single- or mixed-phase conditions exist was also presented.

6.2 Observations and Uncertainties

The EOS in the single-phase region is sensitive to the critical parameters, especially the critical density of UO_2. Consequently the numerical values of the critical parameters and their uncertainty is extremely important to the accuracy of the predictions regardless of suitability of the mathematical model used for the derivation of the EOS. The critical parameters are probably the cause of the most significant uncertainties in the results presented here for the single-phase region. A better experimental and theoretical understanding of intermolecular interactions for UO_2 is required in order to obtain more accurate estimates of the critical parameters and to test the accuracy of the generalized correlations used in the development of the new equation. This knowledge is unfortunately very limited at the present time due to experimental limitations in making the necessary measurements.

In the mixed-phase region, the equation derived was based on the assumption that equilibrium thermodynamics applies to this problem. However, the time scale of events in a disassembly incident may not allow the establishment of true equilibrium conditions. The treatment of this problem by non-equilibrium thermodynamics would be extremely complex especially in view of the very limited information about the thermodynamic behavior at high temperatures and pressures of the molecular species involved. Further experimental information is required both to refine the existing equilibrium thermodynamics calculations and to evaluate the need for non-equilibrium calculations.

The release of fission products from the core is accounted for, to a first approximation, by the introduction of the retention factors α_{ng} and α_{fp}. Possible time delays for gas bubble formation and spatial effects, such as temperature gradients, involved in the calculations of the amount of fission products released from the core could be a potential source of error for the results presented here. The significance of such effects is an unknown factor that merits further consideration.

The scheme proposed to determine the phase-state of the system is believed to be reasonably accurate since the generalized correlations on which it is based involve only the critical temperature. The critical temperature is believed to be the best known of the critical parameters of UO_2. An accurate determination of the transition point from two-phase to single-phase conditions is important for disassembly calculations. The reason is that once single-phase conditions are arrived at, a small increase in temperature induces a large increase in pressure, thus accelerating the disassembly of the reactor.

6.3 Conclusions

Improvements in predictions over currently used EOS were made in both the single- and the mixed-phase regions. In the single-phase region, the model used here is more justified since it is substantiated by more experimental information than previous formulations. In the mixed-phase region, an improved model for the density of molten UO_2 as a function of temperature was introduced. The proposed EOS allows for a more realistic representation of fuel behavior than previous models. The equation can be adapted to a large variety of conditions. Various operating histories can be accounted for by proper selection of burnup and fission product retention factors.

The proposed scheme for the determination of the phase-state of the system is independent of uncertainties in the EOS and could be used with other models as well.

6.4 Recommendations

Implementation of the new equation into a disassembly code such as VENUS-II is a logical continuation of this effort. This would allow one to study the effect of fission products on a disassembly-type accident under a wide variety of conditions. Such a sensitivity-type study would facilitate a better understanding of the accident scenario and would indicate areas that need further development in EOS models. Comparison with previous models would, of course, be called for.

Further studies on the questions of equilibrium vs. non-equilibrium calculations, the significance of time delay for gas bubble formation, and the importance of spatial effects on fission product release are also recommended.

It is the hope of the author that the understanding of reactor safety problems will continue to grow at an accelerated pace, and that we can look with hope towards the peaceful use of the forces stored within the atomic nucleus at minimum risk for mankind.

APPENDIX A

GENERALIZED EOS FOR THE SINGLE-PHASE REGIONS

The EOS developed by Hirschfelder et al. (1958) is presented next:

A.1 Nomenclature

p	reduced pressure
t	reduced temperature
Z_c	critical compressibility
α	slope of the vapor pressure at the critical point (Riedel's parameter)
ρ	reduced density

A.2 Description of the Generalized EOS

The generalized EOS is defined for three regions; namely,

Region I. Gas. All temperatures; $\rho \leq 1$

Region II. High density gas. $t \geq 1$, $\rho \geq 1$

Region III. Liquid. $t \leq 1$, $\rho \geq 1$

The equations for each region are given below:

A.2.1 Region I

$$p_I = t[-w_1(t)\rho^2 - w_2(t)\rho^3 + g(p)], \tag{A.1}$$

where

$$w_1(t) = k_o t + (\beta - k_o)t^{-2} \tag{A.2}$$

$$w_2(t) = 0.5(1-k_o-\alpha + 2\beta) \tag{A.3}$$

$$g(\rho) = \frac{(1+\beta)^3\rho}{\beta(3\beta-1)-(3\beta^2-6\beta-1)\rho + \beta(\beta-3)\rho^2} \tag{A.4}$$

$k_o = 5.5$ and β is related to Z_c by the equation

$$Z_c = \beta(3\beta-1)(1+\beta)^{-3} \tag{A.5}$$

A.2.2 Region II

$$p_{II} = t\{-w_1(t)\rho^2 - w_2(t)\rho^3 + 1 + \beta\rho^2 + S(\rho-1)^5/(\rho + D(\rho,t)\} \tag{A.6}$$

where

$$S = -8.44 + 4.5\beta - 0.363\ \beta^2 \tag{A.7}$$

$$D(\rho,t) = (\rho-1)^3(t-1)\{\rho^{-1}(h_o t^{-1} + h_1) + h_2 t^{-1} + h_3\} \tag{A.8}$$

$$h_o = 88.5 - 3.12\ \beta \tag{A.9}$$

$$h_1 = -44.4 + 5.22\ \beta \tag{A.10}$$

$$h_2 = -47.8 + 4.06\ \beta \tag{A.11}$$

$$h_3 = 23.7 - 3.26\ \beta \tag{A.12}$$

A.2.3 Region III

$$p_{III}(\rho,t) = p_{II}(\rho,t) - P_{II}[\rho_{\ell}(t),t] + p_v(t) \tag{A.13}$$

where $p_v(t)$ and $\rho_{\ell}(t)$ are given by Eqs. (2.5) and (2.7), respectively.

APPENDIX B

MATHEMATICAL DESCRIPTION OF THE VAPOR CODE

The mathematical description of the VAPOR code, reproduced from the paper by Gabelnick and Chasanov, is presented next.

B.1 Nomenclature

a_{ki} = number of metal (non-oxygen) atoms per molecule of condensed species k of fission-product element i.

α_{ki} = activity (mole fraction) of condensed species k of fission-product element i.

b_{ki} = number of oxygen atoms per molecule of condensed species k of fission-product element i.

c_{ji} = number of metal atoms per molecule of vapor species j of fission-product element i.

$\bar{c}_{ki}$ = activity coefficient of species $M_{a_{ki}}O_{b_{ki}}$.

d_{ji} = number of oxygen atoms per molecule of vapor species j of fission-product element i.

fpy_i = fission-product yield of element i (atoms/100 fissions of fuel).

$\Delta\bar{G}(O_2)$ = partial molar free energy of oxygen in fuel matrix.

$\Delta G^{o}_{f,T}(M_{a_{ki}}O_{b_{ji}})$ = free energy of formation of condensed species k of fission-product element i (per gram-atom M).

$\Delta G^{o}{}_{f,T}(M_{c_{ji}}O_{d_{ji}})$ = free energy of formation of vapor species j of fission-product element i (per gram-atom M).

i = index for fission-product elements.

j = index for vapor species.

k = index for condensed species.

K_{ji} = equilibrium constant for reaction

$$\frac{1}{c_{ji}} M_{c_{ji}}O_{d_{ji}}(g) = \frac{d_{ji}}{2c_{ji}} O_2 + M_{c_{li}}$$

$[\equiv M(g)]$.

K_{ki} = equilibrium constant for reaction

$$\frac{1}{a_{ki}} M_{a_{ki}}O_{b_{ki}}(c) = \frac{b_{ki}}{2a_{ki}} O_2 + M_{c_{li}}$$

$[\equiv M(g)]$.

$[M_{c_{ji}}O_{d_{ji}}]$ = vapor pressure (atm) of vapor species $M_{c_{ji}}O_{d_{ji}}$.

nc_i = number of condensed species of fission-product element i.

nv_i = number of vapor species of fission-product element i.

[O] = vapor pressure of monatomic oxygen (atm).

$[O_2]$ = vapor pressure of diatomic oxygen (atm).

p = subscript for properties or variables related to plutonium.

PV_{ji} $\equiv [M_{c_{ji}} O_{d_{ji}}]$.

R = gas constant.

T = temperature (^{o}k).

u = subscript for properties or variables related to uranium species.

XC_{ki} = molar concentration (moles/cm^3) of condensed species k of fission-product element i.

XV_{ji} = molar concentration (moles/cm^3) of vapor species j of fission-product element i.

y_i = concentration (gram atoms/cm^3) of fission-product element i.

y_o = concentration (gram atoms/cm^3) of oxygen.

y_u = concentration (gram atoms/cm^3) of uranium.

YS_{ki} = sum of molar concentrations of all condensed oxide species if $b_{ki} \neq 0$.

= sum of molar concentrations of all condensed non-oxide species if $b_{ki} = 0$.

Z = factor for converting gas-phase pressures to molar concentrations = XV_{ji}/PV_{ji}.

B.2 Mathematical Basis of the VAPOR Code

For each vapor species j of each fission-product (or fuel) element i, the equilibrium constant for the reaction

$$\frac{1}{c_{ji}} M_{c_{ji}} O_{d_{ji}}(g) \rightarrow M(g)(\equiv M_{c_{1i}}) + \frac{d_{ji}}{2c_{ji}} O_2(g) \quad \text{(B.1)}$$

is calculated from the free energies of formation of the appropriate species as

$$K_{ji} \equiv \frac{[M][O_2]^{\frac{d_{ji}}{2c_{ji}}}}{[M_{c_{ji}} O_{d_{ji}}]^{\frac{1}{c_{ji}}}} = \exp\left\{ \frac{\Delta G^o_{f,T}(M_{c_{1i}}) - \Delta G^o_{f,T}(M_{c_{ji}} O_{d_{ji}})}{-RT} \right\} \quad \text{(B.2)}$$

where the free energies, $\Delta G^o_{f,T}$, are per gram-atom M. Similarly, the equilibrium constant for the reaction involving each condensed species,

$$\frac{1}{a_{ki}} M_{a_{ki}} O_{b_{ki}}(c) \rightarrow M(g) \ (\equiv M_{c_{1i}}) + \frac{b_{ki}}{2a_{ki}} O_2(g) \quad \text{(B.3)}$$

is given by

$$K_{ki} = \frac{[M][O_2]^{b_{ki}/2a_{ki}}}{(\alpha_{ki})^{1/a_{ki}}} = \exp\left\{ \frac{\Delta G^o_{f,T}(M_{c_{1i}}) - \Delta G^o_{f,T}(M_{a_{ki}} O_{b_{ki}})}{-RT} \right\} \quad \text{(B.4)}$$

where α_{ki} is the activity (= mole fraction) of species $M_{a_{ki}} O_{b_{ki}}$ (c) in its appropriate condensed phase. Bracketed equations [ ] signify pressures of gaseous species in atmospheres.

The mass constraints for each fission-product element on a gram atom/cm^3 basis, y_i, are related to the fission-product yields (fpy_i)(i.e., atom concentration per 100 fissions), the per cent burnup, and the density of the fuel as follows:

$$y_i = fpy_i \cdot (\text{fuel smear density}) \cdot (\%\ \text{burnup}) \cdot \frac{10^{-4}}{270} \quad (B.5)$$

Also, the mass constraints for uranium, plutonium, and oxygen for fuel of initial composition $(U_y Pu_{1-y})O_{2-z}$ are given by

$$y_u = (\text{fuel smear density}) \cdot (100 - \%\ \text{burnup}) \cdot \frac{10^{-2}}{270} \cdot y \quad (B.6)$$

$$y_p = (\text{fuel smear density}) \cdot (100 - \%\ \text{burnup}) \cdot \frac{10^{-2}}{270} \cdot (1-y) \quad (B.7)$$

$$y_o = (\text{fuel smear density}) \cdot \frac{1}{270} (2-z) \quad (B.8)$$

The factor Z, relating the pressure of a vapor species, PV_{ji} ($\equiv [M_{c_{ji}} O_{d_{ji}}]$), to its molar concentration XV_{ji}, is given by

$$Z = \frac{XV_{ji}}{PV_{ji}} = \frac{\text{void fraction} \times 1\ \text{cm}^3}{RT} = \frac{[1-(\text{fuel smear density})/}{RT}$$

$$\frac{(\text{theoretical fuel density at temperature, T})]}{RT}$$

$$\frac{\times 1\ \text{cm}^3}{RT} \quad (B.9)$$

The activity for a given condensed species, α_{ki}, is given by

$$\alpha_{ki} = \frac{XC_{ki}}{YS_{ki}} \tag{B.10}$$

where XC_{ki} is the molar concentration of the condensed species $M_{a_{ki}}O_{b_{ki}}$ and

$$YS_{ki} = \sum_{i}\sum_{k,\text{oxides}} XC_{ki} \text{ if } b_{ki} \neq 0 \tag{B.11a}$$

or

$$= \sum_{i}\sum_{k,\text{non-oxides}} XC_{ki} \text{ if } b_{ki} = 0 \tag{B.11b}$$

Thus, for each fission-product element, one may write from the mass balance

$$\sum_{j=1}^{nv_i} c_{ji} \cdot XV_{ji} + \sum_{k=1}^{nc_i} a_{ki} \cdot XC_{ki} = y_i \tag{B.12}$$

where nv_i and nc_i are the numbers of vapor and condensed species of fission-product-element i, respectively. Substituting in Eq. (12) for XV_{ji} using Eqs. (B.2) and (B.9) and for XC_{ki} using Eqs. (B.4), (B.10), and (B.11), one may write a polynomial in [M] ($\equiv PV_{1i}$) as follows:

$$\sum_{j=1}^{nv_i} c_{ji} \cdot Z \cdot \left(\frac{[O_2]^{\frac{d_{ji}}{2c_{ji}}}}{K_{ji}} \right)^{c_{ji}} [M]^{c_{ji}} + \sum_{k=1}^{nc_i} a_{ki} \cdot YS_{ki} \cdot \left(\frac{[O_2]^{\frac{b_{ki}}{2a_{ki}}}}{K_{ki}} \right)^{a_{ki}} [M]^{a_{ki}} - y_i = 0 \tag{B.13}$$

The O_2 partial pressure is obtained from the partial molar free energy of O_2 in $(U_yPu_{1-y})O_{2\pm z}$ according to

$$[O_2] = \exp\left\{ \frac{\Delta\bar{G}_{T,(U_yPu_{1-y})O_{2\pm z}}(O_2)}{RT} \right\} \qquad (B.14)$$

and is a strong function of both y and z. Further, one calculates the amount of monatomic oxygen from the free energy of dissociation of O_2:

$$\frac{[O]}{[O_2]^{1/2}} = \exp\left\{ \frac{-\Delta G^o_{f,T}(O)}{RT} \right\} \qquad (B.15)$$

Thus, for a particular value of $[O_2]$, we may solve for $[M](\equiv PV_{li})$, having estimated YS_{ki}. For oxides one initially sets $YS_{ki} = y_u + y_p$ and for the non-oxide $YS_{ki} = y_{Mo} + y_{Pd} + y_{Ru}$, i.e., the yields of the most abundant metals least likely to be oxidized. Having solved for PV_{li} for each fission-product element, one substitutes back into the appropriate equations to obtain revised values of YS_{ki}. These new values are substituted back into Eq. (B.13) which is solved again for each PV_{li}, and the procedure is repeated until the PV_{li}'s do not change. (Three iterations usually suffice.)

A new O/(U + Pu) ratio may then be calculated using the mass constraints y_u, y_p, and y_o as follows:

$$\frac{O}{(U+Pu)} = \frac{y_o - 2\cdot[O_2]\cdot z - [O]\cdot z \sum_i \sum_{j=1}^{nv_i} d_{ji}\cdot XV_{ji} - \sum_{k=1}^{nc_l} b_{ki}\cdot XC_{ki} - \sum_{j=1}^{nu_u} d_{ju}\cdot XV_{ju} - \sum_{j=1}^{nv_p} d_{jp} XV_{jp}}{y_u + y_p - \sum_{j=1}^{nv_u} c_{ju}\cdot XV_{ju} - \sum_{j=1}^{nv_p} c_{jp} XV_{jp}} \qquad (B.16)$$

The value of z in Eq. (B.14) is then changed [O/(U+Pu) = 2 $\pm$ z] and the entire procedure repeated until the O/(U+Pu) ratio calculated from Eq. (B.16) agrees with the trial value to within a specified limit.

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