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Summary

The thermodynamic data of liquid uranium are reviewed, with special attention to the density, for which dynamic measurements were carried out in 1988. The density data are extrapolated to the critical point, assuming that the Law of Rectilinear Diameter holds. This extrapolation provides an alternative to earlier evaluations available in the literature. The critical temperature of the present work is lower than the earlier estimates. The problems and uncertainties are discussed.

In the frame of the present work, density and enthalpy values on the saturation line are evaluated. In spite of still existing uncertainties, these values can be recommended for use in fast reactor accident analysis codes, e.g. SIMMER-III.

Dichte des flüssigem Urans und daraus abgeleitete Zustandsgleichung

Zusammenfassung

Die thermodynamischen Daten des flüssigen Urans werden zusammengestellt und diskutiert, insbesondere die Dichte, für die dynamische Messungen aus dem Jahr 1988 vorliegen. Unter der Annahme, dass das Gesetz des Rectilinear Diameter gilt, werden die Dichtewerte bis zum kritischen Punkt extrapoliert. Damit ist eine Alternative zu früheren Auswertungen gegeben. Die hier errechnete kritische Temperatur ist niedriger als frühere Daten. Die mit der Auswertung verbundenen Probleme und Unsicherheiten werden diskutiert.

Im Rahmen dieser Auswertung werden Daten für Dichte und Enthalpie auf der Sättigungslinie erzeugt. Trotz noch vorhandener Unsicherheiten werden diese Daten für die Verwendung in Codes für die Analyse von schweren Reaktorunfällen empfohlen.

Contents

1 Introduction

In the frame of the CAPRA project, fast reactor designs suitable for plutonium burning are presently under study, in cooperation with the Centre d'Etudes Nucleaire in Cadarache, France. Different fuel types are of interest, and as the project involves also safety investigations, thermodynamic data of these fuels are required. This report deals with thermodynamic data and the equation of state of uranium metal. Besides for the project, the equation of state is also of basic interest.

High-temperature thermodynamic properties of uranium were measured already in the 1960's, during the period when metallic uranium was used as a fuel in both thermal and fast nuclear reactors. Later on, when oxides were the preferred reactor fuel, the main interest of thermodynamicists shifted towards oxides of uranium and plutonium.

In 1976, an IAEA international team, Ref (1) carried out a critical analysis, and summarized their results. They also produced tables of the standard thermodynamic functions, i.e. essentially heat capacity, enthalpy and entropy of the liquid and the gas. The liquid density, however, was not included in their analysis. More recently, their results were updated by the CODATA team, Cox et al, Ref (2), and later on by Cordfunke and Konings, Ref (3). The tables in the three publications show very similar data. This is not surprising because very few additional results pertaining to the standard thermal functions became available in the meantime. However, new measurements of the liquid density were performed, Ref (4,5); they will be discussed later because of their importance, and their bearing on the equation of state.

The properties of the different solid phases are well known. This paper is concerned with the liquid phase (above the melting point, assumed to be at 1408K). A summary and a critical discussion of the available data will be given, and their consistency examined. Furthermore, there are now enough data on the liquid density available to warrant an extrapolation to the critical point by the method of rectilinear diameter. Such an extrapolation will be carried out, and the resulting critical parameters will be compared to earlier extrapolations. In addition, the densities and enthalpies will be calculated.

2 Vapor Pressure

Early vapor pressure measurements suffered from the influence of oxygen contamination, which lead to a partial pressure of UO, and from the tendency of uranium to creep out of the crucible. In addition, data had to be corrected for dissolved crucible material (e.g. tantalum). However, as discussed in the IAEA summary by Oetting et al, Ref (1), later measurements are more reliable. Thus, the vapor pressure curves produced by Ackermann and Rauh, Ref (6) (1980 to 2420K)

$$\log p(atm) = -(25230 \pm 370)/T + (5.71 \pm 0.17) \tag{1}$$

and by Pattoret et al, Ref (7) (1720 to 2340K)

$$\log p(atm) = -(26210 \pm 270)/T + (5.920 \pm 0.135) \tag{2}$$

are compatible with each other, and with data points obtained by DeMaria, and by Storms, see Ref (1). Oetting et al derived an enthalpy of sublimation at 298K of 531.37 kJ/mol from these data.

More recently, Das et al, Ref (8) performed additional vapor pressure measurements, and obtained (2200 to 2900K)

$$\log p(atm) = -(26420 \pm 410)/T + (6.295 \pm 0.164) \tag{3}$$

Including these results in the analysis leads to an enthalpy of sublimation of 533.0 kJ/mol, Ref (2), which is nearly the same as in Ref (1). It is interesting to observe that the three vapor pressure curves differ from their weighted average up to two standard deviations. Thus, they are just about compatible. The three curves are shown in Fig.1.

3 Enthalpy and Entropy of Liquid and Gaseous Uranium

The melting point and the heat of fusion of uranium are well established, see Oetting et al, Ref (1). From this reference, the melting temperature is 1408K, and the heat of fusion 9.142 kJ/mol. The heat capacity in the liquid state was measured by several authors; the most reliable data are those by Stephens, Ref (9), who used levitation calorimetry, and this way avoided errors due to reactions with a container. His value for Cp is 48.66 J/mol/K, and is assumed to be constant. In this paper, the molecular weight is assumed to be 238.0 g/mol.

According to Ref (1) and (3), the standard enthalpy of liquid uranium is

$$H^0 - H^0(298) = 58347 + 48.66(T - 1408) \quad (J/mol) \tag{4}$$

The enthalpy and entropy of uranium monatomic gas were calculated by Oetting et al, Ref (1). The important point is the contribution from electronic excitation, because the uranium atom has a complicated electronic structure, as dicussed e.g. by Rand, Ref (10). The ground state configuration is $(5f)^3(6d)(7s)^2$, and the spectroscopic term is $^5L_6$. Thus, it has an orbital angular momentum L=8, a total spin S=2, and odd parity. L and S can combine to J values between 6 and 10. The ground state has J=6, and the other levels are significantly above it. Therefore, the ground state multiplicity is 2J+1=13, which contributes to the entropy at low temperatures, see the tables in Ref (1). In this reference, the spectroscopic data by Steinhaus (1133 levels) were used. Data up to 6000K are tabulated, but, clearly, the high temperature data must be regarded as provisional. The later evaluations, Ref (2,3), included additional levels in their calculations, based either on measurements or estimates. However, the standard thermal data differ very little from those in Ref (1). The tables show that the heat capacity of the gas (at constant pressure) is very close to the one of the liquid.

This fact has a consequence on the extrapolation of the vapor pressure curve. Usually, curves which are valid over an extended temperature range are represented by a three-term equation of the following type

$$\log p = A - B/T - C\,ln(T) \tag{5}$$

Some authors add a linear term in T, but this does not improve the accuracy sigificantly. In this equation, the logarithmic term is related to the difference in specific heat of liquid and gas. For uranium, this term does not appear because the heat capacities are nearly equal. This means that the two-term equations usually provided by experimenters over a short temperature range can be directly used for extrapolation to higher temperatures.

4 Density of Liquid Uranium

Several measurements of the density of liquid uranium are available. However, they are not included in the critical analysis of thermodynamic data, published by an IAEA team, Ref (1), nor are they mentioned in the later data summaries, Ref (2,3). Therefore, a somewhat detailed discussion will be presented in this report. Besides, the results will be used, in a later Section, to estimate the critical point data, using the Law of Rectilinear Diameter.

First, the static measurements of the liquid density will be discussed. Grosse et al measured, in 1961, in a range of about 500K above the melting point, Ref (11). They obtained

$$\rho = 17904 - 1.0328 * (T - 1408) \quad (kg/m^3) \tag{6}$$

with a standard deviation of $21 kg/m^3$, or 0.116 percent. Later on, Rohr and Wittenberg, Ref (12), measured in a range of about 100K, and found

$$\rho = 17269 - 1.6010 * (T - 1408) \quad (kg/m^3) \tag{7}$$

with a standard deviation of $16 kg/m^3$. The difference between the two results at the melting point is much larger than the combined standard deviations, so there must be a systematic error in at least one of them. Rohr and Wittenberg argue in favor of their data: First, they indicate a volume expansion of 2.2 percent upon melting, which is similar to the behavior of most metals, while Grosse's data would involve a contraction. Besides, there is circumstantial evidence from other experimental results; and, finally, the Archimedian method used by Grosse et al is liable to error due to surface tension forces. Therefore, we take the value of Ref (12) at the melting point as a reference value, as did other workers, see Ref (4).

For the slopes, we use the fact that Rohr and Wittenberg quote measured data points, rather than just a linear fit to their data, to estimate the uncertainty in the slope. Assuming for simplicity that the statistical error is due only to scattering in the density data, and the temperatures are correct, one finds for the slope

$$-1.601 \pm 0.21 \quad (kg/m^3 K) \tag{8}$$

The rather large standard deviation is due to the fact that the temperature range is limited to 100K, and the density change is very small in this interval.

The conclusion now depends on the weight that is attached to the Grosse measurements, which show a much flatter temperature dependence. Either one can ignore them because there seems to be a systematic error in them. On the other hand, one can argue that the error is in the absolute value, and not in the slope. In the second case, assuming a similar uncertainty as for Rohr and Wittenberg, one finds that the two results differ by 1.9σ. Therefore, they are marginally compatible.

More recently, dynamic experiments by the exploding wire technique were performed by Mulford and Sheldon, Ref (4,5), in 1988. The wires which were placed in an argon atmosphere, were transiently heated to high temperatures (up to ca 5300K) by an electric current pulse, on a microsecond time scale. It was observed that they were at constant temperature for about 100 microseconds until they disintegrated. During this period, the temperature was measured by a pyrometer, and the density by snapshot photographs. The authors fitted the data, which show a fairly large scatter, to an analytic equation assuming a constant thermal expansion coefficient, i.e.

$$\frac{dV}{dT} = bV \tag{9}$$

where b was assumed constant. They found $b = 0.99*10^{-4}$ (1/K) in their original paper. Later on the result was modified using more recent data on the emissivity of uranium, Ref (5). The new result is $1.00 * 10^{-4}$. Similar measurements, but not as extensive, were carried out by Gathers et al, Ref (13). Both data are consistent, though the points show a rather large scatter. Besides, they are closer to the static results by Rohr and Wittenberg, than to those of Grosse et al. The data by Mulford and Sheldon, converted to a function of temperature (see Appendix), are shown in Fig.2.

5 Critical Data Reported in the Literature

A model which is frequently used to estimate the critical temperature is the Principle of Corresponding States. If one assumes that the binary interaction potential between two atoms has the same shape for different materials, and differs only by scaling parameters, then it follows that the equation of state, written in dimensionless variables, is the same for these materials. While this principle was used with some success for non-metals, it proved to lead to fairly large errors when applied to metals, Ref (14). Both Grosse et al, Ref (15), and Fortov et al, Ref (14), used a special version of this principle for uranium, and other metals: The molar entropy of vaporization of various liquids should be equal at corresponding temperatures, i.e. at the same reduced temperature (T/T_c). Grosse used mercury, for which the critical temperature is known from experiment, as a reference material to predict critical temperatures for a number of metals. They adjusted at the atmospheric boiling point. Fig.3 shows the vaporization entropy for some materials. There are large differences between the curves of metals and non-metals, but also the two metals, mercury and sodium, for which the critical point is known from experiment, differ significantly. Grosse finds a critical temperature of 12500K for uranium. However, his value for the vaporization enthalpy, which was available at that time (1961), is known now to be too low. With the current data, one obtains 14250K, see Section 7. Using the same method, Fortov et al, Ref (14), reported 11630K. It is not clear which value for the vaporization enthalpy they used.

A different method was used by Young and Alder, Ref (16). They started from a mean-field, hard sphere equation of state of the van der Waals type, and adjusted the parameters to known data at low temperatures. They obtained a critical temperature of 13600K. However, it is known that the van der Waals equation is rather inaccurate.

As a concluding remark, we note that the method by Grosse is valid only if the vaporization entropy curves have a standard shape. It seems that this is fairly well fulfilled for alkali metals, which are in the same group of the periodic system, are all low-boiling, and are one-electron systems. The fact that the gas specific heat is lower than that of the liquid clearly influences the shape of this curve. Uranium, on the other hand, is a refractory metal, and the gas has a rather complex electronic configuration, which means there is a high density of electronic states, leading to a high specific heat. This is probably the reason why the specific heats of liquid and vapor are nearly the same, and so the vaporization entropy curve has a shape which differs from the alkali metals, see Fig.3. Therefore, when using this method, the result depends rather strongly on the reduced temperature where the adjustment is made. Thus, the prediction is inaccurate, but, furthermore, the difference in shape suggests that effects come into play which are not present in most low-boiling metals, thus casting doubt on the validity of the method, notwithstanding the trivial fact that a large extrapolation involves large uncertainties.

6 Critical Data from the Law of Rectilinear Diameter

In view of the problems the Principle of Corresponding States poses, and of the fact that liquid density measurements are now available up to rather high temperatures, it is tempting to apply the Law of Rectilinear Diameter for an alternative assesment of the critical temperature. Both methods are practically independant. If the data used are consistent, then the results of both methods should be compatible, as discussed in Ref (15). The empirical Law of Rectilinear Diameter by Cailletet and Mathias states that the average density between liquid and saturated vapor is a linear function of temperature, and, at the critical point, is equal to the critical density. Well below the critical point, the vapor density is negligible, and then the liquid density is a linear function of temperature. This law was confirmed experimentally for a variety of non-metal liquids, for example for noble gases, simple inorganic compounds, and for hydrocarbons, see Ref (15). With liquid metals, the experimental results are not as abundant. While the law seems to hold adequately for the alkali metals studied in Ref (17), there is evidence for a deviation of about 7 percent for mercury, in the vicinity of the critical point. Though the validity of the law is not strictly established for metals, it is proposed now to apply it to uranium. Generally, application to a refractory metal requires an extrapolation over a large temperature range. However, in the case of uranium, the dynamic density measurements extend to rather high temperatures, so that the extrapolation is not excessive. Then, the accuracy is limited by the experimental uncertainties, and possibly by deviations from the Law of Rectilinear Diameter.

The density measurements by Mulford and Sheldon, Ref (4,5), were adjusted by the authors to an analytic function of the enthalpy, assuming that the volume expansion coefficient is constant. To use these data with the Law of Rectilinear Diameter, an adjustment of the data points to a linear function of temperature was prepared, assuming that the density at the liquidus has the known value $17270 kg/m^3$. This is justified because the vapor density is negligible compared to the liquid density, see Appendix. Fig.2 shows the data points and a linear fit, which is given by

$$\rho(T) = 17270 - (1.4485 \pm 0.0567) * (T - 1408) \tag{10}$$

The rectilinear diameter is half of the liquid density.

In an attempt to carry out the extrapolation to the critical point, it is first observed that straight-forward recipes do not produce reasonable results. E.g., Grosse uses the rule of thumb that the ratio between the density at the boiling point and the critical density is 4.35. Applying this rule with the above density, and assuming the Ackermann vapor pressure curve, one finds that the boiling point is at 4418K, and the critical point at $T_c = 9233K$, and $\rho_c = 2968 kg/m^3$. The corresponding vapor pressure is 96.2Mpa, and then the critical compressibility is 0.100, which is unreasonably low. Besides, the critical temperature is very low compared to earlier estimates. Note that the critical compressibility is defined by the equation

$$Z_c = \frac{p_c V_c}{R T_c} \tag{11}$$

Its standard value for metals is around 0.28, see Ref (14), but values down to 0.20 are still reasonable, whereas 0.100 is much too low. An alternative simple estimate is to assume the standard value for the critical compressibility. Combining with the above density, and the Ackermann vapor pressure curve, one finds $T_c = 10530K$, and $\rho_c = 2028kg/m^3$. In this case, the density is unrealistically low. In view of this situation, it was decided to allow the experimental data (density and vapor pressure) to vary within a reasonable uncertainty range, and to try to define a range for the critical point data, rather than exact numbers.

The density data by Mulford and Sheldon, i.e. the slope $d\rho/dT$, will be varied by 1.6 standard deviations. This defines the 90 percent confidence interval, and a value at the edge of this interval is still consistent with the experimental results. The above estimates indicate that the slope should be somewhat flatter than in the above equation. Thus, the slope assumed is $-1.358kg/m^3K$ instead of $-1.448kg/m^3K$. The static density measurements by Grosse, Ref (11), and by Rohr and Wittenberg, Ref (12), gave $d\rho/dT$ of $-1.033kg/m^3K$ and $-1.601kg/m^3K$, respectively. Clearly the uncertainty is rather large, but the latter value seems to be more reliable. If one decides to include Grosse's measurements in the analysis despite some doubt on their validity, the obvious thing to do is to take a straight average of the three different experimental results. One finds a value of -1.361, which is very close to the modified Mulford and Sheldon value suggested above. This is an additional argument that the value selected is reasonable. Thus, the extrapolation will be carried out using the density

$$\rho(T) = 17270 - 1.358 * (T - 1408) \tag{12}$$

Oetting et al, Ref (1), in their evaluation of the thermal functions, calibrated their data to the vapor pressure curve of Ackermann and Rauh, Ref (6). Thus, the latter curve can be considered as a reference curve. Both the vapor pressure measurements by Pattoret et al, Ref (7), and by Das et al, Ref (8), are consistent with the reference at the temperatures where the measurements were conducted. However, both arrive at a slightly larger slope. The Pattoret curve, though slightly lower at 2000K, leads to higher values when extrapolated to temperatures where the critical point is expected. The Das curve is still a lot higher, and there is indication in the paper Ref (8) that the slope may be too steep. Even if one looks at the weighted average between the three curves, it extrapolates to values above the Pattoret data. In view of this, it was decided to consider the Ackermann data as reference, the Pattoret curve as a plausible variant, and the average curve as an upper limit.

It remains to define the critical compressibility. A standard value for metals, used e.g. by Fortov et al, Ref (14), is 0.28. However, for the alkali metals it is lower, typically around 0.20. Thus, we assume that Z_c is in the range 0.20 to 0.28.

The two density lines in Fig.4 show the rectilinear diameter as a function of temperature, in the range where the critical point is expected. The (lower) nominal line is defined as one half of the density of equation (10), and the line shifted by 1.6σ is half of the density of equation (12). From the above considerations, one expects the critical point to lie on the shifted line. In addition, the ranges of extrapolated critical points compatible with the vapor pressure curves are indicated by short straight lines, which bracket the range of Z_c between 0.20 and 0.28. The two full lines belong to the Ackermann curve, the two broken lines to the Pattoret curve, and the dotted ones to the averaged curve. As a reference value, the point on the Ackermann section with 0.20 is chosen, so that

$$T_c = 10320K \qquad \rho_c = 2584kg/m^3 \tag{13}$$

$$Z_c = 0.20 \qquad p_c = 186.6Mpa \tag{14}$$

Considering the data uncertainties, one can define a reasonable upper limit assuming $Z_c = 0.28$, which leads to a critical temperature of 10790K, and a critical density $2262kg/m^3$. As a lower limit, the point $Z_c = 0.20$ on the average curve is chosen, which gives a critical temperature of 9730K, and density of $2983kg/m^3$.

7 Discussion of the Results

First, the uncertainty range of about 1000K in the predicted critical temperature seems to be rather large. However, it is connected with the uncertainties of the different density measurements, and the fact that they are at best marginally consistent. Besides, there are uncertainties due to the extrapolation (which, however, is rather moderate because data cover a large temperature range), and in the critical compressibility. Thus, the range of 1000K is probably realistic. Note also that extrapolations to the critical point by different methods involve a check on the consistency of different experimental data.

Second, the method of rectilinear diameter predicts significantly lower critical temperatures than the Principle of Corresponding States (PCS), see Ref (14,15). It is, however, believed that the results of this work are more reliable, as will be discussed below.

The present evaluation represents a compromise between different arguments. With the lower limit, the density ratio between the boiling point and the critical point is close to the rule of thumb value 4.35, but the critical temperature is very low. At the upper limit, the critical temperature is much nearer to earlier estimates, but the density ratio exceeds the rule of thumb value by about 35 percent. The reference value is a compromise between these two extremes. In addition, it is clear that there is some judgment involved in the selection of the density curve, which deviates by 1.6σ from the nominal experimental results. Thus, the present evaluation shows that the experimental data are just about marginally consistent. The above arguments can help to recommend the density line that emerges from this work. Note that, in view of the rather large scattering of the Mulford and Sheldon data, and the discrepancy between the static measurements, a selection based on experimental density data alone may be difficult.

Another parameter suitable for comparison of rectilinear diameter data is the dimensionless quantity as a function of reduced temperature

$$\Delta = \frac{2\rho_c T}{T_c(\rho_l + \rho_v)} \tag{15}$$

which was used by Fortov, Ref (14), and by McGonigal, Ref (18). For the alkali metals, Δ at the reduced temperature 0.5 assumes about the value 0.30, see Ref (18). However, for mercury it is higher, about 0.4, whereas for refractory metals it appears to be lower. For uranium, if the critical temperature is 9730K, the value turns out 0.24, and with the reference critical temperature 10320K it is even lower. This seems to confirm the general trend that refractory materials have a low Δ value.

A few comments on the Principle of Corresponding States (PCS) should be made. It was used by Grosse, Ref (15) and by Fortov, Ref (14), to estimate the critical temperature of uranium. First, Grosse uses an old value for the vaporization enthalpy of uranium, so the numbers must be updated. Fig.3 shows the vaporization entropy of mercury, Ref (15), of sodium, Ref (19), and of uranium, Ref (1), assuming that the critical temperature is 10320K. Grosse suggests that the vaporization entropy should be evaluated at the atmospheric boiling point, which is taken as 4418K. From the Ackermann vapor pressure curve, and the data in Ref (1), one deduces a vaporization entropy of 26.5 cal/mol/K at this point. Then, using the curves in Fig.3, one finds a critical temperature of 14250K with mercury as a reference material. This is the updated value. Since Grosse's work, new data on the alkali metals became available, and the critical data of sodium are now well known. Therefore, one can also use sodium as a reference material, which gives 12840K for the critical temperature of uranium. Both estimates differ by about 1400K, which is more than the uncertainty range assessed from the law of rectilinear diameter.

There is another difficulty with these results: If one extrapolates the standard vapor pressure curve by Ackermann and Rauh to the predicted critical temperatures, 12840K and 14250K, one finds 563 Mpa and 881 Mpa, respectively. Combining these values with an estimated critical density of $2968 kg/m^3$, the critical compressibilities become 0.42 and 0.60, respectively. Both values are outside the range where other substances lie, indicating that there is an inconsistency in the procedure. Note that the discrepancy becomes worse with the other vapor pressure measurements. Therefore, although the critical pressures involve a large extrapolation, these results cast doubt on the validity of the PCS method for uranium, as it is discussed here.

Moreover, it is obvious that the boiling points of two liquids are not corresponding states. Thus, Grosse's prescription to apply PCS at the boiling point rests on the silent assumption that the vaporization entropies of the two liquids have the same shape, which indeed they should if the PCS is valid. A glance on Fig.3 shows that this is not the case between uranium and sodium, and neither it is between uranium and mercury. And if the adjustment, with sodium as a reference, is carried out at a lower temperature, the predicted critical temperature may be as low as 11700K.

From a theoretical point of view, the PCS is based on assuming a similarity of the particle interaction in different liquids. With liquid metals, the interaction is complicated by the presence of conduction electrons. They screen the Coulomb field of the ion cores, and thus the ions interact via screened Coulomb potentials. Besides, the electrons form a degenerate Fermi gas, and its properties should be included in the interaction potential. Thus, it is not surprising that the PCS does not work as well with liquid metals as it does with other substances, except for metals in the same group of the periodic system. Fortov et al observe that the PCS does not work well between materials in different groups.

8 Compressibility at the Liquidus

The adiabatic compressibility of liquids is usually obtained from measurements of the velocity of sound. However, no such measurements are available for liquid uranium. What is available are rather detailed measurements of the elastic moduli of alpha uranium by McSkimin and Fisher, Ref (20). Therefore, the best one can do at the present state is to attempt to extrapolate the alpha uranium data to the density of the liquid. Clearly, one would prefer to extrapolate from gamma uranium, but no reliable data for this cubic phase are available. Thus, the number produced in this Section must be regarded as provisional.

Before proceding further, we note that the isothermal compressibility, β_T, can be obtained from the adiabatic β_s by the thermodynamic relation

$$\beta_T = \beta_s + \frac{\alpha^2 TV}{C_p} \qquad (16)$$

where α is the thermal expansion coefficient, V is the molar volume, and C_p the specific heat.

The extrapolation is based on a method suggested by Tallon, Ref (21). He observed that for a number of metals the bulk modulus K (which is the inverse of the isothermal compressibility), if regarded as a function of the specific volume (due to dilatation as the crystal is heated), can be represented by the following equation

$$K = K_0(V/V_0)^{-g} \qquad (17)$$

where K_0 is the bulk modulus at absolute zero.

Furthermore, Tallon found that, for the metals examined, the bulk modulus of the melt very nearly lies on the extrapolated solid curve. Thus, he hypothesized that the above equation holds approximately also through the melt transition.

McSkimin and Fisher used single crystals of the orthorhombic phase, with different orientations, and obtained the adiabatic elastic moduli from measurements of ultrasound velocities. Their data cover the range between -200^0C and about 35^0C. However, the diagonal moduli c_{11}, c_{22}, c_{33}, which are associated with the velocities of longitudinal waves along the crystal axes, were determined up to 300^0C. While the Young's moduli E_{010} and E_{001}

show a normal temperature dependence, that is they decrease with rising temperature, the behavior of the Young's modulus E_{100} is highly anomalous, in that it increases at low temperatures, has a maximum at about -45^0C, and then decreases again, so that the behavior approaches the normal one at higher temperatures.

To carry out the extrapolation, the off-diagonal terms of the c matrix were extrapolated linearly to 300^0C. Then, the bulk modulus was calulated as a function of temperature. McSkimin and Fisher also quote a polynomial fit of the unit cell volume as a function of temperature, so the data could be easily converted to functions of the specific volume. The plot at the upper end is nearly linear, so a fit to the above equation (17) could be obtained; it was found that

$$K = 119.3 * 10^9 (V/V_0)^{-6.5393} \tag{18}$$

where K is in Pascals. These data are well consistent with the plots for eight different metals, as given in Ref (21). Then, inserting the volume ratio $V/V_0 = 1.104$ at the liquidus, one finds the bulk modulus of $62.4 * 10^9 Pa$, and the isothermal compressibility of $16.02*10^{-12}(1/Pa)$ for liquid uranium. These values look reasonable. The measured bulk modulus (up to $V/V_0 = 1.0269$) and the linear extrapolation are shown in Fig.5.

Most of the metals examined by Tallon have cubic structure, only one solid phase, and none of them is a transition metal. Therefore, the applicability of equation (17) to extrapolate from the orthorhombic phase of uranium, with its anomalous behavior, to the liquid, with two more phases in between, may be doubtful. On the other hand, the elastic constants for niobium were measured by Ashkenasi et al, Ref (22), up to the melting point. Niobium, being a transition metal, should be more suitable for comparison with uranium than the metals discussed by Tallon. The measured bulk modulus shows a similar temperature dependence as the one of alpha uranium: Anomalous at low temperatures, and monotonically decreasing at higher temperatures. Thus, these measurements should lend at least some support to the procedure used in this paper.

Note that the purpose of this exercise is to provide a number for the liquid compressibility, albeit provisional, for use in reactor accident analysis codes like SIMMER-III, Ref (24). The number suggested is certainly in the expected magnitude, and can be used until more reliable data become available.

9 Extrapolation of the State Variables to the Critical Temperature

Using the reference critical data obtained from the Law of Rectilinear Diameter, quoted in Section 6, the densities and enthalpies of saturated liquid and vapor will now be extrapolated up to the critical temperature. This can be done making the following assumptions:

- The Law of Rectilinear Diameter holds. This is the basis of the assessment of the critical point, as used in this work, and is an alternative to the Principle of Corresponding States, which does not hold between metals of different groups.
- The vapor pressure is given by the Ackermann and Rauh curve.
- The eqation of state on the vapor side can be described by a modified Redlich-Kwong equation of state (MRK EOS). This equation, which is discussed e.g. in Ref (23), is valid for a wide range of temperature and density, and unlike the original Redlich-Kwong EOS, it can be adjusted to different values of the critical compressibility. It is used e.g. in the fast reactor accident analysis code SIMMER-III, Ref (24), which was developed at PNC in Japan, with contributions from Los Alamos Scientific Laboratories, Forschungszentrum Karlsruhe, and other organizations. As this data evaluation is of interest for SIMMER-III, it is logical to use the MRK EOS also in the present work.

The modified Redlich-Kwong EOS reads

$$p = \frac{RT}{V - b_1} - \frac{a(t)}{V(V + b_2)} \tag{19}$$

where $a(t)$ is the function

$$a(T) = a_c(T/T_c)^{\kappa} \tag{20}$$

and a_c, b_1 and b_2 are determined by the critical compressibility. With these assumptions one arrives at the data on the saturation line in a straightforward manner: Combining the above equation with the vapor pressure equation by Ackermann and Rauh, Ref (6), gives the molar volume (or the density) of the saturated vapor. Then, the liquid density follows from the Law of Rectilinear Diameter.

The enthalpy of the dilute gas (at 1 atm) was calculated from the measured parameters of the electronic excitation levels, and tabulated e.g. in Ref (1). We accept these data, but for easier handling we prefer an analytic fit to them. It is based on a model for the density of electronic levels, as suggested in Ref (25). The level density above a lower energy limit is assumed to be a quadratic function of energy, i.e.

$$D(E) = D_0 + D_1E + D_2E^2 \tag{21}$$

so that the electronic partition function, Q_{el},is

$$Q_{el} = g_0 + \int_{E_l}^{+\infty} D(E)exp(-\frac{E}{RT})dE \tag{22}$$

where g_0 is the degeneracy of the ground state. The thermal functions of the dilute gas can then be calculated in the usual way.

To find the internal energy U (or the enthalpy) of the saturated (compressed) vapor, we observe that the thermodynamic relation

$$\frac{\partial U}{\partial V} = T\frac{\partial p}{\partial T} - p \tag{23}$$

when applied to the MRK EOS leads to

$$U_v(T, \rho_v) = U_g(T) - \frac{(1-\kappa)a(T)}{b_2} \ln(1 + b_2\rho_v) \tag{24}$$

where the subscript g refers to the gas at 1 atm, and v refers to the compressed vapor.

In the next step, the Clausius- Clapeyron equation

$$\frac{dp}{dT} = \frac{Q}{T(V_v - V_l)} \tag{25}$$

gives the heat of vaporization, Q, and then the liquid enthalpy.

To carry out this procedure we now introduce the following dimensionless parameters into the MRK EOS

$$b_{10} = b_1/V_c = 0.073948 \qquad b_{20} = b_2/V_c = 2.073948 \tag{26}$$

$$a_0 = a_c/V_cRT_c = 2.704620 \qquad \kappa = -0.054422 \tag{27}$$

The first three parameters follow from the critical compressibility, $Z_c = 0.20$, the fourth parameter is obtained from the requirement that the derivative dp/dT is continuous at the critical point.

The above equation for the density of electronic states was fitted to give the closest possible approximation to the data tabulated in Ref (1). The fit gave

$$g_0 = 16.5 \qquad D_0 = 2.52044 \tag{28}$$

$$D_1 = -0.334275 \qquad D_2 = 0.101263 \tag{29}$$

where g_0 is somewhat larger than the true physical value, 13. These equations are easier to handle than sums over more than a thousend levels.

One additional remark should be made. The vapor pressure obtained from the thermal data in Ref (1) is close to, but not identical to the Ackermann and Rauh values. To make sure that our data can be used in conjunction with Ref (1), we used these data for the liquid enthalpy and free energy function, in the temperature range where the ideal gas law holds, and thus the MRK EOS is not needed; this is up to 5000K. In this range the liquid specific heat is constant, and equal to 48.66 J/mol/K. Then, only a very small, and acceptable difference with Ref (1) exists because of the use of the electronic level density model in the gas partition function.

The results are shown in Table 1. The data represent an alternative to the results obtained from the Principle of Corresponding States, as published in the literature, Ref (14,15). The present work also provides a fairly straightforward way to determine state variables on the saturation line.

It should be mentioned that the enthalpies of liquid and vapor are consistently normalized to 298K in the solid phase. The heat of sublimation at this temperature, 531.37 kJ/mol, is taken from Ref (1).

10 Conclusions

A new interpretation of existing liquid density measurements was used, in conjunction with the Law of Rectilinear Diameter, LRD, to evaluate the equation of state of uranium up to the critical point. The resulting critical temperatures are significantly lower than earlier evaluations, which are based on the Principle of Corresponding States, PCS. While both methods have their problems and uncertainties, the PCS is known to be particularly liable to errors when applied between metals of different groups of the periodic system. Therefore, at the present state of the art, the LRD seems to give more reliable results.

Furthermore, this work indicates that the different available data (density, vapor pressure, enthalpy, which are either measured, or calculated from measured data) are just about compatible within estimated error limits. To cover uncertainties, an attempt was made to quote a range of critical temperatures, in addition to a reference value. Thus, it is expected that the critical temperature of uranium is between 9730K and 10790K, with a reference value of 10320K. The corresponding reference values of the critical pressure and density are 186.6 Mpa, and $2584 kg/m^3$. The corresponding data at the lower limit are 203.0 Mpa and $2983 kg/m^3$, and at the upper limit, 238.7 Mpa, and $2262 kg/m^3$.

With some additional assumptions, the present method allows to evaluate the state variables, density and enthalpy, along the saturation line. These data can be used in fast reactor accident analysis codes like SIMMER-III.

While this evaluation is thermodynamically consistent, uncertainties are still rather large. This is in part due to error limits in experimental data, but mainly to the necessity to use certain models, whose validity is not fully established, to extrapolate to higher temperatures. This could be improved significantly by extending vapor pressure measurements to higher temperatures, and also by experimental data for the speed of sound in liquid uranium.

11 Appendix: Analytic Fits to the Data by Mulford and Sheldon

The density measurements by Mulford and Sheldon were fitted by the authors to an analytic function, assuming that the volume expansion coefficient, $dV/dT/V$, is constant. That fit cannot be used to extrapolate to the critical point, for two reasons. First, their assumption leads to the density being an exponential function of temperature, while the Law of Rectilinear diameter states that it is a linear function, in the temperature range where the vapor density is negligible. Second, the original temperature values in Ref (4) were corrected in Ref (5) due to new values of the emissivity. However, the data in Ref (5) were already smoothed, and lie on a straight line. Therefore, in a first step, the corrected temperature was evaluated at each original data point. The results, together with the measured enthalpy, brightness temperature, and density ratio are shown in Table 2. The measurements extend to about 5300K. One finds, from the vapor pressure curve, that the vapor density at the highest temperature is about $5 kg/m^3$, which is more than three orders of magnitude lower than the liquid density, and thus is negligible compared to the liquid density. In a second step, the density was fitted to a linear function of temperature, assuming that the liquidus point is known. The result is

$$\rho = 17270 - (1.4485 \pm 0.0567) * (T - 1408) \quad (kg/m^3) \tag{30}$$

see Fig.2. The standard deviation was derived from the scatter of the experimental data. It was found that the data are consistent with the assumption that the Law of Rectilinear Diameter holds.

A further comment concerns the enthalpy versus temperature results. The smooth data of Ref (5) lead to the linear equation

$$H = 50.56 + 0.05020 * (T - 1408) \quad (kJ/mol) \tag{31}$$

Thus, the enthalpy at the liquidus is lower than the standard value quoted in Ref (1,3), which is 58.35 kJ/mol. As the majority of the measurements were carried out at temperatures far above the melting point, these data are not well suited for extrapolation down to the melting point. On the other hand, it is desirable to have a function available that reproduces the correct enthalpy at the liquidus. Therefore, an adjustment was carried out with the assumption that C_p is given by

$$C_p = a + bT + c/T^2 \tag{32}$$

as was suggested in Ref (26). The function obtained is

$$H = 58.35 + 0.03528x + 1.59061 * 10^{-6}(T^2 - 1408^2) + 12.5323(1 - 1408/T) \tag{33}$$

where $x = T - 1408$, and H is in kJ/mol. The standard deviation of the data points from this curve is slightly larger than with a straight line. However, it has the advantage that both enthalpy and specific heat at the liquidus point are correctly represented.

Note, however, that this is an ad hoc adjustment based only on the Mulford and Sheldon data. It cannot be recommended for use outside this context.

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TABLE 1 DATA ON THE LIQUID AND VAPOR SATURATION LINES

TEMP (K)	RHL (KG/M**3)	RHV (KG/M**3)	LIQ.ENTH (J/MOL)	VAP.ENTH (J/MOL)	PRESS (PA)
2000.0	.164660E+05	.297919E-07	.871540E+05	.577691E+06	.107402E-01
2500.0	.157870E+05	.105358E-04	.111484E+06	.597556E+06	.379823E+01
3000.0	.151080E+05	.514237E-03	.135814E+06	.620418E+06	.185386E+03
3500.0	.144290E+05	.824659E-02	.160144E+06	.645408E+06	.297295E+04
4000.0	.137500E+05	.664564E-01	.184474E+06	.671589E+06	.239579E+05
4500.0	.130710E+05	.339233E+00	.208804E+06	.698238E+06	.122296E+06
5000.0	.123920E+05	.125778E+01	.233134E+06	.724900E+06	.453437E+06
5500.0	.117059E+05	.709635E+01	.274118E+06	.749993E+06	.134414E+07
6000.0	.110181E+05	.159213E+02	.306002E+06	.774460E+06	.324128E+07
6500.0	.103233E+05	.317049E+02	.340765E+06	.797340E+06	.682619E+07
7000.0	.961821E+04	.577921E+02	.379054E+06	.818148E+06	.129250E+08
7500.0	.889825E+04	.987507E+02	.421397E+06	.836331E+06	.224759E+08
8000.0	.815670E+04	.161304E+03	.468168E+06	.851229E+06	.364726E+08
8500.0	.738255E+04	.256445E+03	.519659E+06	.861973E+06	.559090E+08
9000.0	.655526E+04	.404742E+03	.576175E+06	.867243E+06	.817304E+08
9500.0	.562775E+04	.653246E+03	.638452E+06	.864527E+06	.114796E+09
10000.0	.443777E+04	.116423E+04	.709899E+06	.846433E+06	.155854E+09
10100.0	.411118E+04	.135502E+04	.726764E+06	.838573E+06	.165081E+09
10200.0	.369315E+04	.163725E+04	.746309E+06	.826808E+06	.174658E+09
10320.0	.258370E+04	.258370E+04	.789920E+06	.789920E+06	.186600E+09

Table 2: Data by Mulford and Sheldon (corrected)

Enth	T(Br)	Temp	V/V0	Rho
172.0	3199.0	3835.0	1.46	13062.
223.0	3834.0	4705.0	1.61	11845.
218.0	3814.0	4677.0	1.49	12799.
189.0	3465.0	4197.0	1.44	13243.
231.0	4082.0	5050.0	1.47	12973.
226.0	4001.0	4938.0	1.51	12629.
193.0	3497.0	4241.0	1.38	13819.
170.0	3022.0	3596.0	1.35	14126.
121.0	2538.0	2955.0	1.28	14898.
154.0	2902.0	3436.0	1.32	14447.
147.0	2933.0	3477.0	1.32	14447.
216.0	4007.0	4946.0	1.72	11087.
246.0	4231.0	5257.0	1.62	11772.
158.0	2991.0	3550.0	1.40	13621.
195.0	3406.0	4117.0	1.41	13525.
119.0	2431.0	2816.0	1.28	14898.

Fig.1 Vapor Pressure above Uranium Metal

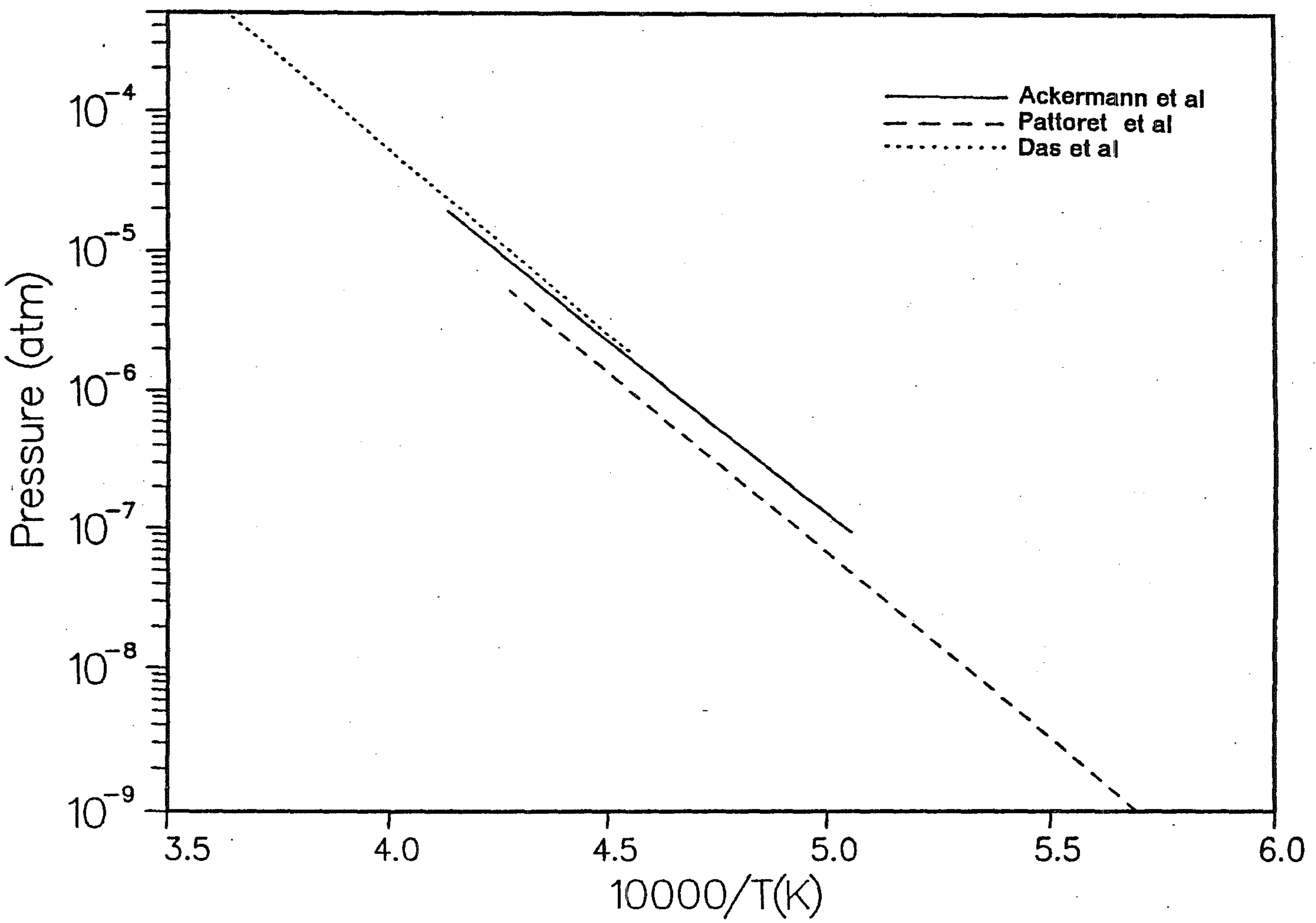

Fig.2 Density of Liquid Uranium

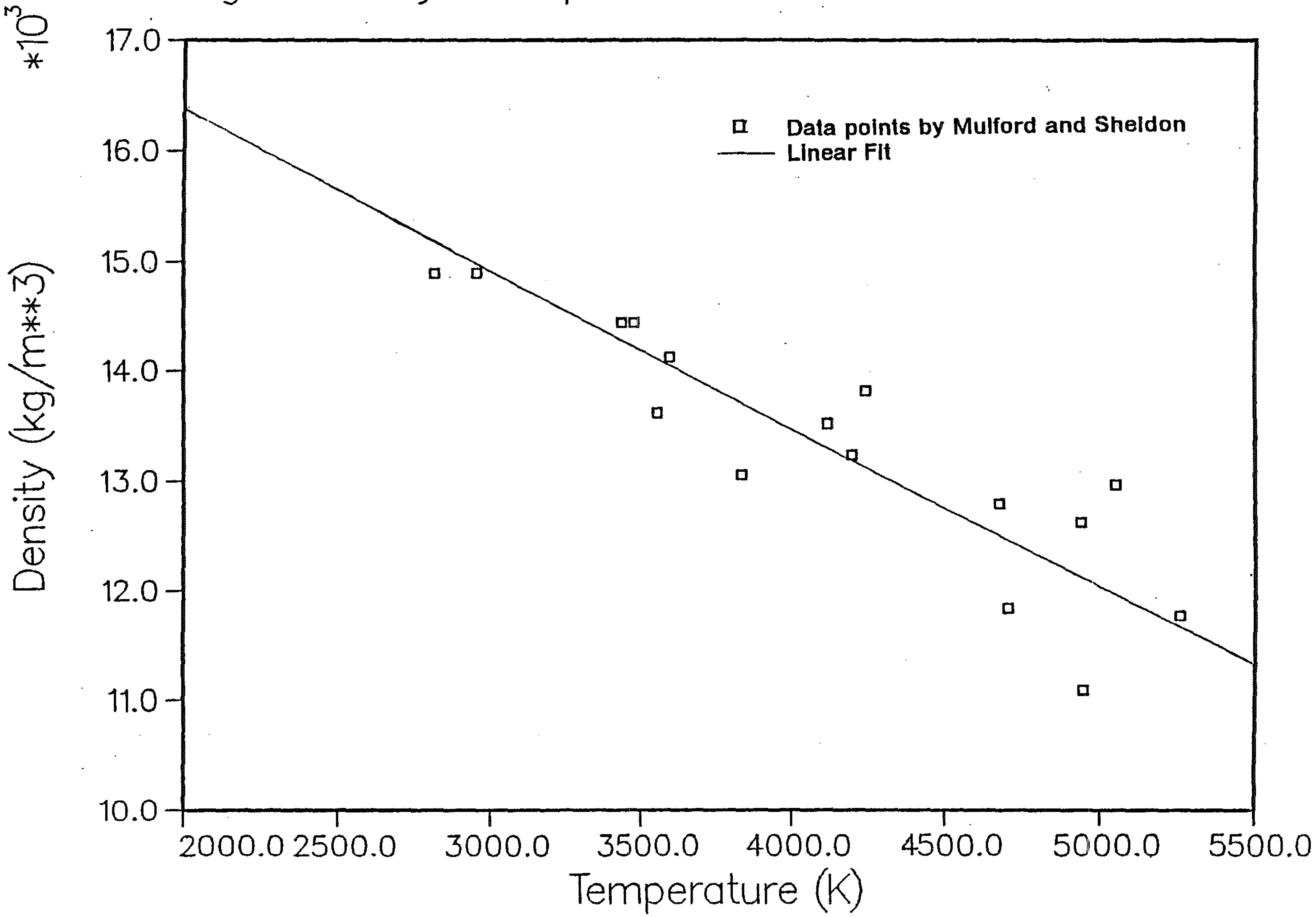

Fig.3 Entropy of Vaporization

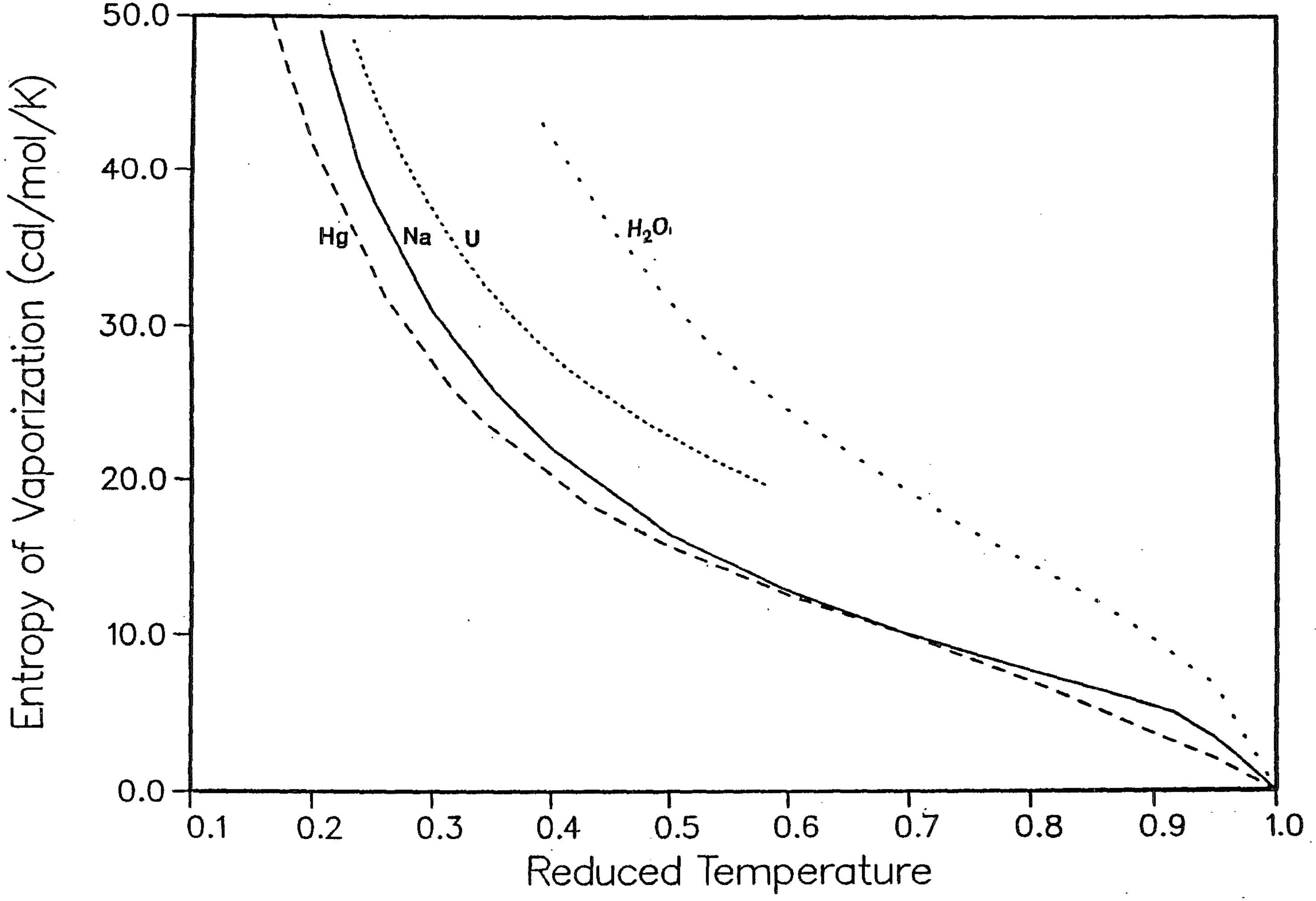

Fig.4 Critical Temperature and Density

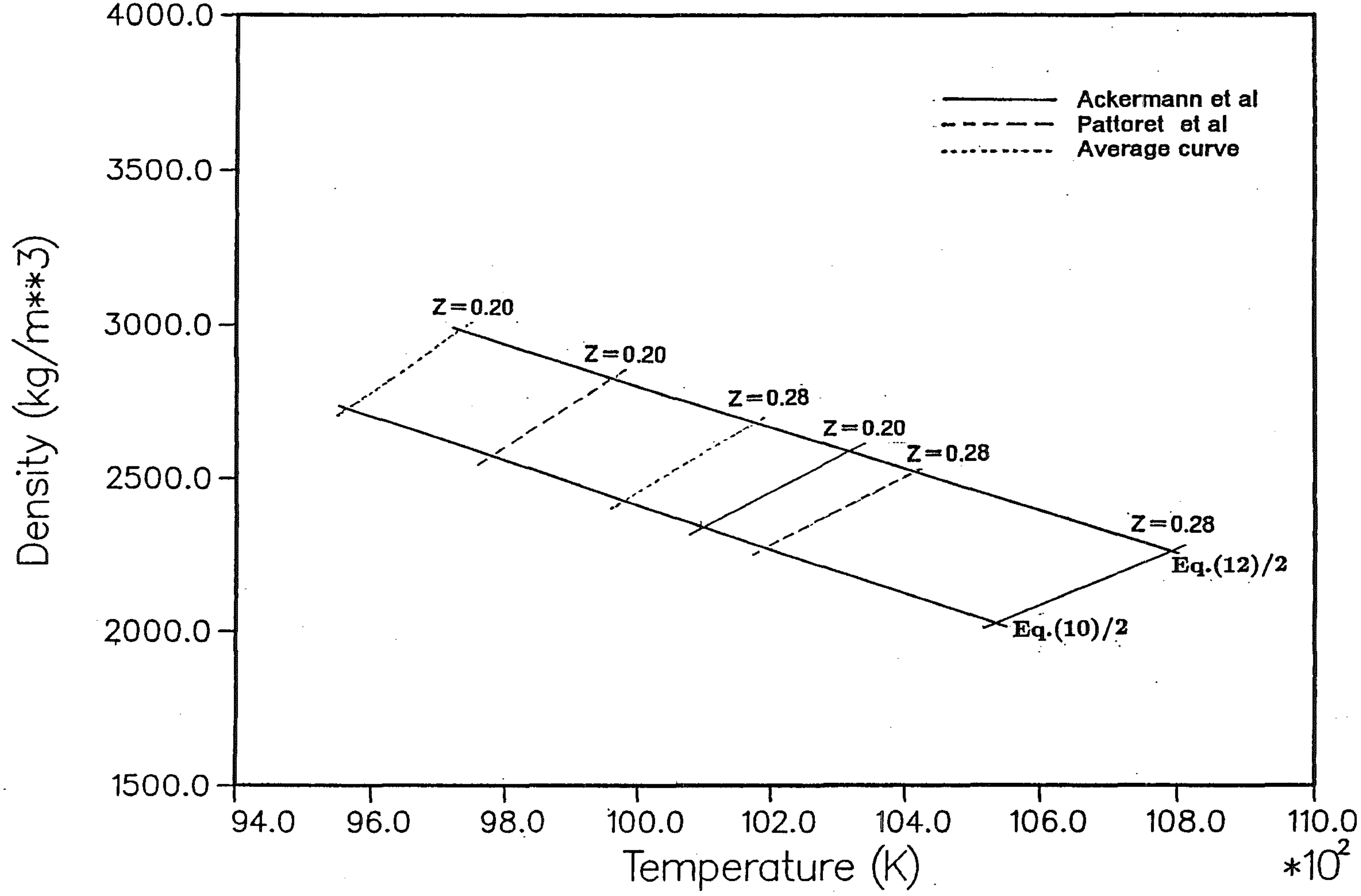

Fig.5 Bulk Modulus of Uranium versus Specific Volume