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VAPOR PRESSURES AND VAPOR COMPOSITIONS IN EQUILIBRIUM WITH HYPOSTOICHIOMETRIC URANIUM-PLUTONIUM DIOXIDE AT HIGH TEMPERATURES

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ABSTRACT

Vapor pressures and vapor compositions in equilibrium with a hypostoichiometric uranium-plutonium dioxide condensed phase $(U_{1-y}Pu_y)O_{2-x}$, as functions of T, x, and y, have been calculated for $0.0 \leq x \leq 0.1$, $0.0 \leq y \leq 0.3$, and for the temperature range $2500 \leq T \leq 6000$ K. The range of compositions and temperatures was limited to the region of interest to reactor safety analysis. Thermodynamic functions for the condensed phase and for each of the gaseous species were combined with an oxygen potential model to obtain partial pressures of O, O_2, Pu, PuO, PuO_2, U, UO, UO_2, and UO_3 as functions of T, x, and y. Thermodynamic functions for the condensed phase were calculated from available information for urania and plutonia using the ideal solution approximation. Thermodynamic functions for the vapor species were calculated previously. Suitable oxygen potential models for the individual urania and plutonia systems, which have been used previously, were combined to provide an oxygen potential model for the mixed-oxide system. The uncertainties in calculated results arising from approximations and incomplete data have been evaluated. One important conclusion of this work is that the vapor composition differs markedly from that of the condensed phase in both oxygen-to-metal and uranium-to-plutonium ratios. A second conclusion is that the total pressures calculated do not differ greatly from those calculated for the urania system. The limitations of this approach, an estimate of uncertainties and some suggestions for additional work are presented.

I. INTRODUCTION

Reactor safety analysis requires thermophysical property data up to very high temperatures which, in some extreme cases, may reach 6000 K. One of the most important properties is the vapor pressure of reactor fuel. We have previously calculated the vapor pressures and vapor compositions in equilibrium with hypostoichiometric uranium dioxide (Green and Leibowitz 1981, 1982) and with hypostoichiometric plutonium dioxide (Green, Fink, and Leibowitz 1982a, 1982b). We present here a similar analysis for the hypostoichiometric uranium-plutonium dioxide system.

Because of its technological importance, considerable attention has been devoted to the vaporization of $(U_{1-y}Pu_y)O_{2-x}$ which has been well summarized in a recent review (Potter and Rand 1981). The procedure we have followed is conceptually identical to that of the urania and plutonia studies and is outlined in Fig. 1. Thermodynamic functions for the gaseous species were obtained previously (Green 1980) from experimental spectroscopic data and estimates of molecular parameters. The functions for the condensed mixed-oxide phase have been calculated from an assessment of the available data on urania and plutonia (Fink 1982) and the approximation of ideal solution behavior. The oxygen potential has been calculated (following Blackburn 1972, 1973, 1974, 1975 and Blackburn and Johnson 1974) from a simultaneous solution to the combined urania and plutonia oxygen potential models, the parameters for which were determined in the previous studies (Green and Leibowitz 1981, 1982 and Green, Fink, and Leibowitz 1982a, 1982b).

In this report we describe: (1) the gas-phase and condensed-phase thermodynamic functions; (2) the oxygen potential model; and (3) the calculated vapor pressures and vapor compositions as functions of temperature and composition. We have limited the composition range studied to that of interest to nuclear reactor technology *viz.* $0.0 \leq x \leq 0.1$ and $0.0 \leq y \leq 0.3$. A more detailed explanation of the methods and results is given elsewhere (Green, Fink, and Leibowitz 1982c).

II. METHODS

A. General

The methods we have used for the mixed oxide system are identical to those followed in the two previous studies of the individual systems (Green and Leibowitz 1981, 1982 and Green, Fink, and Leibowitz 1982a, 1982b). The total pressure, $p(total)$, in equilibrium with a $(U_{1-y}Pu_y)O_{2-x}$ condensed phase is:

$$p(total) = \sum_i p_i = p(O) + p(O_2) + p(Pu) + p(PuO) + p(PuO_2) + p(U) + p(UO) + p(UO_2) + p(UO_3) \quad (1)$$

where only neutral species are considered. [Ions were considered previously (Green and Leibowitz 1981, 1982 and Green, Fink, and Leibowitz 1982a, 1982b) and their contributions were negligible.] The oxygen-to-metal ratio in the gas phase, *R(gas)*, is:

$$R(gas) = \frac{p(\mathrm{O}) + 2p(\mathrm{O_2}) + p(\mathrm{PuO}) + 2p(\mathrm{PuO_2}) + p(\mathrm{UO}) + 2p(\mathrm{UO_2}) + 3p(\mathrm{UO_3})}{p(\mathrm{Pu}) + p(\mathrm{PuO}) + p(\mathrm{PuO_2}) + p(\mathrm{U}) + p(\mathrm{UO}) + p(\mathrm{UO_2}) + p(\mathrm{UO_3})} \tag{2}$$

In the mixed oxide system there is also the possibility of plutonium or uranium enrichment of the vapor relative to the condensed phase. For the condensed phase of composition $(\mathrm{U}_{1-y}\mathrm{Pu}_y)\mathrm{O}_{2-x}$, we define

$$y(gas) = \frac{p(\mathrm{Pu}) + p(\mathrm{PuO}) + p(\mathrm{PuO_2})}{p(\mathrm{Pu}) + p(\mathrm{PuO}) + p(\mathrm{PuO_2}) + p(\mathrm{U}) + p(\mathrm{UO}) + p(\mathrm{UO_2}) + p(\mathrm{UO_3})} \tag{3}$$

to measure the overall metal composition of the vapor phase. Thus, for $y(gas) < y$, the vapor is uranium rich.

We shall treat the mixed oxide condensed phase here as an ideal solution of y moles of PuO_{2-x} and $1 - y$ moles of UO_{2-x}. Alternatives to this treatment are discussed in section IV.A.

The set of partial pressures given by Eq. (1) must satisfy equilibria among themselves and with the condensed phase. There are a number of possible choices of independent equilibria, and we have chosen the following set as a convenient one:

$$\mathrm{O_2}(g) \rightleftarrows 2\mathrm{O}(g) \tag{4}$$

$$\frac{x}{2}\mathrm{O_2}(g) + \mathrm{UO}_{2-x}(c) \rightleftarrows \mathrm{UO_2}(g) \tag{5}$$

$$\frac{x}{2}\mathrm{O_2}(g) + \mathrm{PuO}_{2-x}(c) \rightleftarrows \mathrm{PuO_2}(g) \tag{6}$$

$$\mathrm{UO_2}(g) \rightleftarrows \mathrm{UO}(g) + \frac{1}{2}\mathrm{O_2}(g) \tag{7}$$

$$\mathrm{PuO_2}(g) \rightleftarrows \mathrm{PuO}(g) + \frac{1}{2}\mathrm{O_2}(g) \tag{8}$$

$$\mathrm{UO_2}(g) \rightleftarrows \mathrm{U}(g) + \mathrm{O_2}(g) \tag{9}$$

$$\mathrm{PuO_2}(g) \rightleftarrows \mathrm{Pu}(g) + \mathrm{O_2}(g) \tag{10}$$

$$\mathrm{UO_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \rightleftarrows \mathrm{UO_3}(g) \tag{11}$$

where c represents the condensed phase (solid or liquid) and g represents the gas phase.

The equilibrium constant for Eq. (5) is

$$K = \frac{\mathrm{p(UO_2)}}{\mathrm{a(UO_{2-x})\,p(O_2)}^{x/2}} \tag{12}$$

where the activity of UO_{2-x}, $a(UO_{2-x})$, may be taken as $1 - y$ for the ideal mixed oxide. Similarly for the equilibrium of Eq. (6) we have for the activity of PuO_{2-x}, $a(PuO_{2-x}) = y$.

If we know the oxygen pressure, $p(O_2)$, from the oxygen potential (Section II.C.), the required partial pressures may be obtained from Eqs. (4)-(11) by using the following relationships:

$$\ln p(O) = \frac{1}{2}\ln p(O_2) - \Delta G_f^0(O)/RT \tag{13}$$

$$\ln p(UO_2) = \frac{x}{2}\ln p(O_2) + [\Delta G_f^0(UO_{2-x}, c) - \Delta G_f^0(UO_2, g)]/RT + \ln(1-y) \tag{14}$$

$$\ln p(PuO_2) = \frac{x}{2}\ln p(O_2) + [\Delta G_f^0(PuO_{2-x}, c) - \Delta G_f^0(PuO_2, g)]/RT + \ln(y) \tag{15}$$

$$\ln p(UO) = [\Delta G_f^0(UO_2, g) - \Delta G_f^0(UO, g)]/RT - \frac{1}{2}\ln p(O_2) + \ln p(UO_2) \tag{16}$$

$$\ln p(PuO) = [\Delta G_f^0(PuO_2, g) - \Delta G_f^0(PuO, g)]/RT - \frac{1}{2}\ln p(O_2) + \ln p(PuO_2) \tag{17}$$

$$\ln p(U) = [\Delta G_f^0(UO_2, g) - \Delta G_f^0(U, g)]/RT - \ln p(O_2) + \ln p(UO_2) \tag{18}$$

$$\ln p(Pu) = [\Delta G_f^0(PuO_2, g) - \Delta G_f^0(Pu, g)]/RT - \ln p(O_2) + \ln p(PuO_2) \tag{19}$$

$$\ln p(UO_3) = [\Delta G_f^0(UO_2, g) - \Delta G_f^0(UO_3, g)]/RT + \frac{1}{2}\ln p(O_2) + \ln p(UO_2) \tag{20}$$

All thermodynamic data required to apply Eqs (13)-(20) are available from the individual systems (Green and Leibowitz 1981, 1982 and Green, Fink, and Leibowitz 1982a, 1982b).

B. Thermodynamic Functions

Tabulated data were used in a least-squares fitting procedure to derive an analytical equation for ΔG_f^0 of each of the vapor species as a function of temperature. The coefficients of the equations for ΔG_f^0 of the gaseous species are given in Table 1. Also included in Table 1 are the coefficients for the equation for $\Delta G_f^0(UO_2, c)$ and $\Delta G_f^0(PuO_2, c)$. The methods and data used to obtain these values have been described previously (Green and Leibowitz 1981, 1982 and Green, Fink, and Leibowitz 1982a, 1982b).

C. Oxygen Potentials

Considerable attention has been devoted to the temperature and composition dependence of the oxygen potential, $\Delta\overline{G}^0(O_2)$, for solid $(U_{1-y}Pu_y)O_{2-x}$ (Potter and Rand 1981, Blackburn 1972, 1973, 1974, 1975 and Blackburn and Johnson 1974). We have chosen the model devised by Blackburn, which is essentially a combination of the Blackburn models we also used for UO_{2-x} (Green and Leibowitz 1981, 1982) and

PuO_{2-x} (Green, Fink, and Leibowitz 1982a, 1982b). This model agrees well with the available experimental data and has a reasonable physical basis which allowed extention into the liquid region. In the following section we outline this model for $(U_{1-y}Pu_y)O_{2-x}$ and discuss the basis for its extrapolation.

We consider the following equilibria to exist in the condensed material:

$$2U^{4+} \rightleftarrows U^{2+} + U^{6+} \tag{21}$$

$$2U^{2+} + O_2(g) \rightleftarrows 2U^{4+} + 2O^{2-} \tag{22}$$

$$4Pu^{4+} + 2O^{2-} \rightleftarrows 4Pu^{3+} + O_2(g) \tag{23}$$

with the respective equilibrium constants; K_1, K_2, and K_3. We have previously demonstrated (Green, Fink, and Leibowitz 1982a 1982b) that the effect of Pu^{2+}, which was included by Blackburn (1972, 1973, 1974, 1974 and Blackburn and Johnson 1974), is insignificant in the region of our concern (small values of x), and we shall not consider it further. In addition to these equilibrium constants, we have for $(U_{1-y}Pu_y)O_{2-x}$, equations for conservation of uranium, plutonium, and charge.

To evaluate these constants, we assume that $\ln K_j = A_j + B_j/T$ where the subscript $j(= 1, 2, 3)$ refers to the equilibria given by Eqs. (21)-(23), respectively; T is the absolute temperature, and A_j and B_j are constants. Values for A_j and B_j for the solid phase were found previously by Blackburn (1972, 1973, 1974). Corresponding values for the liquid phase were found from estimates of entropies and enthalpies of fusion. These values for A_j and B_j are given in Table 2 along with corresponding values for the liquid (A_j^{ℓ} and B_j^{ℓ}). We now have a set of six equations (the three equilibrium constant equations and the three conservation equations) with the unknowns: $p(O_2)$, $[U^{6+}]$, $[U^{4+}]$, $[U^{2+}]$, $[Pu^{4+}]$, $[Pu^{2+}]$, and $[O^{2-}]$. We take $[O^{2-}] = 2 - x$ and solve the set of equations simultaneously to calculate $p(O_2)$ for any x, y, and T. Details on this method are given elsewhere (Green, Fink, and Leibowitz 1982c).

D. Phase Boundaries

In the previous calculations for the separate urania and the plutonia systems, the phase boundaries affected results in two different ways: (1) to provide a means of deriving the values of the oxygen potential model parameters for the liquid phase from those of the solid and (2) to decide which parameters were appropriate for calculation of the oxygen potentials. For the mixed oxide, the values of the model parameters are identical with those used previously and the phase boundaries are of importance only in determining which model parameters (solid or liquid) are to be used. Errors in the phase boundaries selected will cause errors only in the immediate region of the solidus or liquidus (to the extent that the wrong parameters were selected) but will cause no errors away from the region of melting. Because of the absence of reliable data on the phase boundaries for the range of x and y being considered here we have chosen a line to describe the y dependence of the melting region with no two phase region being considered. We have chosen the curve given for the liquidus of the mixed oxide system by Aitken and Evans (1968) corrected for more recent values of the melting points of UO_2 (3120 K) and PuO_2 (2701 K). In addition, we have assumed no dependence of the phase boundary on x. While these choices are obviously approximations, the effect on calculated oxygen potentials will be small and will be confined to the region between 3000 and 3100 K. If reliable data on the phase boundaries were to become available, this approximation could be improved.

III. RESULTS

The partial pressures of O, O_2, U, UO, UO_2, UO_3, Pu, PuO, and PuO_2 in equilibrium with the condensed phase $(U_{1-y}Pu_y)O_{2-x}$ were calculated as functions of temperature ($2500 \leq T \leq 6000$ K), x ($0 \leq x \leq 0.1$), and y ($0 \leq y \leq 0.3$). From these partial pressures, the total pressure in equilibrium with $(U_{1-y}Pu_y)O_{2-x}$ was determined by Eqs. (1) and (13)-(20).

The presence of U^{6+} in the oxygen-potential model for the mixed oxide limits the pressure of O_2 so that the calculated total pressures at high temperature are similar to those calculated for the U/O system (Green and Leibowitz 1981 1982) and are much lower than those calculated for the Pu/O system (Green, Fink, and Leibowitz 1982a 1982b). Figure 2 shows the effect of the U^{6+} state by comparing the total pressure as a function of inverse temperature for $UO_{1.96}$, $Pu_{1.96}$, and $(U_{0.8}Pu_{0.2})O_{1.96}$. It is clear from this comparison that the presence of U^{6+} has a major impact on the calculated pressures. Indeed the mixed oxide and the urania pressures are quite similar.

The vapor composition in equilibrium with a $(U_{0.8}Pu_{0.2})O_{1.98}$ condensed phase, a typical composition for a reactor fuel, is shown in Fig. 3. Below about 4200 K, UO_3 and UO_2 are the most important vapor species, with UO_2 being the dominant species below about 2550 K. Above 4700 K, the vapor is largely O and O_2. Note that the plutonium-containing vapor species are never dominant for this composition in the temperature range considered. Examination of other compositions indicates that this domination of the uranium-bearing species is general. At O/M = 1.90, UO, UO_3, and O are the dominant species. As was shown previously for the Pu/O system (Green, Fink, and Leibowitz 1982a, Tables 9, 10, and 11), the partial pressures of metal-bearing species are not very different in the U/O and Pu/O systems whereas, the partial pressures of O_2 are very different. The behavior of the metal-bearing species in the mixed-oxide system is therefore completely consistent with previous results for the individual systems.

The comparison of *y(gas)*, Eq. (3), with *y* for the condensed phase in Fig. 4 indicates that the vapor is uranium rich relative to the condensed phase except at low temperature and low O/M. This result was anticipated from the results of the individual systems.

The vapor in equilibrium with $(U_{1-y}Pu_y)O_{2-x}$ is very oxygen rich at high temperature, *i.e.* $R(gas) > 2$. Figure 5 gives the oxygen-to-metal ratio (O/M) of the gas phase, *R(gas)* as defined in Eq. (2), as a function of O/M of the condensed phase. The oxygen-rich equilibrium vapor phase is comparable to that for the U/O system (Green and Leibowitz 1981, 1982) and is less like that of the Pu/O system (Green, Fink, and Leibowitz 1982).

The total pressure is relatively insensitive to variation with either *x* or *y* in the condensed phase. Variation of total pressure with *x* is shown in Fig. 6. Note that the pressures are closer as the temperature increases. Figure 7 shows variation in total pressure with *y*. Here also, the variation in total pressure with *y* is greater at lower temperatures. In fact, the total pressure in equilibrium with $UO_{2.00}$ is very nearly equal to the total pressure in equilibrium with $(U_{0.8}Pu_{0.2})O_{1.98}$. Thus, in reactor safety experiments that are solely assessing the effect of pressure, UO_2 would serve as a good substitute for $(U_{0.8}Pu_{0.2})O_{1.98}$ for the fuel in the experiment. This approximation to the total pressure of $(U_{0.8}Pu_{0.2})O_{1.98}$ would not be valid for thermophysical properties that depend upon vapor composition.

Comparisons have been made of the total pressures calculated by this procedure with the total pressures calculated by Bober, Breitung, and Karow (1978) and with the experimental measurements by Ohse, Berrie, Brumme, and Kinsman (1975). Figure 8 compares results for the composition $(U_{0.8}Pu_{0.2})O_{1.95}$. Agreement of our results with the calculations of Bober, Breitung, and Karow is good for the composition shown in Fig. 8 and for others that were calculated. In all cases, total vapor pressures of the experiments by Ohse, Berrie, Brumme, and Kinsman (1975) are significantly higher than these calculations. This result is consistent with the previous results for the U/O system for which the total pressures in equilibrium with UO_2 measured by Ohse, Berrie, Bogensberger, and Fischer, (1975) are significantly higher than those calculated with this method (Green and Leibowitz 1981 1982). Note, however, that measurements of total pressure in equilibrium with UO_2 by Tsai (1981) using a laser pulse technique are significantly lower than the values measured by Ohse, Berrie, Bogensberger, and Fischer (1975) and the values calculated by this method (Green and Leibowitz 1981, 1982) fall between these two experimental results.

IV. DISCUSSION AND CONCLUSIONS

A. Uncertainties and Limitations

The uncertainties in application of this method of determination of the vapor pressures in equilibrium with $(U_{1-y}Pu_y)O_{2-x}$ fall into two areas. First, uncertainties arise that are related to the use of an ideal solution model for the mixed oxide condensed phase. Secondly, uncertainities arise that exist in the calculations of the vapor in equilibrium with UO_{2-x} and with PuO_{2-x}; these have been discussed previously (Green and Leibowitz 1981, 1982 and Green, Fink, and Leibowitz 1982a, 1982b).

An ideal solution model has been chosen to represent the condensed phase because the lack of experimental data for the range of temperature and composition of interest precludes alternatives. Using an ideal solution approximation, there are several ways to treat the mixed oxide, including:

$$(U_{1-y}Pu_y)O_{2-x} = (1-y)UO_{2-x} + yPuO_{2-x} \tag{24}$$

$$(U_{1-y}Pu_y)O_{2-x} = (1-y)UO_2 + yPuO_{2-z} \tag{25}$$

$$(U_{1-y}Pu_y)O_{2-x} = (1-y)UO_{2-z} + yPuO_2 \tag{26}$$

Only the approximation given in Eq.(24) is consistent with the use of the Blackburn oxygen potential model. However, the other approximations have been used; for example the method given by Eq. (25) has been used in the solid solution model of Rand and Markin (1967). It is not clear that one method of representation of an ideal solution is preferable. Because we are limited in our choice of oxygen potential models and because only one method of representation of an ideal solution is compatible with our choice of oxygen potential, it is impossible for us to assess accurately the uncertainties that arise from the choice of Eq. (24) to represent the ideal solution.

The uncertainties generated by the assumption of an ideal solid solution are most likely far greater than those resulting from choice of a particular ideal solution model. Analysis of the available enthalpy data on solid $(U_{1-y}Pu_y)O_{2-x}$ (Fink 1982) indicate that the ideal solution approximation is inadequate for the enthalpy. Mole averages of the enthalpy of PuO_2 and UO_2 consistently underestimate the enthalpy relative to 298.15 K of $(Pu_{0.2}U_{0.8})O_2$ and of $(Pu_{0.25}U_{0.75})O_2$ by about 10% .

While we cannot evaluate the effect of the ideal solution model on the vapor pressure, we can compare the error in the use of an ideal solution model for the heat capacity (10 %) with other uncertainties in the heat capacity whose effects on pressure have been examined previously. These uncertainties include: (1) extrapolation of the condensed phase functions for PuO_{2-x} from the solid to the liquid, (2) failure to include a possible solid-solid phase transition in PuO_{2-x}, (3) extrapolation of the condensed phase functions for UO_{2-x} in the liquid region, and (4) use of a constant heat capacity for the entire liquid range for both PuO_{2-x} and UO_{2-x} (Green, Fink, and Leibowitz 1982). The gas phase thermodynamic functions are well established and have the smallest uncertainties in the calculation. These uncertainties have been discussed previously (Green 1980 and Green, Fink, and Leibowitz 1982b).

The phase diagram that has been chosen for these calculations consists of a single line rather than a surface. The errors introduced by this simplification are significant only for a few points of the calculation that fall into this region, and the phase diagram has been used only to determine which set of equilibrium constants (liquid or solid) are to be used. For the mixed oxide, errors of a factor of two to three in the total pressure (for T near 3100 K only) will be introduced by incorrect phase assignments.

Uncertainties related to the oxygen-potential model include uncertainties due to the neglect of Pu^{6+} and Pu^{2+} as well as the method of determining the entropy of fusion for PuO_{2-x}. Uncertainties in the last two are the same as for the Pu/O system (Green, Fink, and Leibowitz 1982a, 1982b). The neglect of Pu^{6+} is not as important in these calculations as it was in the PuO_{2-x} calculations (Green, Fink, and Leibowitz 1982a, 1982b) because the presence of a higher oxidation state in UO_{2-x} limits the oxygen pressure of the mixed oxide system.

B. Implications for Reactor Safety Analysis

Total pressures in equilibrium with $(U_{1-y}Pu_y)O_{2-x}$ condensed phases are not very sensitive to either x or y. For example, the total pressure in equilibrium with $UO_{2.00}$ is virtually identical with that in equilibrium with $(U_{0.8}Pu_{0.2})O_{1.96}$. The U/O and Pu/O systems are also similar in that, at high temperature, both produce vapors which are very rich in oxygen, as is illustrated in Fig. 5. However, the effects of changes in the plutonium content of the condensed phase during vaporization, as shown in Fig. 4, should be considered in cases where appreciable vaporization takes place. This uranium enrichment of the vapor could produce a significant increase in plutonium concentration in the condensed phase.

C. Suggested Additional Experimental Work

There is a notable lack of data on properties of $(U,Pu)O_{2-x}$ above the melting point. All the areas discussed in Section IV.A. as sources of error are reasonable candidates for additional work. Measurements on the phase diagram and heat capacity, for example, are clearly needed. The principal uncertainty in these calculations is a direct consequence of the lack of reliable experimental data on oxygen potentials over a wide temperature and composition range. Even measurements over a relatively small temperature and composition range would do much to improve the reliability of the calculated pressures. Indeed, without improved data on the oxygen potentials, other data would be of relatively little value in improving the results obtained with this approach.

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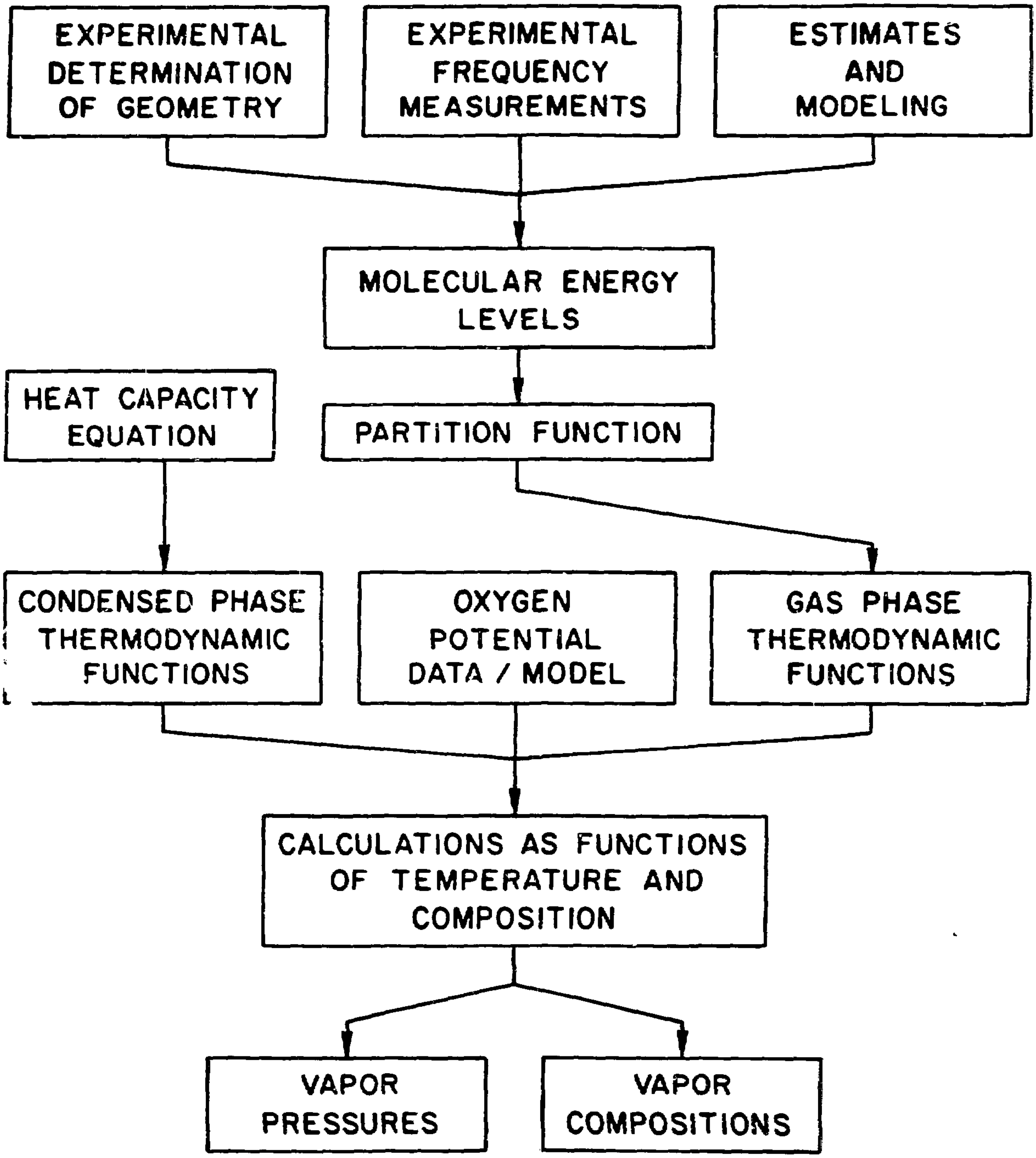
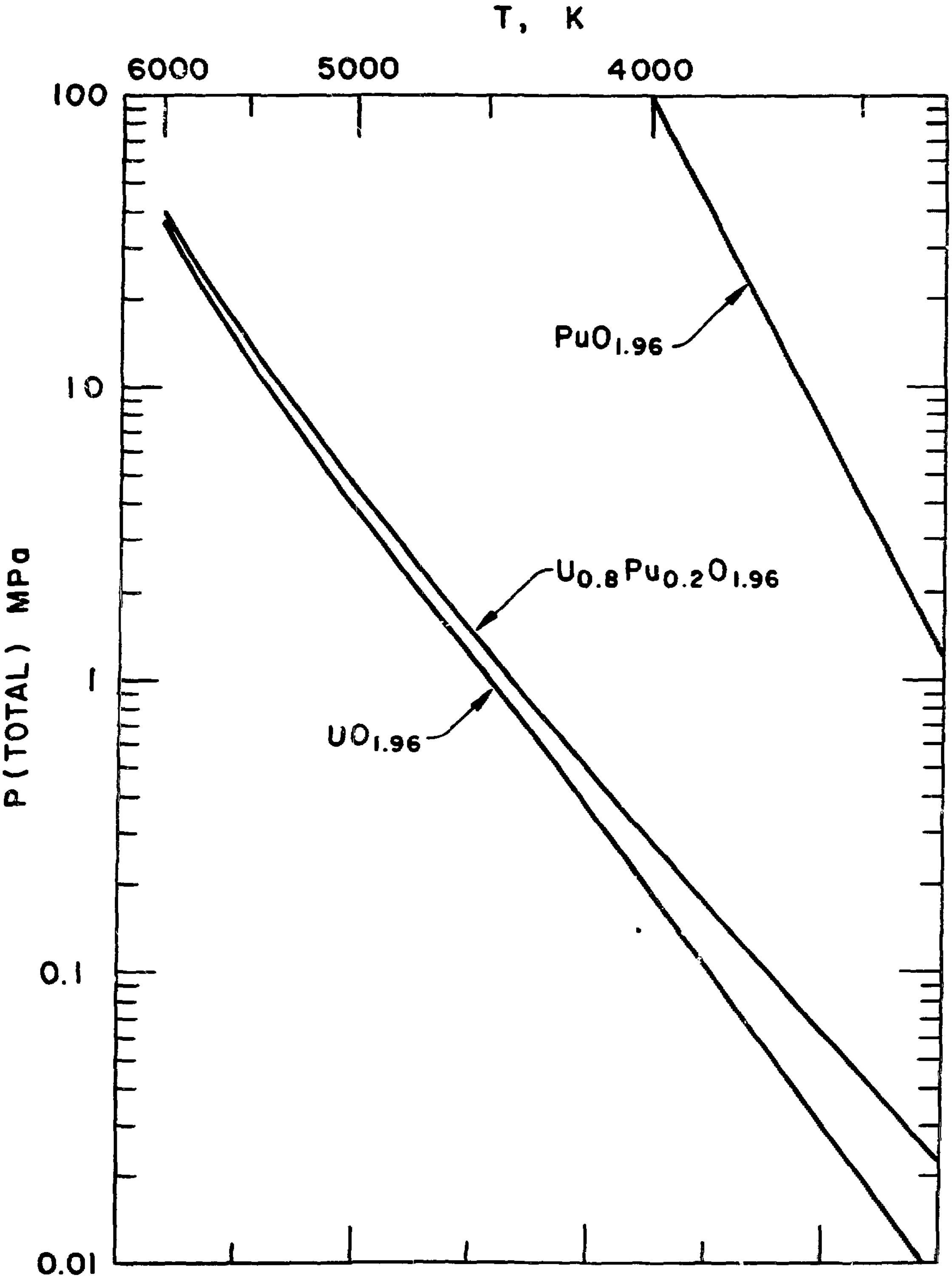
Table 1. Coefficients of the Equations ΔG_f° (in $kJ \cdot mol^{-1}$) = A + BT + CT^2 + D/T + E·ln (T) + FT^3. (θ represents 298.15 K.)

Species	T-range, K	A	B	C	D	E	F
O (g)	θ-1400	252.36	-6.2747×10^{-2}	-1.3294×10^{-6}	-527.60	—	—
	1400-6000	259.03	-6.7710×10^{-2}	-1.6525×10^{-8}	-3747.4	—	—
U (g)	θ-1400	539.11	-1.6007×10^{-1}	1.7321×10^{-5}	-1046.4	—	—
	1400-4435	749.73	-8.3008×10^{-2}	-2.0904×10^{-6}	—	-40.548	—
	4435-6000	0.0	—	—	—	—	—
UO (g)	θ-1400	26.863	-1.0515×10^{-1}	1.6100×10^{-5}	-1002.4	—	—
	1400-4435	179.98	-4.2342×10^{-2}	2.0064×10^{-6}	—	-29.432	—
	4435-6000	-521.65	5.8124×10^{-2}	2.4020×10^{-6}	—	—	—
UO_2 (g)	θ-1400	-501.42	-4.2567×10^{-2}	1.4530×10^{-5}	—	7.5475	—
	1400-4435	-367.02	1.4476×10^{-2}	1.7735×10^{-6}	—	-18.571	—
	4435-6000	-989.24	1.1823×10^{-1}	2.0798×10^{-6}	—	—	—
UO_3 (g)	θ-1400	-822.97	2.5295×10^{-2}	1.4770×10^{-5}	—	4.9754	—
	1400-4435	-707.37	9.0256×10^{-2}	1.9058×10^{-6}	—	-18.131	—
	4435-6000	-1321.1	1.8201×10^{-1}	2.4230×10^{-6}	—	—	—
UO_2 (c)	θ-1400	-1131.0	1.4405×10^{-1}	8.1068×10^{-6}	—	9.7445	—
	1400-2670	-1079.8	1.5714×10^{-1}	1.2365×10^{-5}	—	—	-2.6564×10^{-9}
	2670-3120	-1167.1	2.4280×10^{-1}	-1.4569×10^{-5}	—	—	—
	3120-4435	-1002.7	1.6163×10^{-1}	-5.4369×10^{-6}	—	—	—
	4435-6000	-1453.7	2.5458×10^{-1}	-3.4634×10^{-6}	—	—	—
Pu (g)	1000-3605	260.58	-7.9957×10^{-2}	-2.4343×10^{-6}	12715	6.8126	—
	3605-6000	0.0	—	—	—	—	—
PuO (g)	1000-3605	-106.88	-6.4867×10^{-2}	3.4979×10^{-6}	—	—	—
	3605-6000	-452.62	3.0418×10^{-2}	3.6209×10^{-6}	—	—	—
PuO_2 (g)	1000-3605	-481.09	2.1026×10^{-2}	2.3283×10^{-6}	—	—	—
	3605-6000	-783.92	8.9630×10^{-2}	7.6481×10^{-6}	—	—	-2.9487×10^{-10}
PuO_2 (c)	913-2701	-1060.9	2.0521×10^{-1}	-6.0130×10^{-6}	—	—	—
	2701-3605	-918.62	1.3644×10^{-1}	—	—	—	—
	3605-6000	-1241.0	2.1943×10^{-1}	2.0882×10^{-6}	—	—	-8.9622×10^{-11}

Table 2. Values for Constants in Oxygen-Potential Model

	Solid	Liquid
A_1	7.680	7.680
A_2	−28.786	−25.986
A_3	20.8	18.0
B_1	−60805	−57576
B_2	159317	147352
B_3	−101600	−89166


EXPERIMENTAL DETERMINATION OF GEOMETRY
EXPERIMENTAL FREQUENCY MEASUREMENTS
ESTIMATES AND MODELING
MOLECULAR ENERGY LEVELS
HEAT CAPACITY EQUATION
PARTITION FUNCTION
CONDENSED PHASE THERMODYNAMIC FUNCTIONS
OXYGEN POTENTIAL DATA / MODEL
GAS PHASE THERMODYNAMIC FUNCTIONS
CALCULATIONS AS FUNCTIONS OF TEMPERATURE AND COMPOSITION
VAPOR PRESSURES
VAPOR COMPOSITIONS


T, K
6000
5000
4000
100
10
1
0.1
0.01
P (TOTAL) MPa
$PuO_{1.96}$
$U_{0.8}Pu_{0.2}O_{1.96}$
$UO_{1.96}$
1.6
2.0
2.4
2.8
$10^4/T$

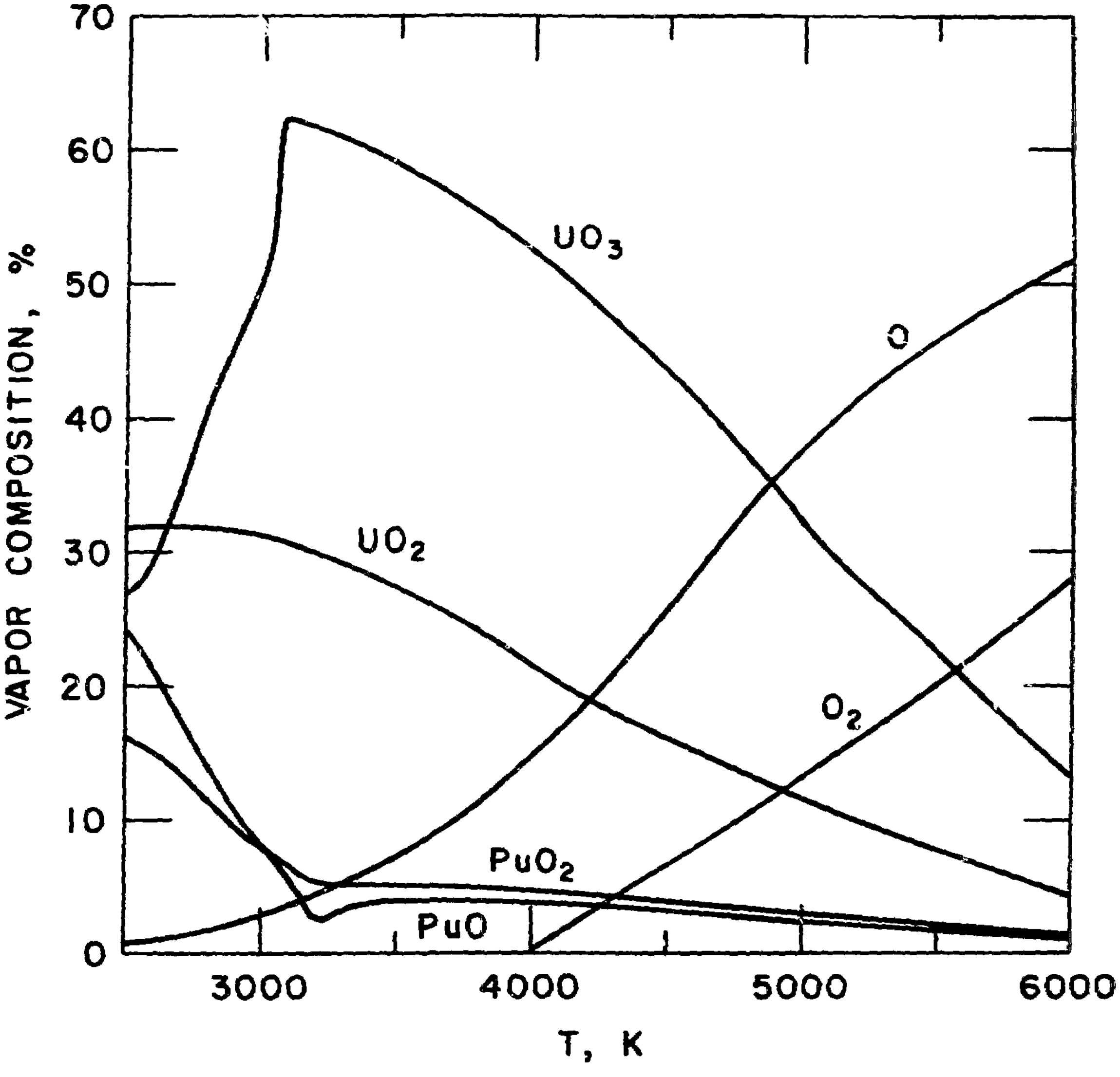

70
60
50
40
30
20
10
0
VAPOR COMPOSITION, %
3000
4000
5000
6000
T, K
UO3
UO2
O
O2
PuO2
PuO

Fig ~~5~~ 4

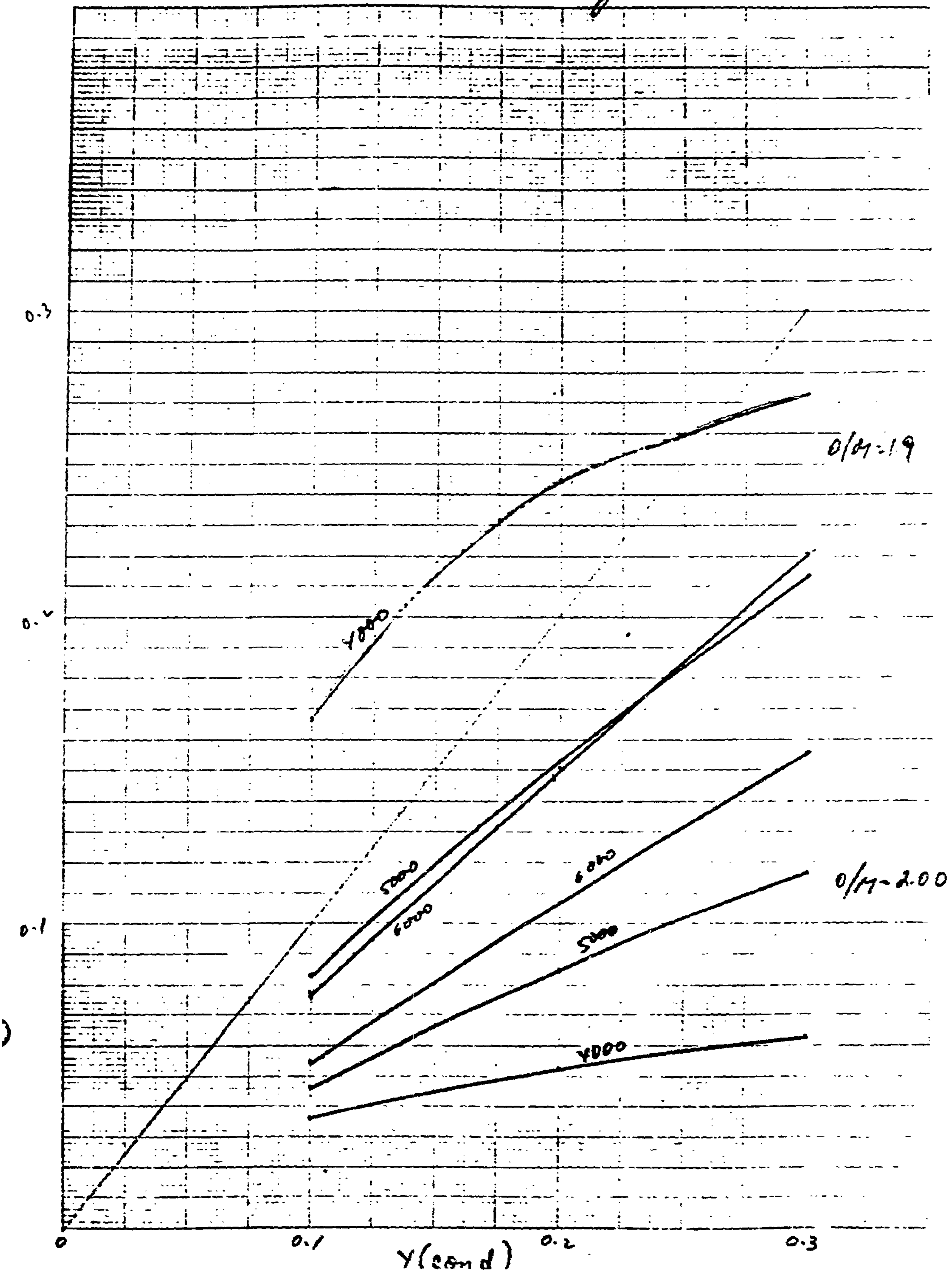
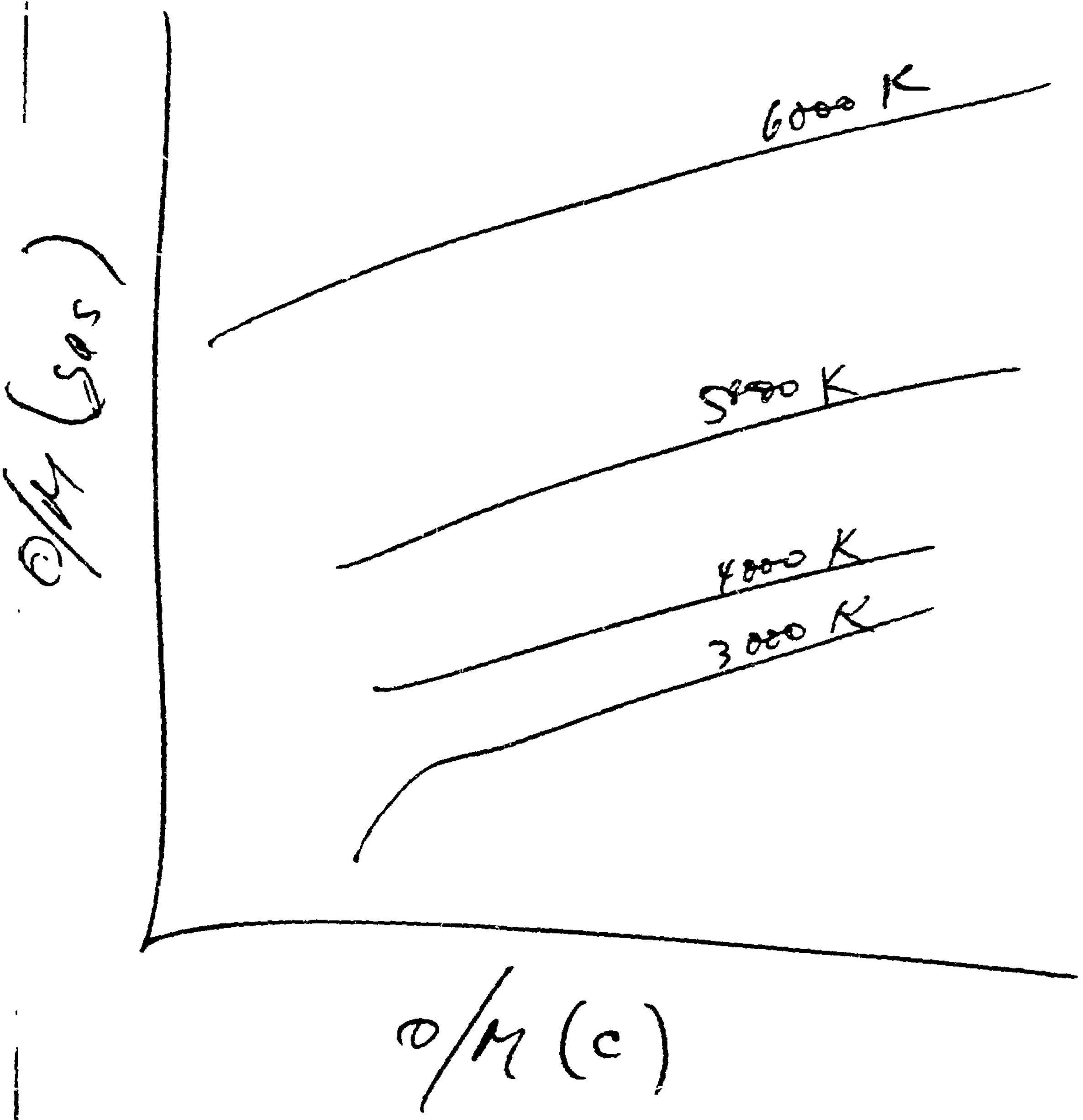
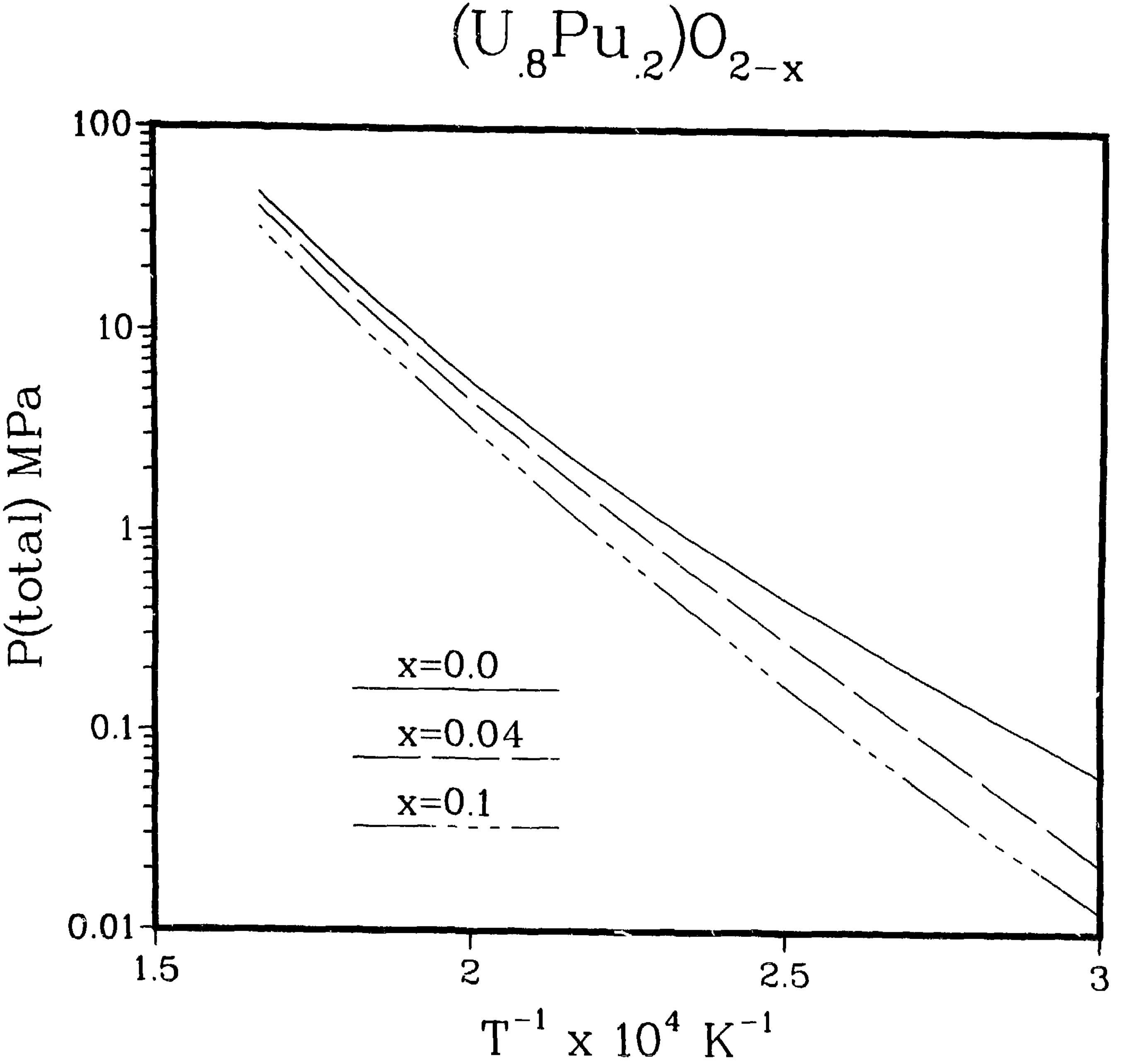
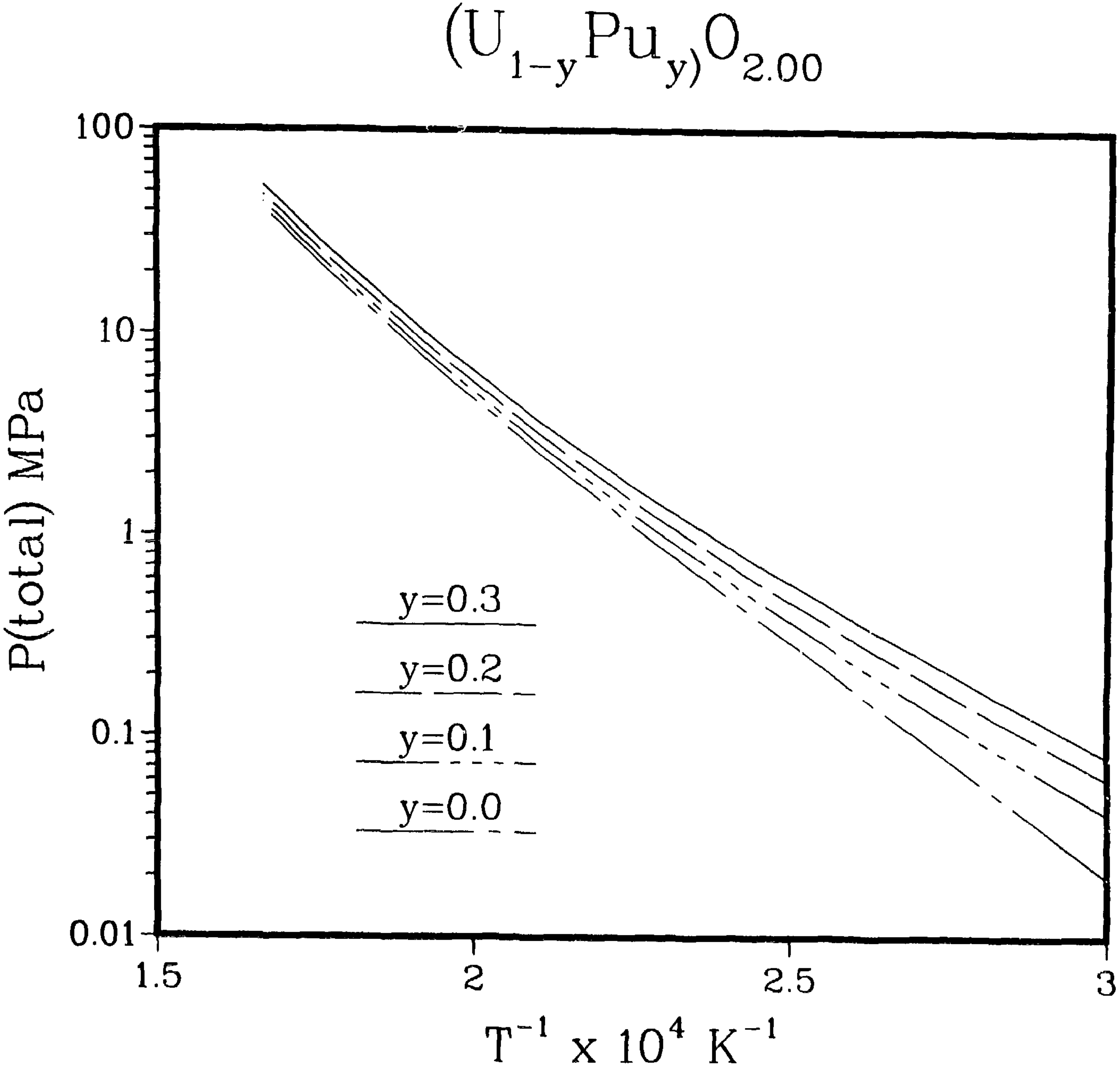
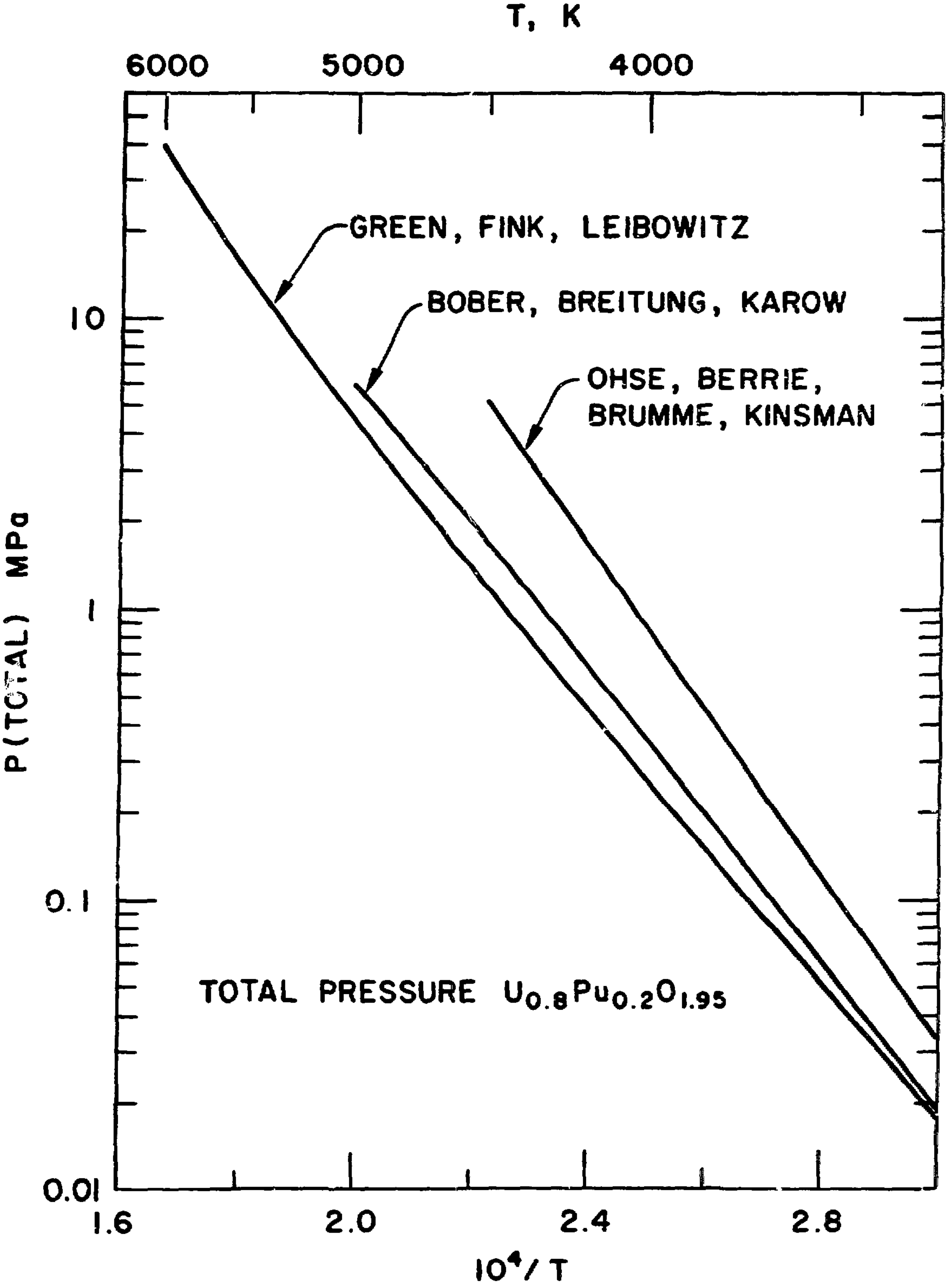

0.3
0.2
0.1
y(gas)
0
0.1
0.2
0.3
Y(cond)
O/M-1.9
4000
5000
6000
6000
5000
4000
O/M-2.00

Fig 5




$(U_{.8}Pu_{.2})O_{2-x}$
P(total) MPa
100
10
1
0.1
0.01
1.5
2
2.5
3
T^{-1} x 10^4 K^{-1}
x=0.0
x=0.04
x=0.1


$(U_{1-y}Pu_y)O_{2.00}$
P(total) MPa
100
10
1
0.1
0.01
1.5
2
2.5
3
$T^{-1} \times 10^4\ K^{-1}$
y=0.3
y=0.2
y=0.1
y=0.0



T, K
6000
5000
4000
GREEN, FINK, LEIBOWITZ
BOBER, BREITUNG, KAROW
OHSE, BERRIE, BRUMME, KINSMAN
P (TOTAL) MPa
10
1
0.1
0.01
TOTAL PRESSURE $U_{0.8}Pu_{0.2}O_{1.95}$
1.6
2.0
2.4
2.8
$10^4/T$