# Solidus/Liquidus of Uranium-Plutonium Dioxide

## Recommendation

The recommended solidus and liquidus curves for stoichiometric, unirradiated $UO_2$-$PuO_2$ solutions are those reported by Adamson et al. [1] from their reanalysis of the data from their laboratory [2,3] using the IAEA-recommended melting point of 3120 K for $UO_2$ [4]. The solidus, $T_S$, and liquidus, $T_L$, in K are represented by the polynomial equations of Adamson et al.

$$T_S(K) = 3120.0 - 655.3x + 336.4x^2 - 99.9x^3 \quad \textbf{(1)}$$

$$T_L(K) = 3120.0 - 388.1x - 30.4x^2 \quad \textbf{(2)}$$

where $x$ is the mole fraction of $PuO_2$. The recommended solidus and liquidus curves are shown in Figure 1 along with the experimental data. The solidus and liquidus are tabulated as a function of $PuO_2$ content in Table 1.

## Uncertainty

Adamson et al. state that these curves fit the available data with a standard deviation of $\pm$ 27 K. For mole fractions of $PuO_2$ from 0 to 0.6, measurement errors are in the range of 20 to 30 K. At mole fractions greater than 0.6, the uncertainty in the measurements increases with increasing Pu content. Thus, the overall reliability of these curves, which includes both experimental and fitting uncertainties, decreases above 0.6 moles of $PuO_2$. For $PuO_2$ contents from 0 to 0.6 moles, the two standard deviation uncertainties (that include the uncertainties in the measurements and the fits) are $\pm$35 K for the solidus and $\pm$55 K for the liquidus. For $PuO_2$ contents above 0.6 mole, the two standard deviation uncertainties are $\pm$50 K for the solidus; $\pm$75 K for the liquidus.

## Discussion

### Experimental Data

Lyon and Baily [3] measured the solidus and liquidus of $(U,Pu)O_2$ contained in sealed tungsten capsules heated by electromagnetic induction. Temperatures were determined using an optical pyrometer focused on a black-body cavity. Measurements were made at frequent intervals as the temperature was increased or decreased. The change in the slopes of the temperature-time curve were used to determine the solidus and the liquidus in the system. Aitken and Evans [2] used the same apparatus as used by Lyon and Baily but included a silicon detector for continuous temperature measurement. Data from these two sets of measurements are shown in Figure 1.

As shown in Figure 1, the temperatures for the solidus and liquidus obtained by Aitken and Evans[2] are, on the average, somewhat higher than the Lyon and Bailey [3] values at similar compositions. It is believed that these differences arise from the differences in response time in the optical pyrometer systems used in the two experiments. Although the data of Aitken and Evans have fewer compositions than the Lyon and Bailey data for the stoichiometric mixed oxide, the numerous Aitken and Evans data for the hypostoichiometric mixed oxide provide a large degree of internal consistency. Because of the improvements in the continuous optical pyrometer system, the data of Aitken and Evans are considered more reliable. However, the uncertainties in both sets of data are such that differences between the two sets of measurements are mainly within the experimental uncertainties of $\pm$35 K for the solidus and $\pm$55 K for the liquidus.

Although melting measurements on this system have been made using the tungsten V-filament technique [5,6], these data are considered unreliable because of problems in the V-filament method [1]. The main problem is that the incongruent vaporization near the melting point of the small, uncontained specimens causes compositional changes and results in significantly lower values for the solidus and liquidus compared to sealed capsules. In addition, because it is difficult to achieve black-body conditions for these small V-filament samples, the surface emissivity is used in temperature measurement. The compositional changes caused by the incongruent vaporization lead to changes in the surface emissivity and thus to errors in temperature measurements. The unreliability of the V-filament technique is illustrated by comparison of V-filament measurements on unirradiated, stoichiometric $UO_2$ made by Christensen [7,8] and by Bates [9] with the precise measurements by Latta and Fryxell [10]. Melting points (3063 - 3073 K) obtained with the V-filament technique were approximately 50 K lower than the true melting point of $UO_2$ (3120 K)[4].

**Data Analysis**

Adamson et al. analyzed the data of Aitken and Evans and of Lyon and Bailey using the ideal solution model of Epstein [11]. In this analysis, the melting point for $UO_2$ was 3120 K, the IAEA-recommended value [4]; the melting point for $PuO_2$ was 2701 K, the corrected value from measurements of Aitken and Evans. The enthalpy of fusion for $UO_2$ obtained from this analysis is 86.9 kJ $mol^{-1}$. It is 14% lower than the recommended value (74.8 kJ $mol^{-1}$) obtained from enthalpy measurements [4, 12-14]. The enthalpy of fusion of $PuO_2$ obtained from this analysis ( 90.5 kJ $mol^{-1}$) is only 4% lower than the value (94.3 kJ $mol^{-1}$) calculated by Fink [15] from solid enthalpy data and estimates of the enthalpy of liquid $PuO_2$.

**Comparison with Other Equations**

Equations given in MATPRO [16] for the solidus and liquidus of the mixed oxide are based on a least square fit to the data of Lyon and Baily [3] and a $UO_2$ melting point of 3113.15 K, from Brassfield et al.[17]. The MATPRO solidus ($T_{sol}$) and liquidus ($T_{Liq}$) are

$$T_{Sol}(K) = 3113.15 - 5.41395\,C + 7.46390\times10^{-3}\,C^2 - 3.2\times10^{-3}\,\mathrm{FBu} \qquad \textbf{(3)}$$

$$T_{Liq}(K) = 3113.15 - 3.21660C - 1.448518\text{x}10^{-3}C^2 - 3.2\text{x}10^{-3}\,\text{FBu} \quad (4)$$

where C is the $PuO_2$ content in wt%; FBu is the burnup in MWd/tU. These curves give 2647 K for the melting point of $PuO_2$. The curves from Eqs.(3) and (4) are shown in Figure 2 along with the experimental data of Lyon and Baily [3] and of Aitken and Evans [2]. A comparison of these equations with the recommended equations derived by Adamson et al.[1] is shown in Figure 3. Agreement between the two sets of equations is within $\pm$ 7 K up to a mole fraction of 0.6 $PuO_2$ where differences increase to 11K. The two sets of curves continue to diverge at higher mole fractions of $PuO_2$ until they differ by 55 K at the melting point of $PuO_2$. This large deviation is related to the fit by MATPRO to the data of Lyon and Baily, which give 2663 K for the melting point of $PuO_2$ compared to the fit by Adamson et al. to both the Lyon and Baily data and the data of Aitken and Evans. Values of the liquidus calculated using the MATPRO equation differ from values obtained with the liquidus equation of Adamson et al. by less than the experimental uncertainties for the liquidus. Only for mole fractions of $PuO_2$ greater than 0.8, do the MATPRO solidus values differ by more than the experimental uncertainty ($\pm$35 K) from the solidus values of Adamson et al.

Komatsu et al.[18] derived an equation for the solidus and liquidus of irradiated mixed oxide fuel as a function of burnup and as a function of oxygen-to-metal ratio from their extension of the ideal solution model of Epstein for $(U,Pu)O_2$ to the ternary system $UO_2$-$PuO_2$-$PuO_{1.61}$. In this theory, they used:

77.8 kJ $mol^{-1}$ for the enthalpy of fusion of $UO_2$,
66.5 kJ $mol^{-1}$ for the enthalpy of fusion of $PuO_2$,
66.9 kJ $mol^{-1}$ for the enthalpy of fusion of $PuO_{1.61}$,
3138 K for the melting point of $UO_2$,
2718 K for the melting point of $PuO_2$,
2553 K for the melting point of $PuO_{1.61}$.

The enthalpies of fusion for $UO_2$ and $PuO_2$ used in this analysis are those obtained in the Epstein model [11]. The value for $UO_2$ is closer to the value (74.8 kJ $mol^{-1}$) obtained from measurements than the value obtained by Adamson et al.[1]. The value for $PuO_2$ is 30% lower than the value calculated by Fink [15] from solid enthalpy data and estimates of the liquid enthalpy. It is 27% lower than the value obtained by Adamson et al.[1]. Komatsu et al.[18] incorporated Adamson's model for the effects of soluble fission products on the melting point of irradiated fuel by expressing the melting temperature as a function of burnup. Melting points for $UO_2$, $PuO_2$, and $PuO_{1.61}$ used by Komatsu et al.[18] are, respectively, from data of Latta and Fryxell [10], data of Aitken and Evans[2] and V-filament measurements of Pijanovski and DeLuca [6]. The melting point formula given by Komatsu et al.is:

$$T_m = \frac{1 - A(2 - O/M)}{1 + BY + CY^2} T_m(UO_2) \quad (5)$$

where

| | |
|---|---|
| $T_m$ | = melting temperature (solidus/liquidus) of irradiated (U,Pu)$O_2$ in °C |
| $T_m(UO_2)$ | = melting temperature of $UO_2$ = 2865°C = 3138 K |
| $A$ | = 0.2388 for the solidus; 0.1403 for the liquidus |
| $B$ | = 0.1811 for the solidus; 0.1068 for the liquidus |
| $C$ | = - 0.01100 for the solidus; 0.06316 for the liquidus |
| $O/M$ | = oxygen-to-metal ratio of the fuel, |
| $Y$ | = X + D BU |
| X | = $X_s$ ($PuO_2$) + $X_s$ ($PuO_{1.61}$) or $X_l$ ($PuO_2$) + $X_l$ ($PuO_{1.61}$) |
| $X_s$ or $X_l$ | = mole fraction of component in solid or liquid phase |
| BU | = burnup in at% |
| D | = 0.016. |

Values for the solidus and liquidus of (U,Pu)$O_2$ calculated from this equation of Komatsu et al. are shown in Figure 4 and compared with the experimental data of Aitken and Evans and of Lyon and Baily. The curves by Komatsu et al. appear to be consistently high relative to both sets of the data. This is surprising because reasonable agreement between their solidus and liquidus and the data of Aitken and Evans (in °C) are shown in a graph in the paper by Komatsu et al.[18] They have used 2718 K from Aitken and Evans original paper for the melting point of $PuO_2$ rather than Aitken and Evan's corrected value, 2701K, which was reported in the reanalysis of the data in the paper by Adamson et al.[1] In Figure 5, the solidus and liquidus of Komatsu et al. is compared with the values by Adamson et al.

The solidus and liquidus given by Adamson et al. is preferred to the values given in MATPRO or the equations given by Komatsu et al. because the equations of Admason et al. have been derived from careful review of two sets of experimental data by the experimentalists and are consistent with the IAEA recommended melting point of $UO_2$. The equations of Adamson et al. have been recommended in the review of mixed oxide data by Harding, Martin, and Potter.[19]

## References


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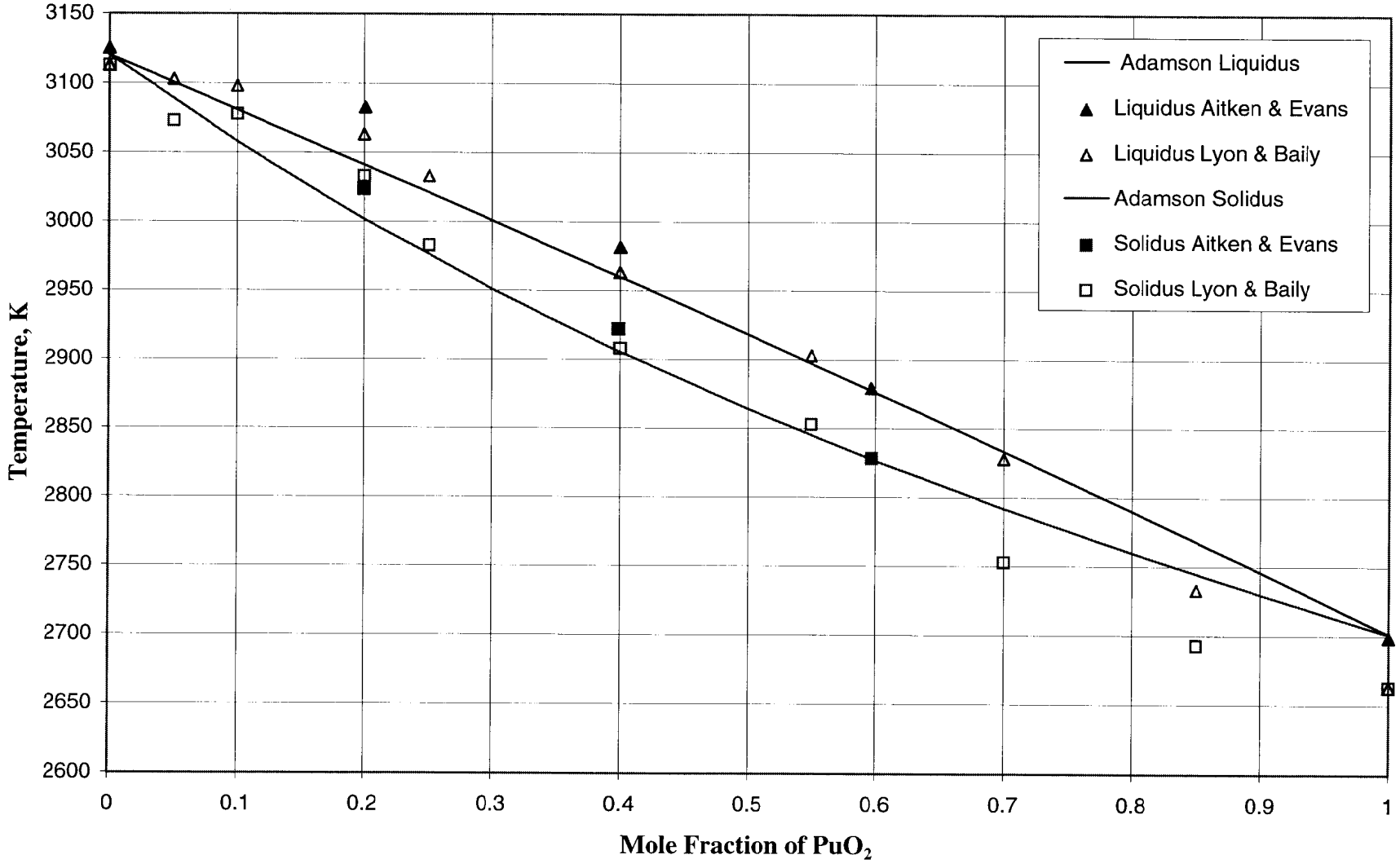
**Table 1 Recommended Solidus and Liquidus of $(U,Pu)O_2$**

| Mole Fraction of $PuO_2$ | Solidus K | Liquidus K |
|---|---|---|
| 0 | 3120 | 3120 |
| 0.1 | 3058 | 3081 |
| 0.2 | 3002 | 3041 |
| 0.3 | 2951 | 3001 |
| 0.4 | 2905 | 2960 |
| 0.5 | 2864 | 2918 |
| 0.6 | 2826 | 2876 |
| 0.7 | 2792 | 2833 |
| 0.8 | 2760 | 2790 |
| 0.9 | 2730 | 2746 |
| 1 | 2701 | 2701 |

## Fig. 1 Recommended Solidus/Liquidus of $(U,Pu)O_2$



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## Fig. 2 MATPRO $(U,Pu)O_2$ Solidus/Liquidus

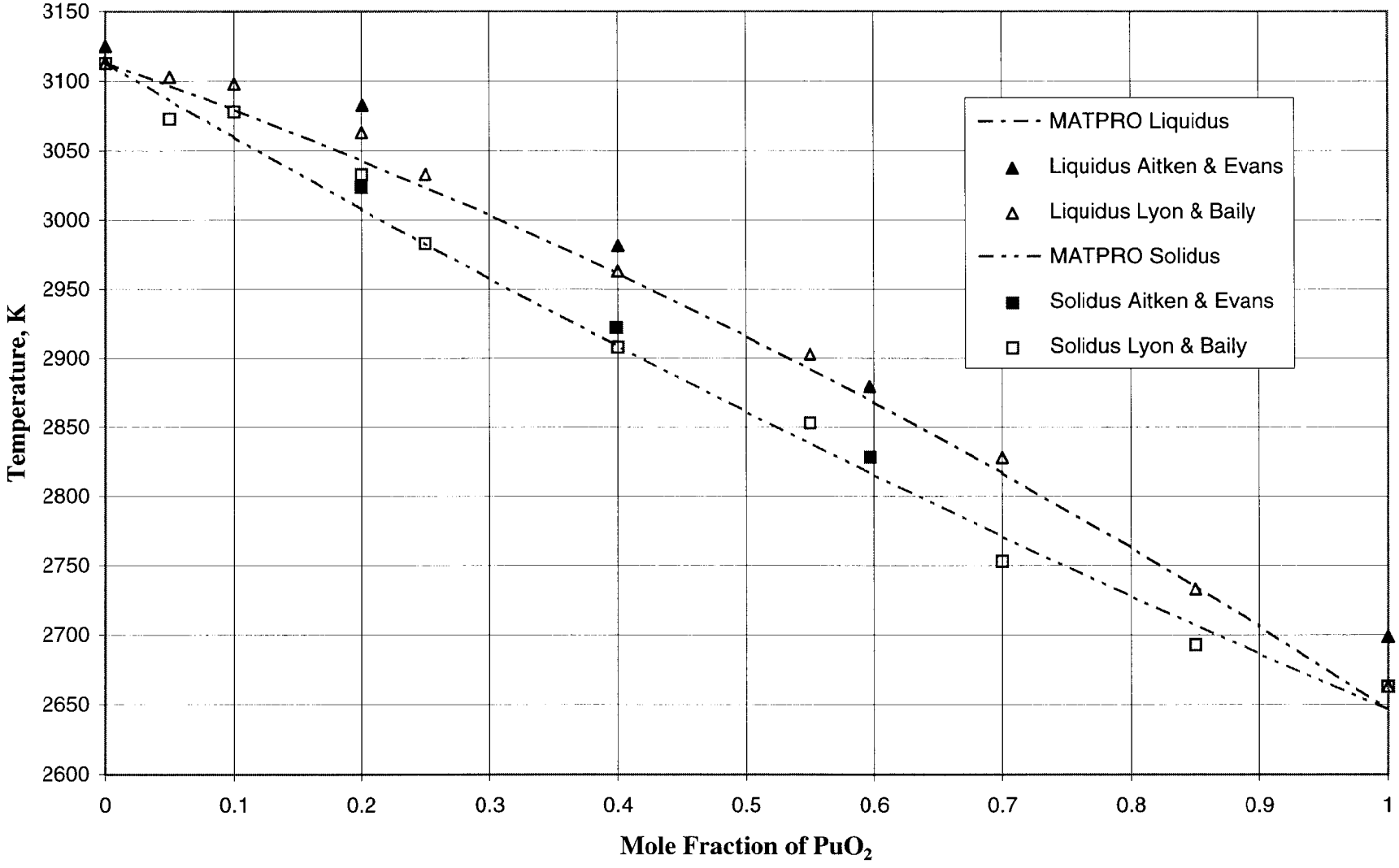
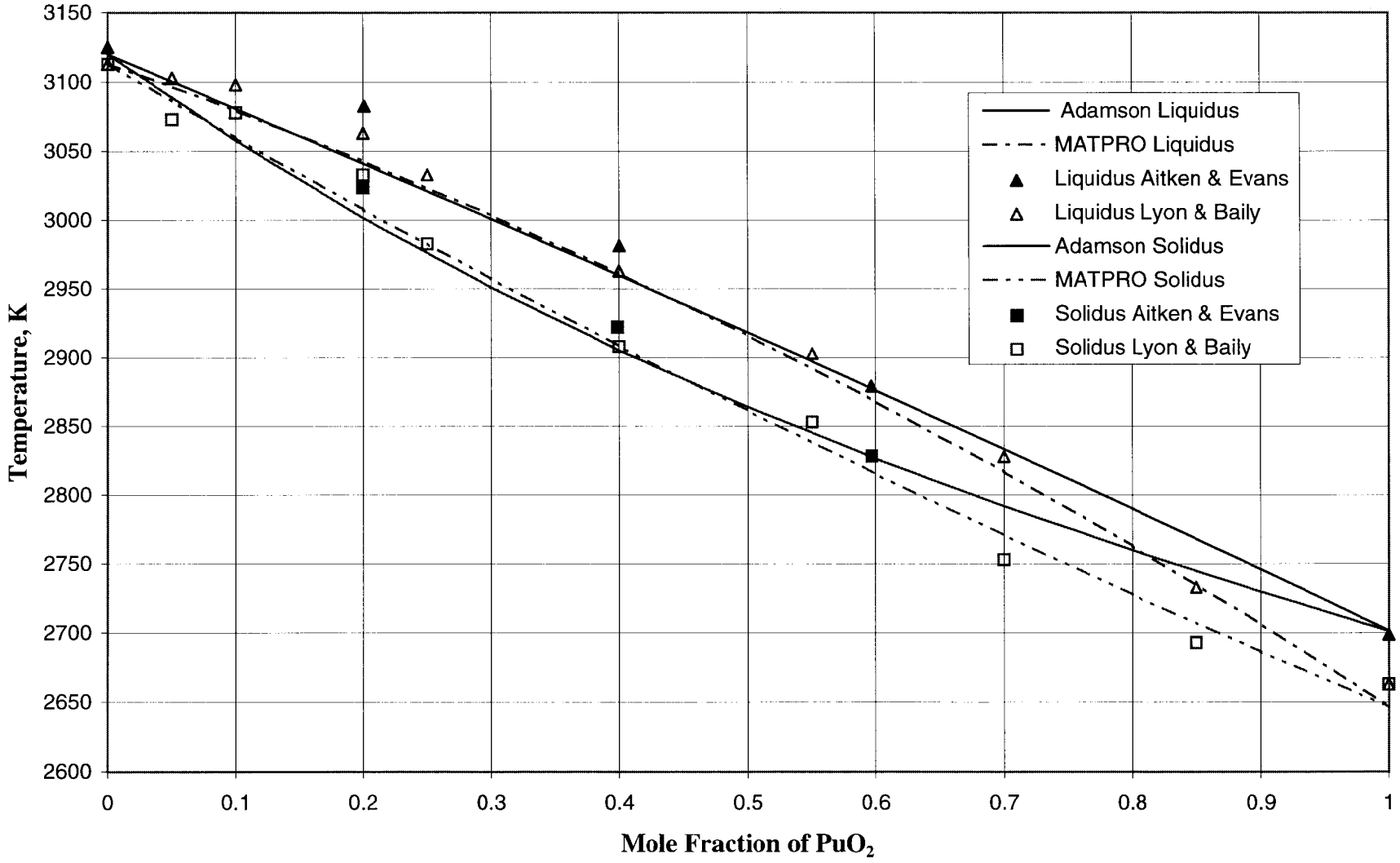


**Fig. 3 Comparison of $(U,Pu)O_2$ Solidus/Liquidus of Adamson & MATPRO**



## Fig. 4 $(U,Pu)O_2$ Solidus/Liquidus of Komatsu

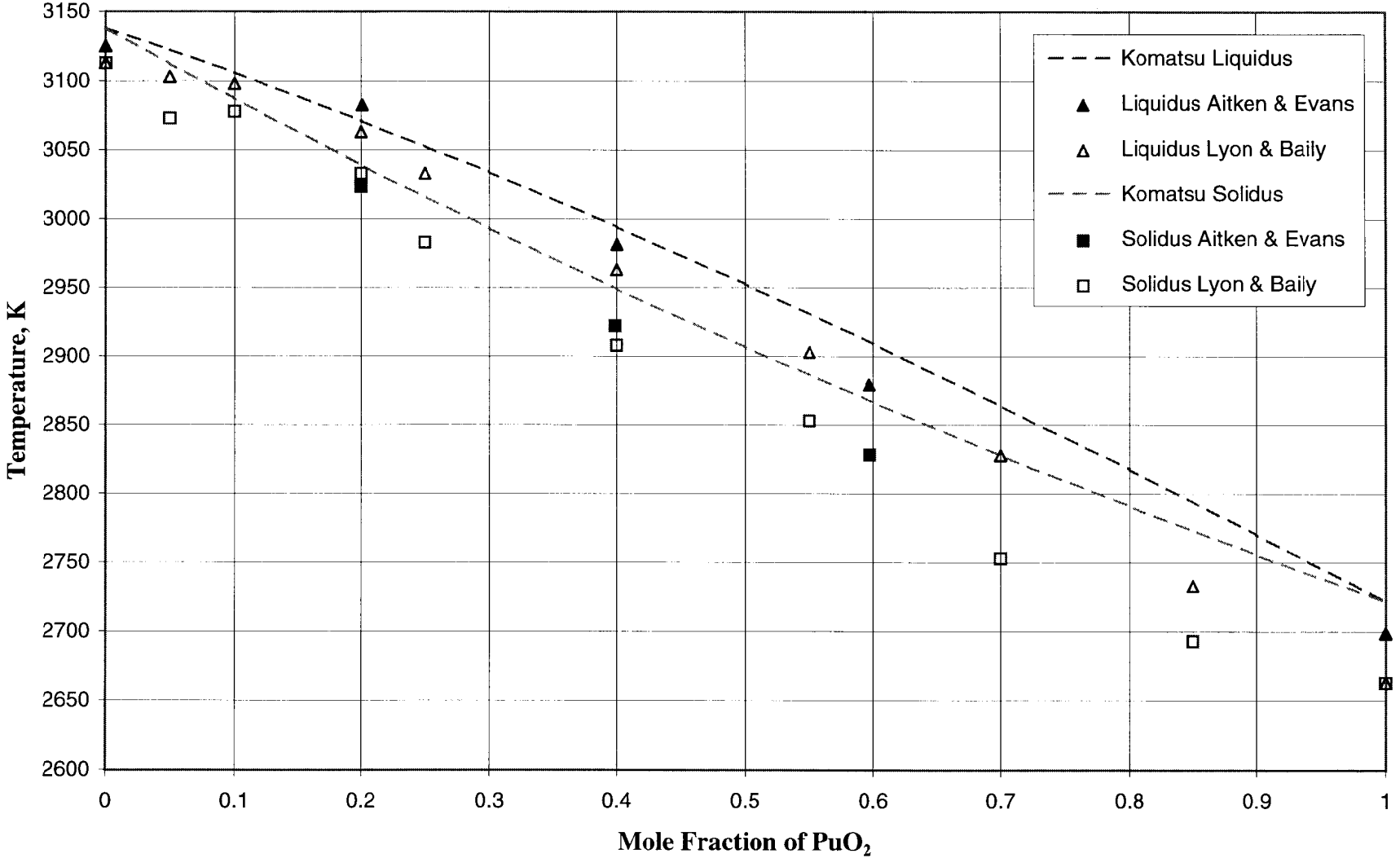


**Fig. 5 Comparison of $(U,Pu)O_2$ Solidus/Liquidus of Adamson & of Komatsu**