

Fig. 11.1 Oxygen—uranium phase-equilibrium system. [After R. K. Edwards and A. E. Martin, in *Thermodynamics*, Symposium Proceedings, July 22-27, 1965, Vienna, International Atomic Energy Agency, Vienna, 1966 (STI/PUB/109).]

**From UO<sub>2</sub> Phase Diagram**

**at T < 1300- 1800 °C  
and O/U < 2.00**

**Then at low temperatures, UO<sub>2</sub> is a mixture of  
UO<sub>2.00</sub> +U (met)**

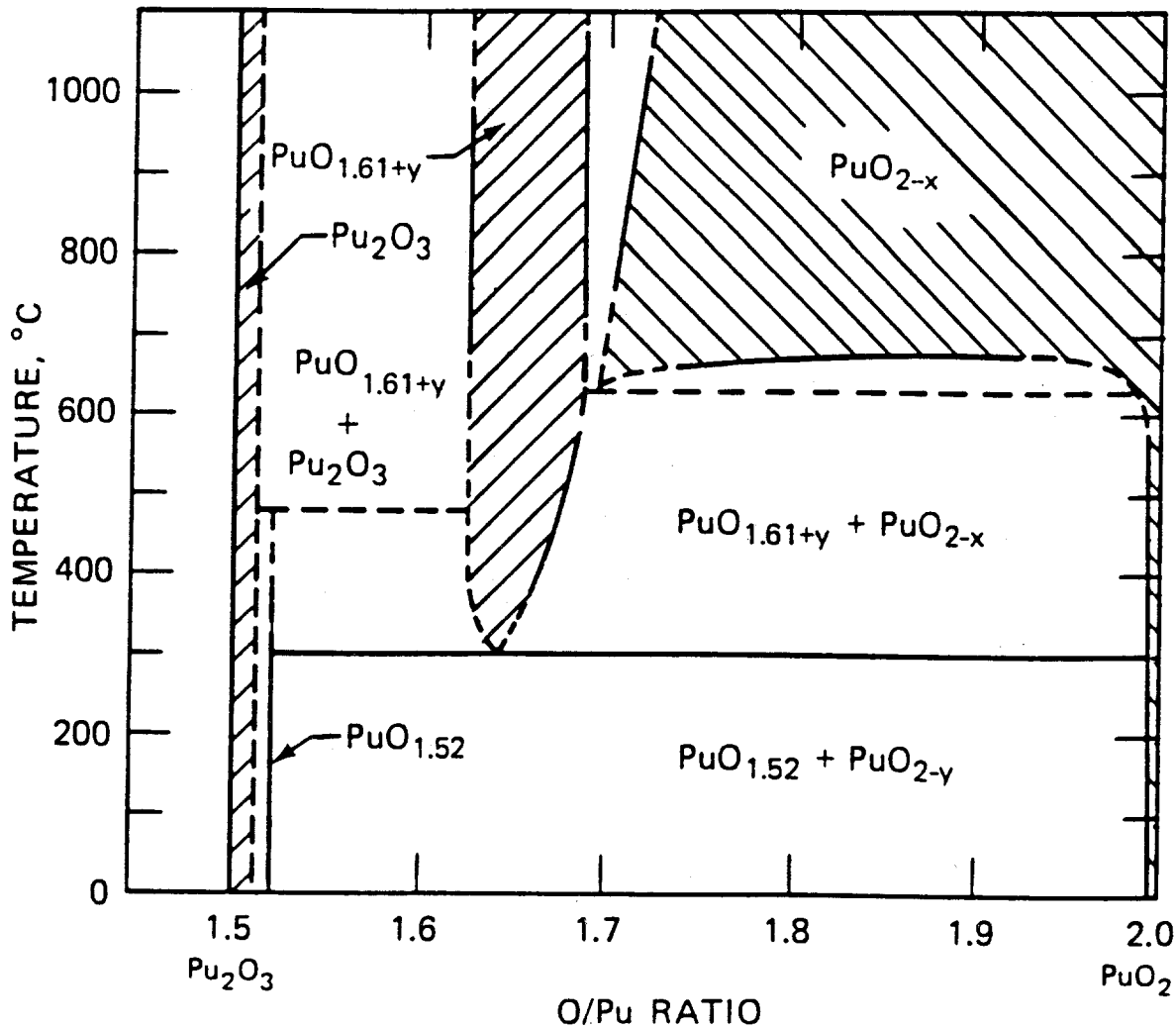
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**From PuO<sub>2</sub> Phase Diagram;**

**Phase    Pu<sub>2</sub>O<sub>3</sub>    PuO<sub>1.52</sub>    PuO<sub>1.61</sub>    PuO<sub>2</sub>**

**O/M    1.5        1.52        1.61        2.00**

**Valence   +3    ----->  
+4**



**Fig. 11.2** Phase diagram of the plutonium—oxygen system. [From H. M. Mattys, *Actinides Rev.*, 1: 165 (1968).]

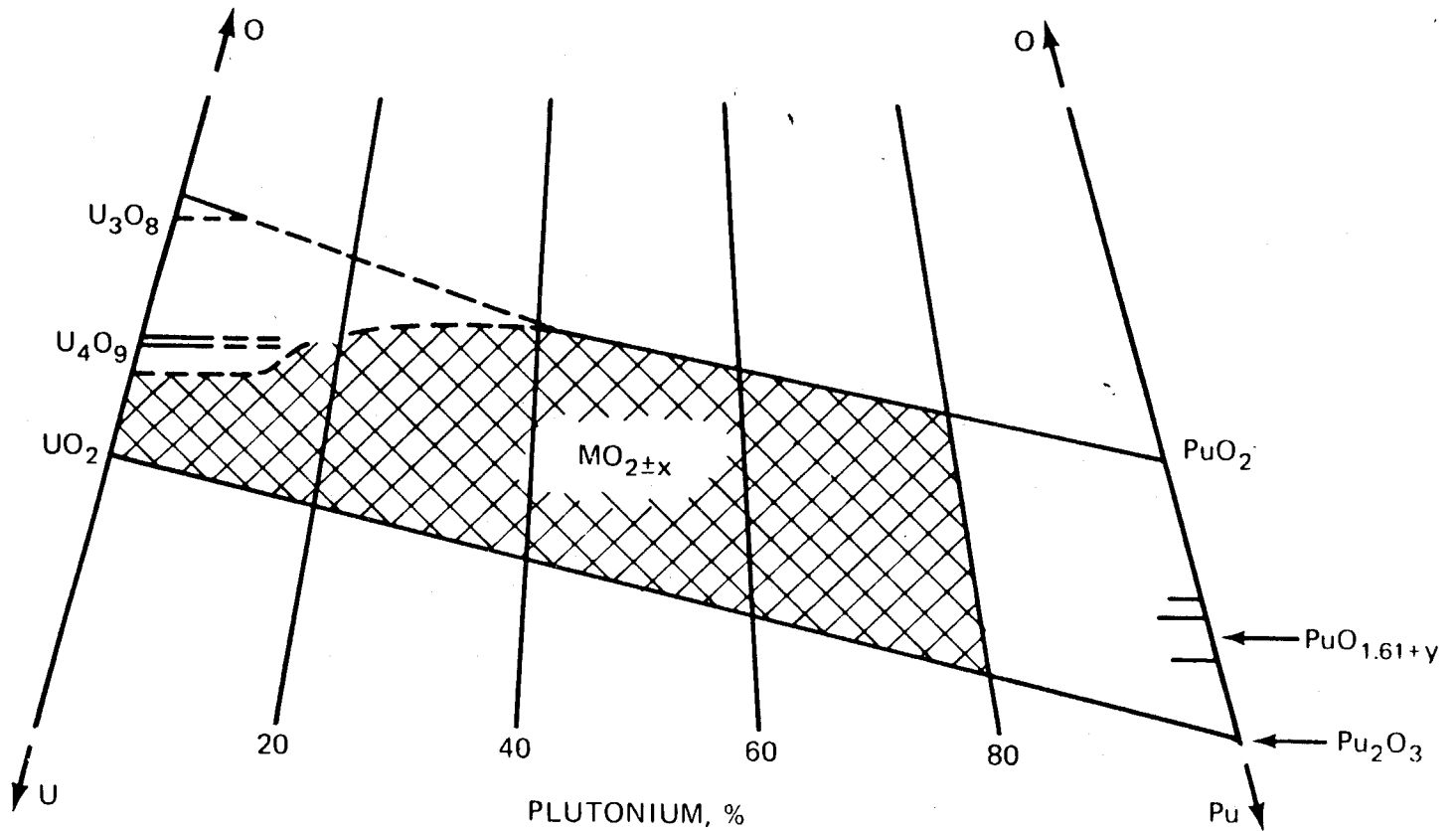


Fig. 11.3 Phase diagram of the uranium-plutonium-oxygen system at 800°C. [From H. M. M. *Actinides Rev.*, 1: 165 (1968).]

## 11.3 Defect Structure

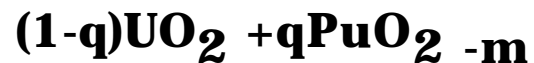
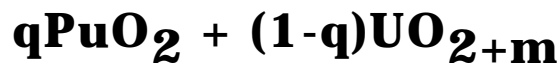


add x oxygen

subtract x oxygen

*Oxidize  $2xU^{+4}$  to  $2xU^{+5}$*

*Reduce  $2xPu^{+4}$  to  $2xPu^{+3}$*



$$m = \frac{x}{(1 - q)}$$

$$m = \frac{x}{q}$$

**Q: Where does the deficiency of oxygen come from?**

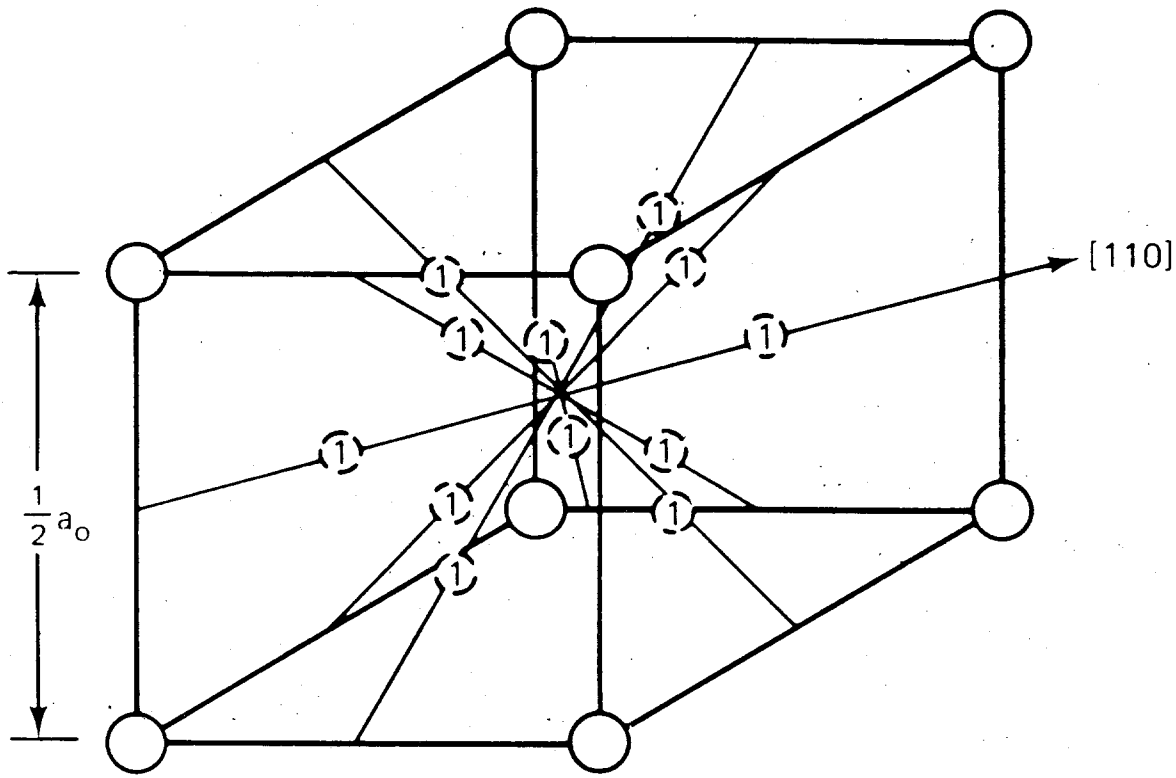
*Figure - Oxygen sublattice*

**Q: Where do the excess oxygen atoms go?**

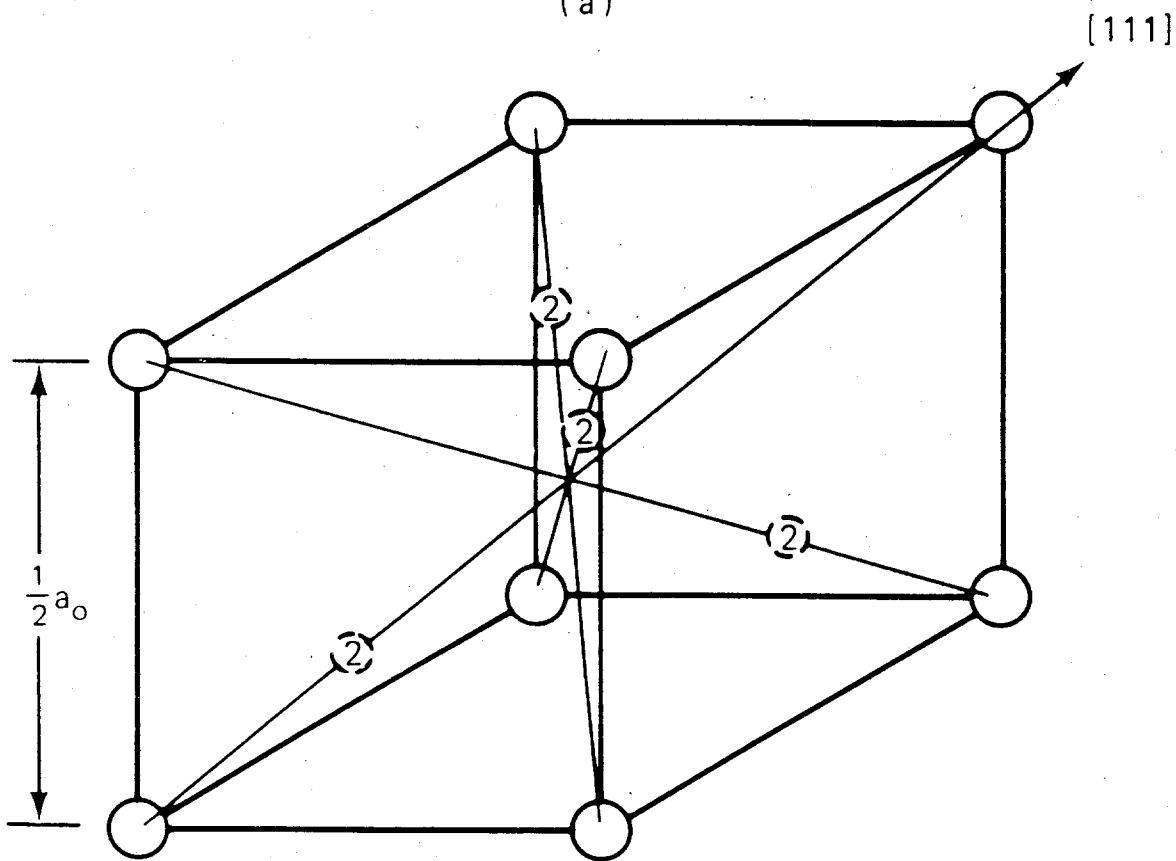
*Figure - 2 types of interstitial positions*

**For example: What happens if we stick two excess oxygen atoms in the matrix?**

- 1.) Force 2 atoms off lattice site-> 2 vacancies**
- 2.) Form two type 1 and two type 2**
- 3.) Change four  $U^{+4}$  to four  $U^{+5}$**



(a)



(b)

Fig. 11.4 Sites for interstitial oxygen in  $\text{UO}_2$ .  $\circ$ , normal oxygen ions.  $(1)$ , type 1 interstitial sites.  $(2)$ , type 2 interstitial sites.

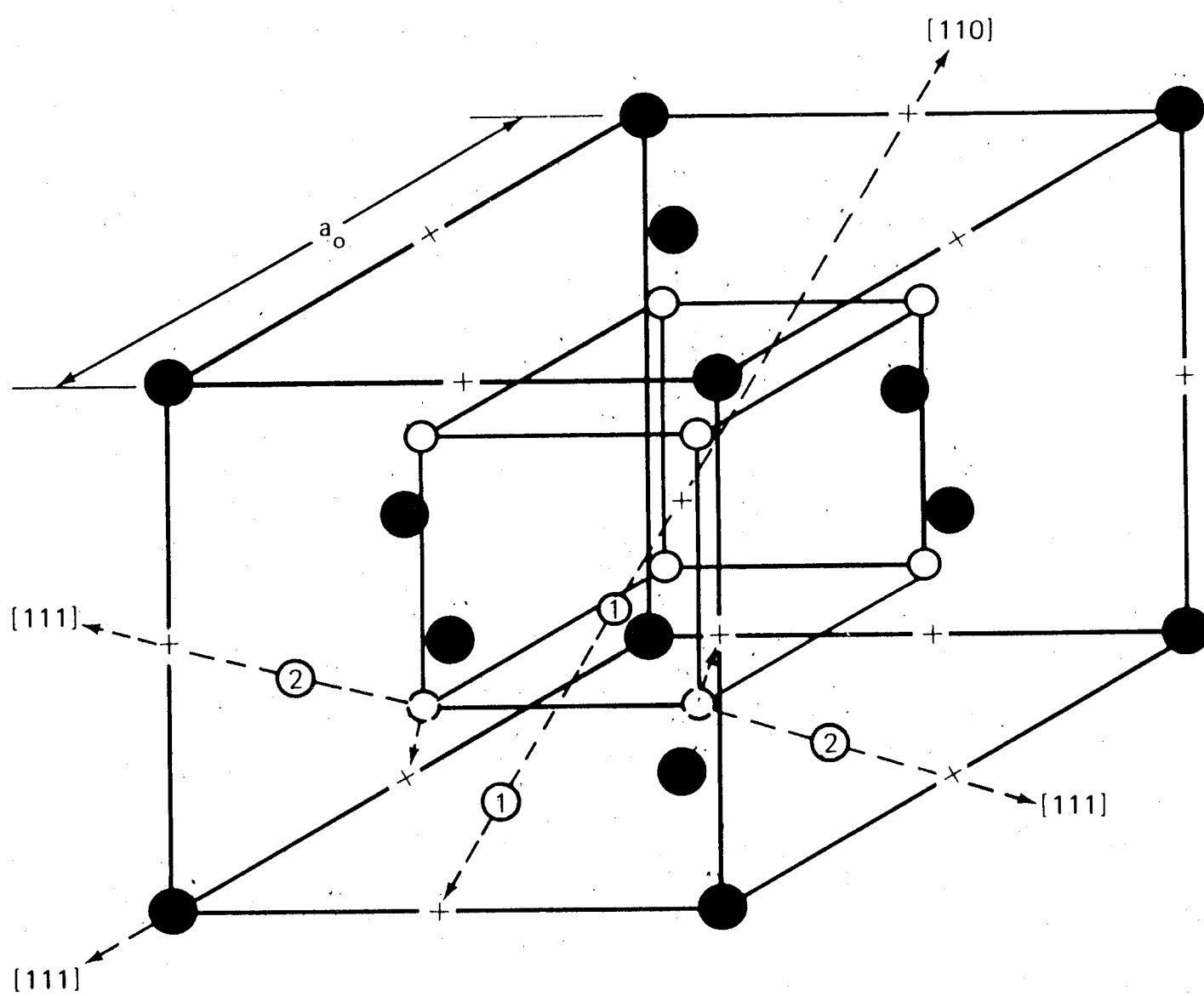


Fig. 11.5 Defect complex in  $\text{UO}_2$ . ●, uranium ions. ○, normal oxygen. (1), type 1 interstitial oxygen. (2), type 2 interstitial oxygen. ( ), vacancy in normal oxygen site. +, interstice at center of cube formed by eight normal oxygen sites.



# 11.4

## Oxygen Potentials

*How can we predict the partial pressure of oxygen around a hot pellet?*

- Use thermodynamics -- see chapter 5
- At equil. all chemical potentials are equal

$$\frac{1}{2} \mu_{O_2}(g) = \mu_O(g)$$

$$\mu_O(g) = \mu_O(\text{solution})$$

$$\mu_{O_2}(g) = G_{O_2}^\circ + RT \ln (p_{O_2})$$

***Gibbs Free Energy of Pure O<sub>2</sub> gas at Temp. T***

***Partial Pressure of O<sub>2</sub> (Figure 11.6)***

=  $\overline{G}_{O_2}$  = partial molar free energy of oxygen in the solid per mole of O<sub>2</sub>

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$$\overline{G}_{O_2} = 2\mu_O(\text{solution}) - G_{O_2}^\circ \quad @ 1 \text{ atm.}$$

= a way of expressing equilibrium partial pressure over the material

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**11.4.1 , 11.4.2 show ways to measure  $\overline{G}_{O_2}$**

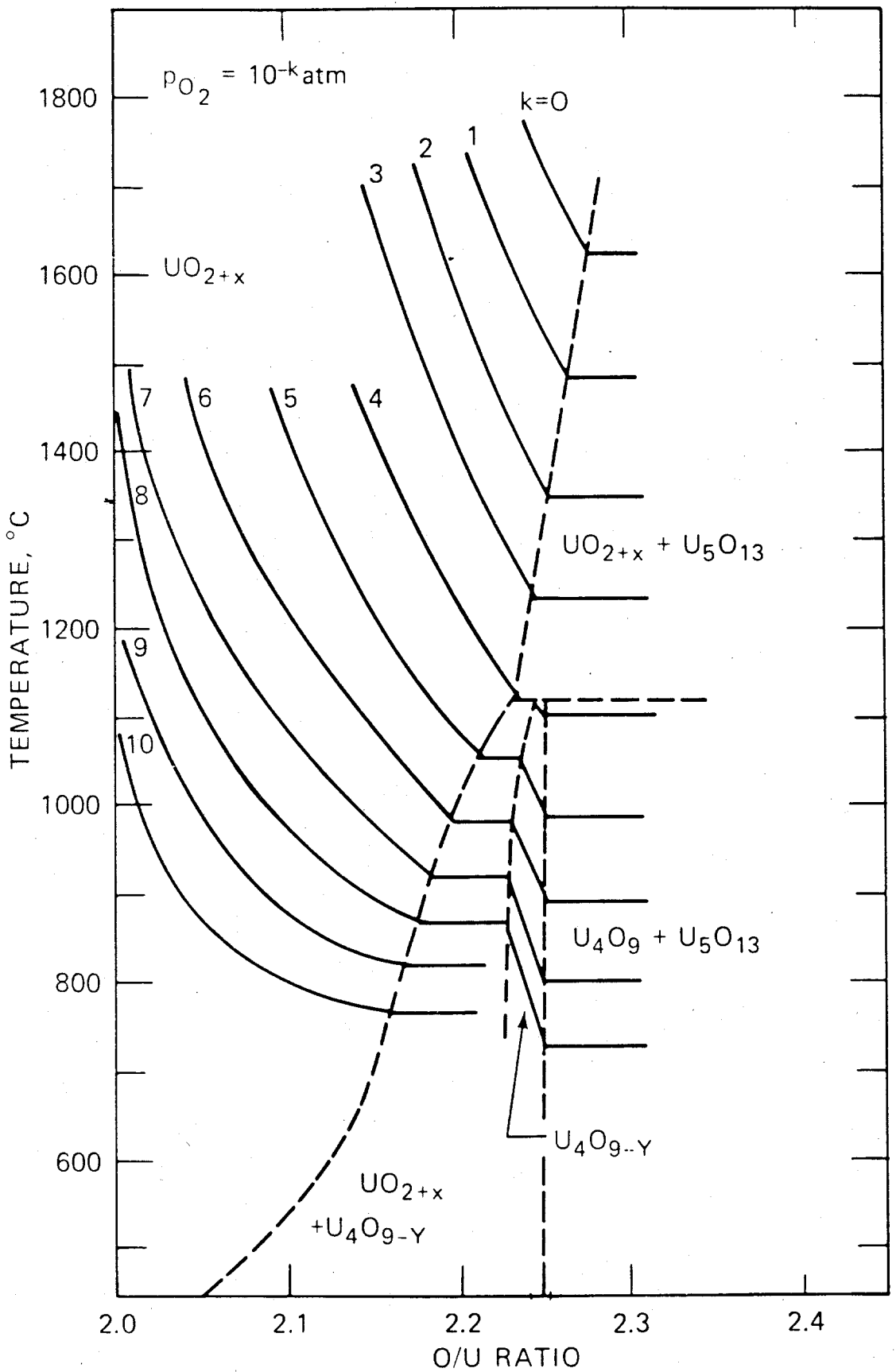


Fig. 11.6 Equilibrium oxygen partial pressure in  $\text{UO}_{2+x}$ . ---, phase-equilibrium line. —, isobar of oxygen. [From I. Tamotsu et al., *J. Nucl. Mater.*, 36: 288 (1970).]

### 11.4.3 Measured Oxygen Potentials

$$\overline{G}_{O_2} = \overline{H}_{O_2} - \overline{S}_{O_2} \left( \frac{T}{1000} \right)$$

partial molal (Enthalpy/entropy) of oxygen in solid oxide

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#### 11.4.4 UO<sub>2</sub>

Can get oxygen partial pressure over hyperstoichiometric UO<sub>2</sub> from figure 11.10

A.) Knowing  $\overline{H}_{O_2}$ ,  $\overline{S}_{O_2}$ ,  $T \implies \overline{G}_{O_2}$

B.) Knowing  $\overline{G}_{O_2} \implies p_{O_2}$

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Can get oxygen partial pressure over hypostoichiometric UO<sub>2</sub> from figure 11.11

<1300°C can get  $p_{O_2}$  over U(l) + UO<sub>2.00</sub>

>1300°C can have some UO<sub>2-x</sub> by converting some U<sup>+4</sup>  $\rightarrow$  U<sup>+2</sup>

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Note - the higher the temperature,

the lower  $\overline{G}_{O_2}$ ,

the higher  $p_{O_2}$

i.e.,  $p_{O_2} = \exp \left( \overline{G}_{O_2} / RT \right)$

as  $x \rightarrow 0$ ,  $p_{O_2}$  increases

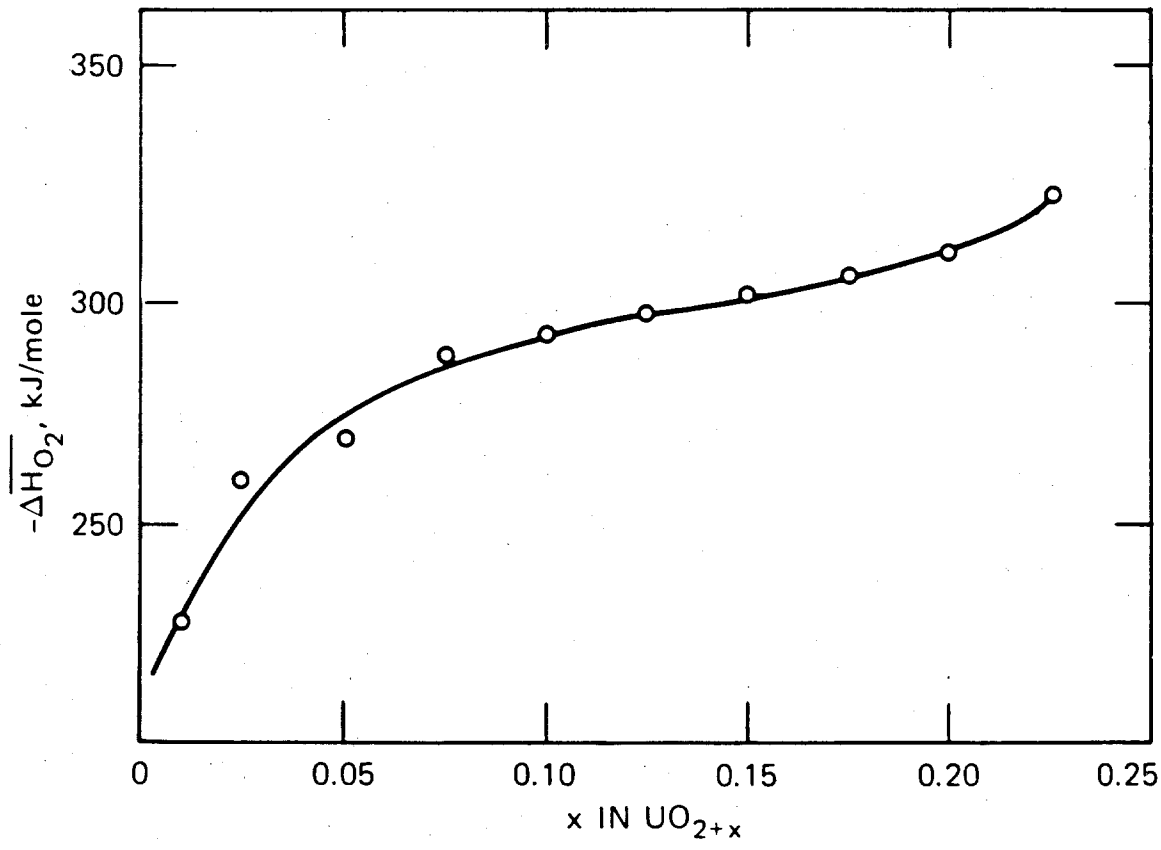
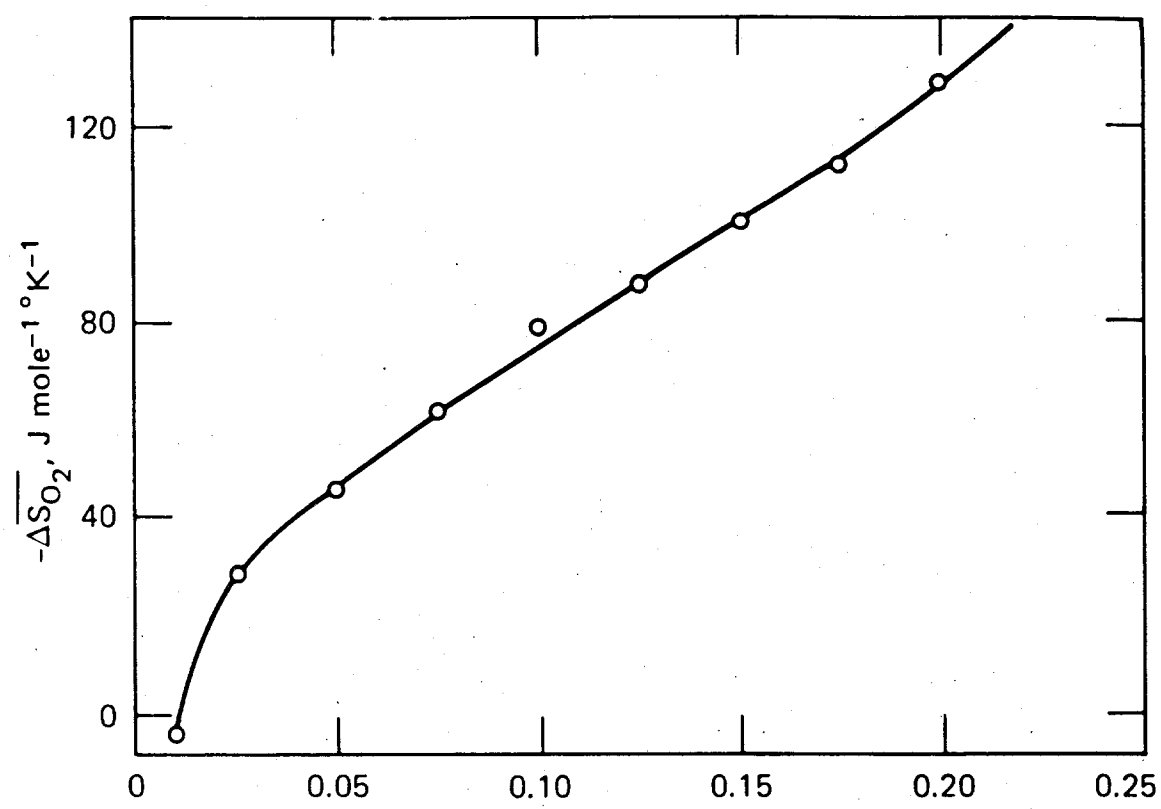


Fig. 11.10 Partial molar entropy and enthalpy of oxygen in  $\text{UO}_{2+x}$ . [From K. Hagemark and M. Broli, *J. Inorg. Nucl. Chem.*, 28: 2837 (1966).]

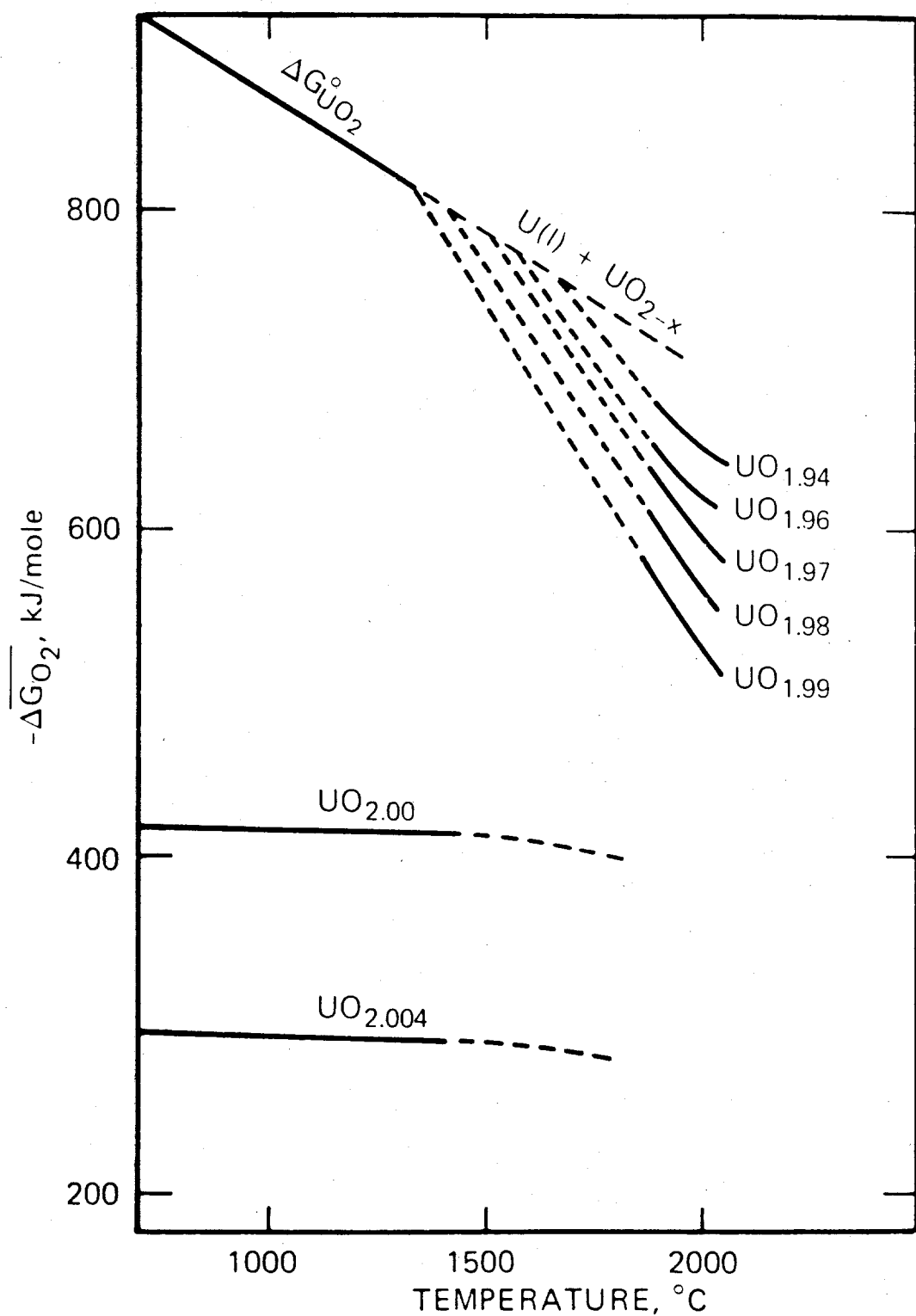


Fig. 11.11 Oxygen potentials of hypostoichiometric and slightly hyperstoichiometric urania. (From T. L. Markin, Chemical Engineering Progress Symposium Series, *Preparation of Nuclear Fuels*, Nuclear Engineering, Part XVIII, Vol. 63, No. 80, p. 43, American Institute of Chemical Engineers, New York, 1967.)

### 11.4.5 Mixed Oxides

Note that the oxygen partial pressure is quite a bit higher for hyperstoichiometric oxide

**Figure 11.12**

$$P_{O_2} = \exp\left(\frac{\overline{\Delta G_{O_2}}}{RT}\right)$$

### 11.4.6 Rand-Markin Model

It was shown that  $\overline{H_{O_2}}$ ,  $\overline{S_{O_2}}$  depend mainly on the valence of the heavy metal ions.

	Hypo	Hyper
$V_U$	4	$4 + \frac{2x}{1-q}$
$V_{Pu}$	$4 - \frac{2x}{q}$	4

See Figures 11.13, 11.14

### 11.4.7 Blackburn's Model

**Main Aim**

1.) To examine the dependence of  $\mu_{O_2}$  on  $V_U$  for hyper and  $V_{Pu}$  for mixed fuel hypo oxides

2.) To allow for some  $\frac{U}{Pu}$  ratio effects.

**Procedure:**

- 1.) Set up rate for U, Pu, and U-Pu
- 2.) Solve for rate constants
- 3.) Use normalization and charge balances to obtain quantitative solutions.

**Example- UO<sub>2</sub>**

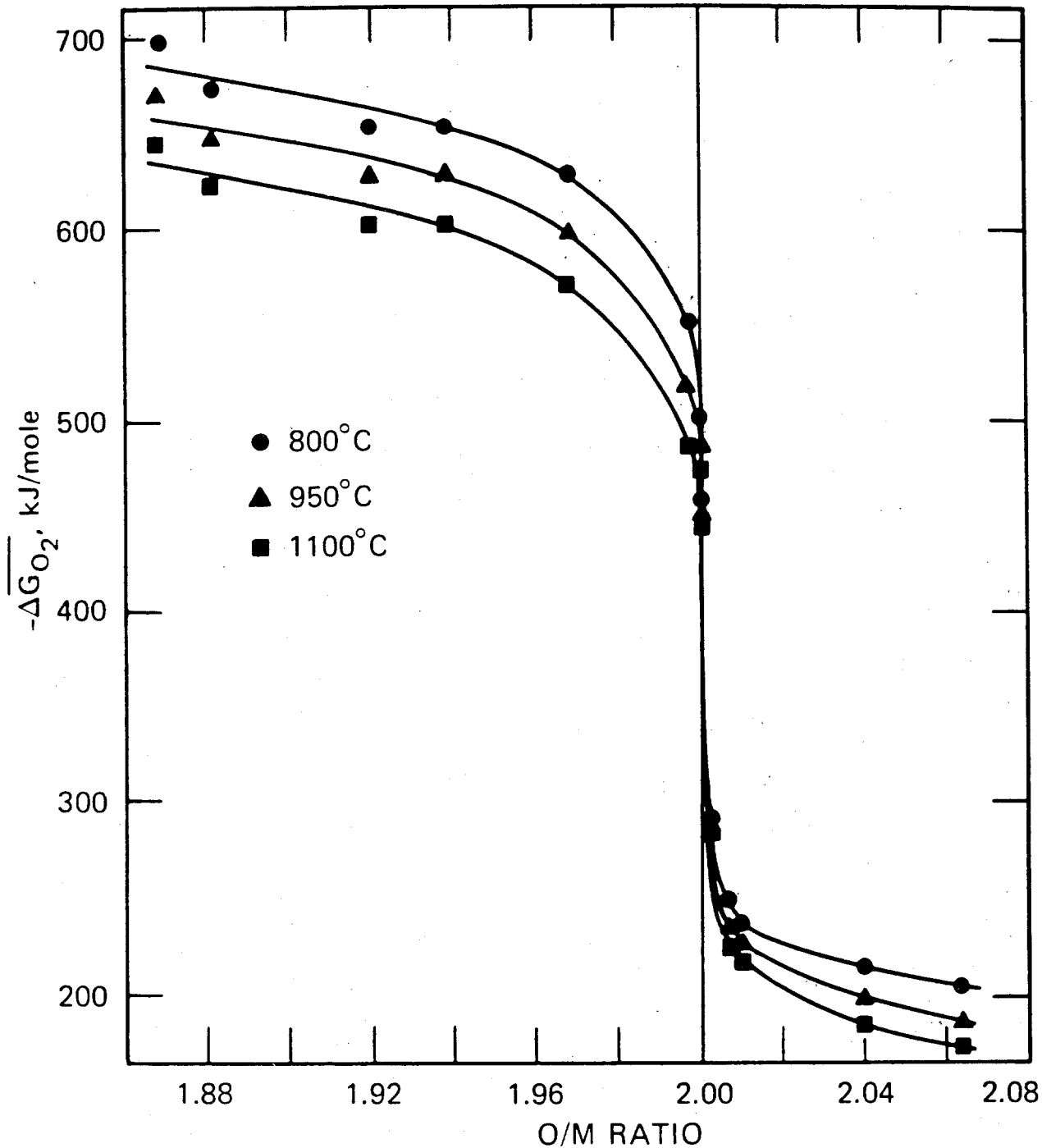


Fig. 11.12  $\Delta\overline{G}_{O_2}$  vs. O/M ratio for  $U_{0.70}Pu_{0.30}O_{2+x}$ . (From T. L. Markin and E. J. McIver, *Plutonium 1965*, A. E. Kay and M. D. Waldron (Eds.), p. 845, Chapman and Hall, London, 1965.)

Hypo	Hyper
$U^{+4} + O^{-2} = U^{+2} + \frac{O_2(g)}{2}$	$U^{+6} + O^{-2} = U^{+4} + \frac{O_2(g)}{2}$
$K_{2,4}^U = \frac{\sqrt{\Pi_{O_2}} \cdot [U^{+2}]}{[U^{+4}] \cdot [O^{-2}]}$	$K_{4,6}^U = \frac{\sqrt{\Pi_{O_2}} \cdot [U^{+4}]}{[U^{+6}] \cdot [O^{-2}]}$

[ ] = ions per U atom

$$\ln K_{2,4}^U = \left( \frac{78,300}{T} \right) + 13.6$$

$$\ln K_{4,6}^U = - \left( \frac{16,400}{T} \right) + 5.0$$

Normalization,

$$[U^{+2}] + [U^{+4}] + [U^{+6}] = 1$$

Electric Neutrality,

$$[O^{-2}] = 2 \pm x$$

$$[U^{+2}] + 2[U^{+4}] + 3[U^{+6}] = [O^{-2}]$$

- Can do the same for Pu oxide
- Can do the same for U-Pu oxide

$$[O^{-2}] = 2 \pm x = [U^{+2}] + [Pu^{+2}] + 3/2[Pu^{+3}] + 2[U^{+4}] + 2[Pu^{+4}] + 3[U^{+6}]$$

Then

- 1.) Solve equations for K's
- 2.) Express  $\Pi_{O_2}$  in terms of Conc. [ ], [ ], ..
- 3.) Sub. for conc. in last eq. above to get  $\Pi_{O_2-x}$  relationship

*Solves differences in figures 11.13 and 11.14*



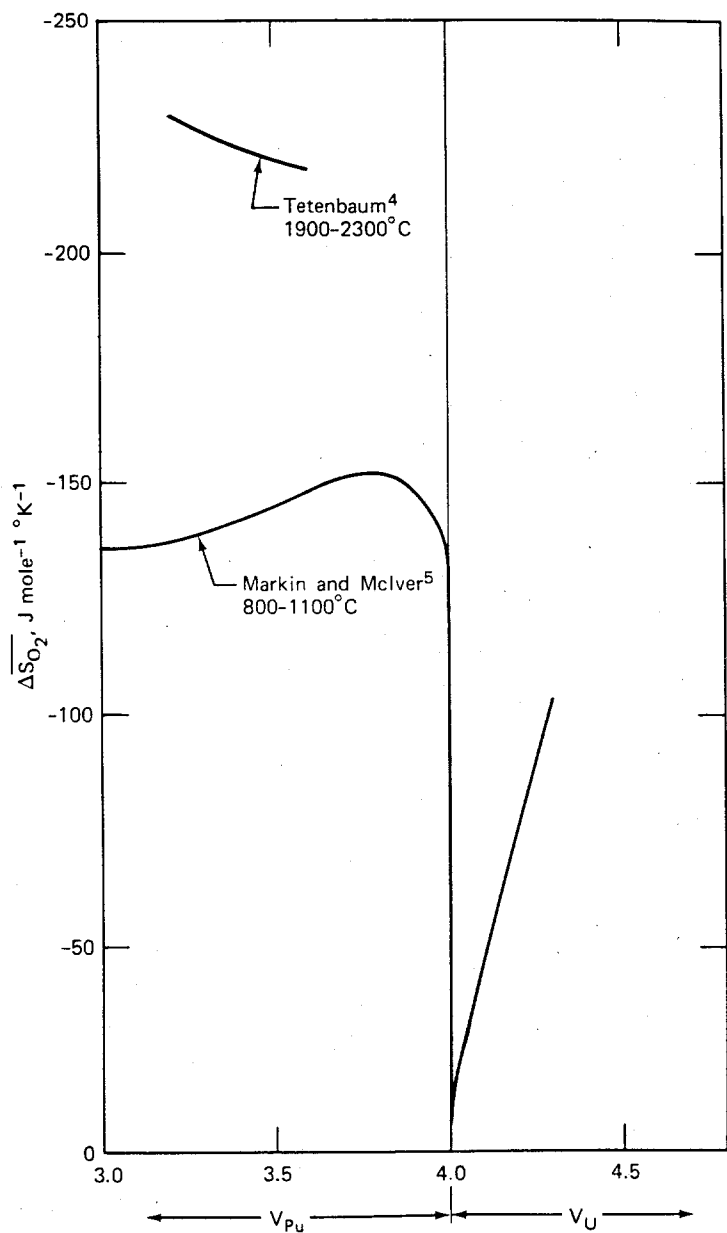


Fig. 11.13 Partial molar entropy of oxygen in mixed uranium-plutonium oxides.

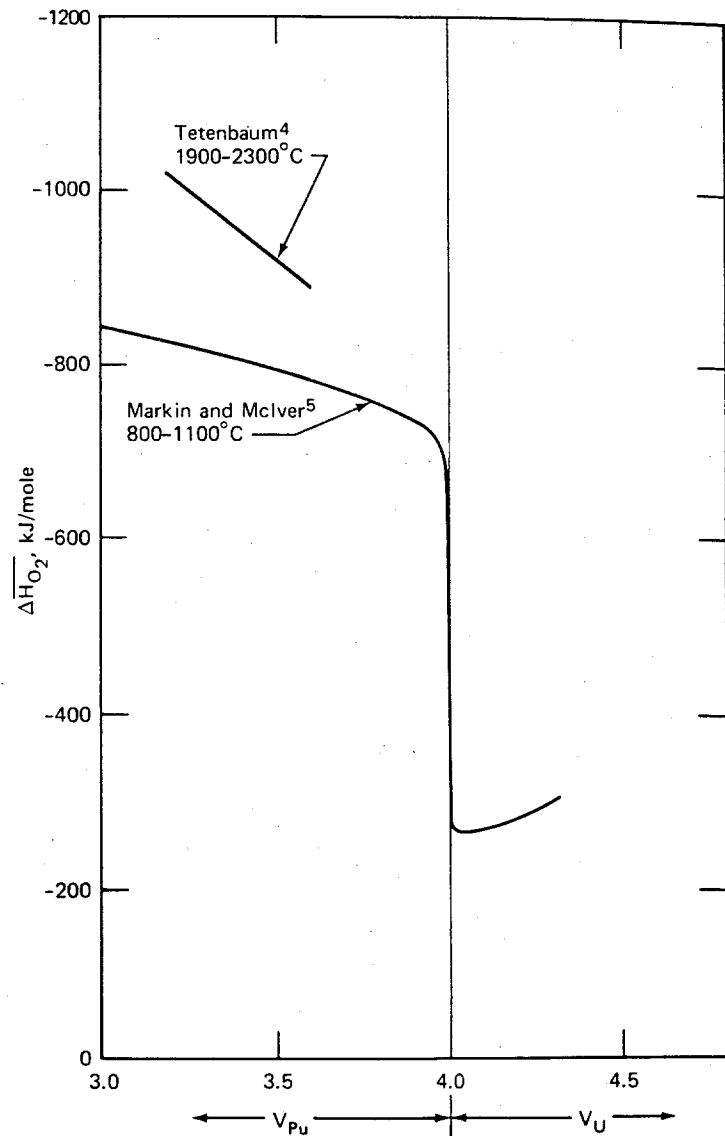


Fig. 11.14 Partial molar enthalpy of oxygen in mixed uranium-plutonium oxides.