

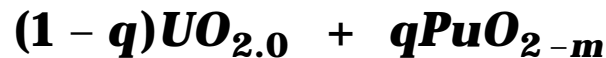
11.5 Thermochemistry of Fuel Vaporization

11.5.1 Gas-Solid Equilibria (Rand Markin)

Look at Other Components Besides Oxygen

Hypostoichiometric Oxides

Consider $(U_{1-q}Pu_q)O_{2-x}$



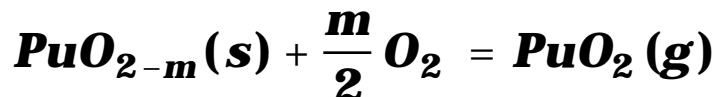
$$\text{where } m = \frac{x}{q}$$

Raoult's Law for partial pressure of UO₂ Over Solid

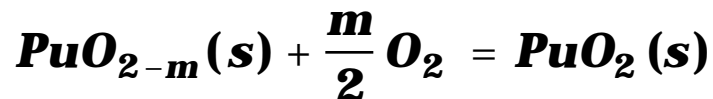
$$P_{UO_2} = (1 - q)P_{UO_2}^\circ$$

$$P_{UO_2} = (1 - q) \exp \frac{-G_{UO_2, \text{vap}}}{RT}$$

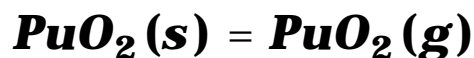
Vapor Pressure, of, pure, solid, UO₂



is the same as the sum of



and



$$PuO_2 = q \left(O_2 \right)^{\frac{m}{2}} \exp \frac{-G_{comp}^{\circ}}{RT}$$

$$G_{comp}^{\circ} = G_{PuO_{2-m}, PuO_{2(s)}}^{\circ} + G_{PuO_{2,vap}}^{\circ}$$

Hyperstoichiometric Oxides



note $UO_{2+m}(s) = UO_2(g) + \frac{m}{2} O_2(g)$

$$UO_2 = \frac{(1-q)}{\left\{ O_2 \right\}^{\frac{m}{2}}} \exp \frac{-G_{Comp}^{\circ}}{RT}$$

$$PuO_2 = q \exp \frac{-G_{PuO_{2,vap}}^{\circ}}{RT}$$

note that

$$G_{comp}^{\circ} = G_{UO_{2+x}(s), UO_2(g)}^{\circ} + G_{UO_{2,vap}}^{\circ}$$

11.5.2 Equilibria in the Gas Phase

(Rand Markin Model)

There are 9 components in the gas phase above the fuel:



To get the Composition of the Vapor

Determine O_2 from the oxygen potential of the fuel (section 11.4)

Get UO_2, PuO_2 from earlier eqs

Get atomic oxygen from 11.56

Get UO, PuO from eqs. 11.58, 11.61

Use monoxide pressures to determine U, Pu (11.57, 11.60)

Get UO_3 from UO_2 (11.59)

11.5.3 Another method of determining heavy metal oxide vapor pressures--- Blackburn

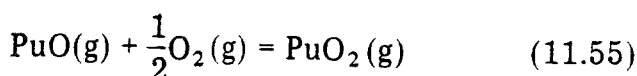
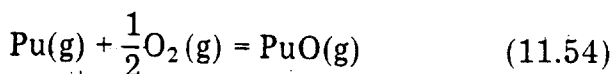
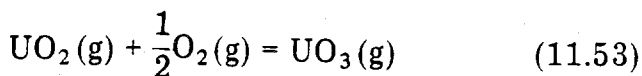
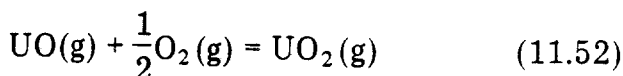
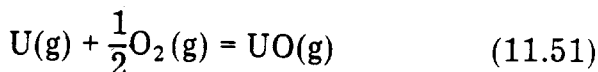
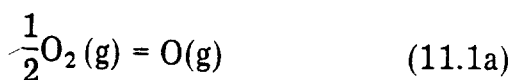
Note that

$$UO \quad [U^{+2}] \quad K_{UO} = \frac{UO}{[U^{+2}] \cdot [O^{-2}]}$$

$$UO_2 \quad [U^{+4}] \quad K_{UO_2} = \frac{UO_2}{[U^{+4}] \cdot 2[O^{-2}]}$$

11.5.2 Equilibria in the Gas Phase (Rand—Markin Model)

To the gas—solid equilibria just discussed we must add the requirements of equilibrium of all nine components in the gas phase above the fuel. These are



The equilibrium constants and standard-state free-energy changes of these reactions are

$$\frac{p_{\text{O}}}{(p_{\text{O}_2})^{1/2}} = \exp\left(-\frac{\Delta G_{\text{O}_2/\text{O}}^\circ}{RT}\right) \quad (11.56)$$

$$\frac{p_{\text{UO}}}{p_{\text{U}} (p_{\text{O}_2})^{1/2}} = \exp\left(-\frac{\Delta G_{\text{U}/\text{UO}}^\circ}{RT}\right) \quad (11.57)$$

$$\frac{p_{\text{UO}_2}}{p_{\text{UO}} (p_{\text{O}_2})^{1/2}} = \exp\left(-\frac{\Delta G_{\text{UO}/\text{UO}_2}^\circ}{RT}\right) \quad (11.58)$$

$$\frac{p_{\text{UO}_3}}{p_{\text{UO}_2} (p_{\text{O}_2})^{1/2}} = \exp\left(-\frac{\Delta G_{\text{UO}_2/\text{UO}_3}^\circ}{RT}\right) \quad (11.59)$$

$$\frac{p_{\text{PuO}}}{p_{\text{Pu}} (p_{\text{O}_2})^{1/2}} = \exp\left(-\frac{\Delta G_{\text{Pu}/\text{PuO}}^\circ}{RT}\right) \quad (11.60)$$

$$\frac{p_{\text{PuO}_2}}{p_{\text{PuO}} (p_{\text{O}_2})^{1/2}} = \exp\left(-\frac{\Delta G_{\text{PuO}/\text{PuO}_2}^\circ}{RT}\right) \quad (11.61)$$

In each of these equations the standard-state free-energy changes can be written

Note
 $p = \pi$
 in my notes

and $\ln K_i = \frac{-A_i}{\frac{T}{1000}} + B_i$

get A_i, B_i from table 11.1

and $[O^{-2}] = 2$

so,

$UO = 2K_{UO} [U^{+2}]$ get from U, O Eqs

$UO_2 = 4K_{UO_2} [U^{+4}]$

" " "

11.5.4 Knudsen Cell Mass Spectrometer Expts.

READ

See Figure 11.17

**Table 11.1 Constants in Eq. 11.74
of Blackburn's Model**

Species	A	B
UO	49.5	11.9
UO ₂	74.0	19.9
UO ₃	44.0	11.9
PuO	44.1	11.5
PuO ₂	72.5	18.8

**Table 11.2 Thermochemical Parameters of Reactions
Among Heavy-Metal Species***

Gas-phase reaction	ΔH° , kJ/mole	ΔS° , J mole ⁻¹ °K ⁻¹
$\frac{1}{2}\text{O}_2 = \text{O}$	257	68
$\text{U} + \frac{1}{2}\text{O}_2 = \text{UO}$	-528	-62
$\text{UO} + \frac{1}{2}\text{O}_2 = \text{UO}_2$	-471	-71
$\text{UO}_2 + \frac{1}{2}\text{O}_2 = \text{UO}_3$	-404	-90
$\text{Pu} + \frac{1}{2}\text{O}_2 = \text{PuO}$	-498	-46
$\text{PuO} + \frac{1}{2}\text{O}_2 = \text{PuO}_2 \dagger$	-352	-69
Vaporization of dioxides		
$\text{UO}_2(\text{s}) = \text{UO}_2(\text{g})$	567	150
$\text{PuO}_2(\text{s}) = \text{PuO}_2(\text{g})$	571	150

Also examine the results of partial Pressures over

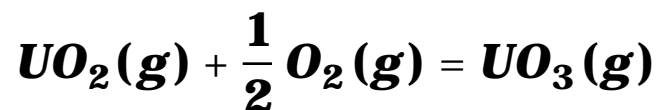


Figure 11.17

Key Features

Hyper-

1.) UO_3 is predominant



2.) $\frac{U}{Pu}$ is larger in vapor than in the solid (10^6 times)

3.) $\frac{O}{M}$ in vapor is higher than in solid which means the solid is losing oxygen.

Hypo-

1.) $\frac{U}{Pu}$ is smaller than in solid for $O/M < 1.96$ (means solid is losing Pu preferentially)

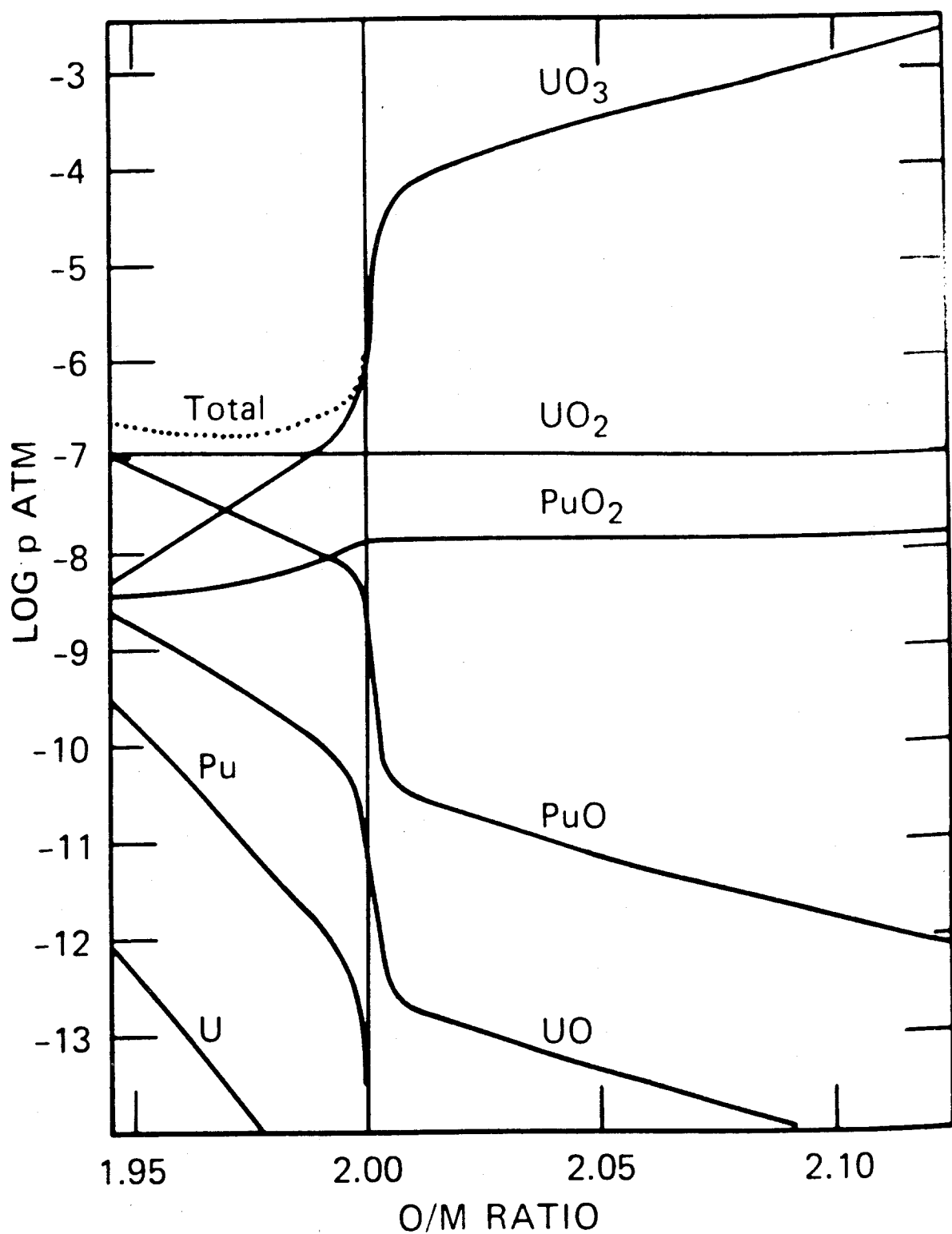


Fig. 11.17 Partial pressures over $\text{U}_{0.85}\text{Pu}_{0.15}\text{O}_{2 \pm x}$ at 2000°K (calculated). [From M. H. Rand and T. L. Markin, *Thermodynamics of Nuclear Materials—1967*, Symposium Proceedings, Vienna, 1967, p. 1007.]

11.6 Oxygen Redistribution

Because:

$$\ln \frac{O_2}{M} = \frac{\overline{G_{O_2}}}{RT} = \frac{\overline{H_{O_2}}}{RT} - \frac{\overline{S_{O_2}}}{R}$$

then

$O_2(r)$ and oxygen can move in the temperature gradient. If that happens, then the $\frac{O}{M}$ ratio is changed affecting;

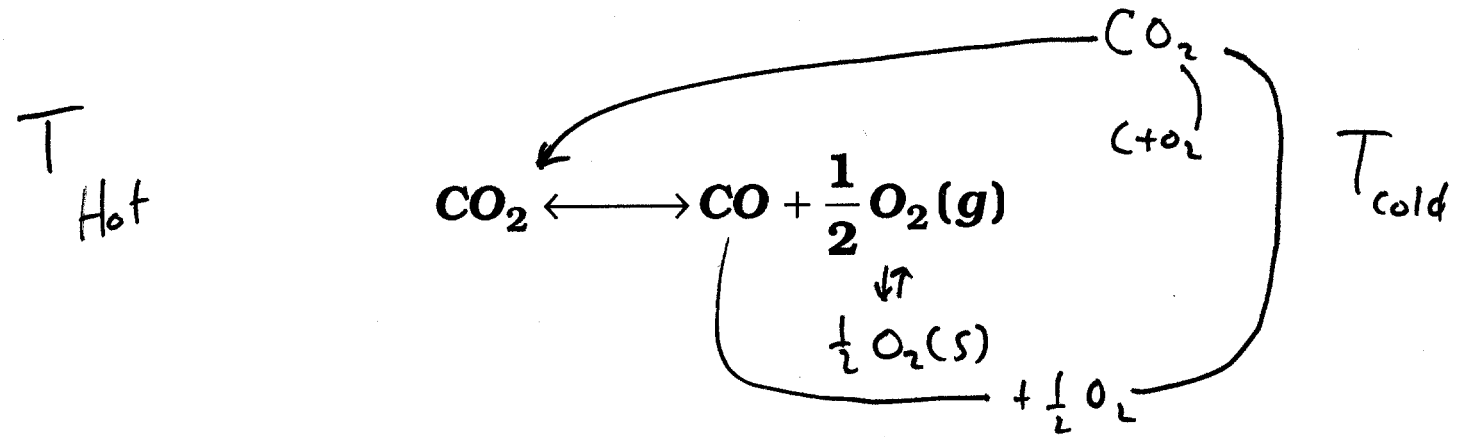
- **Thermal Conductivity (hence temperature)**
- μ_{O_2} (hence cladding corrosion)
- **creep strength of UO_2 (e.g., dimensional stability)**
- **Diffusion coefficients (e.g., bubble growth, solid element redistribution)**

11.6.1) Markin-Rand-Roberts Model

Assumes that carbon can transport oxygen through gas phase to one part of the fuel or another (H_2 diffuses out)

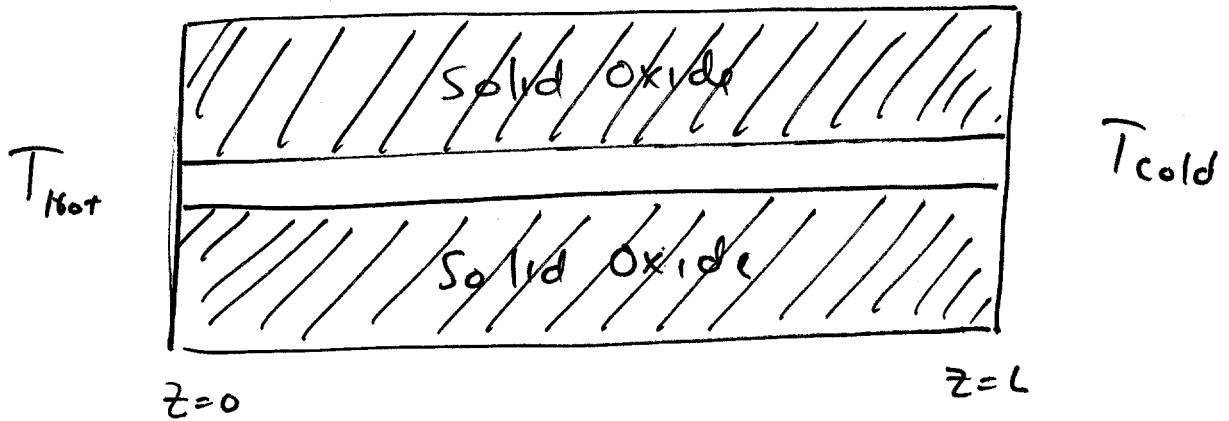
Note the type of data that comes out of the Knudsen Cell measurements ! (Table 11.2)

Hyperstoichiometric Fuel-Proposed Model



Model

(Assume rectangular coordinates + no net oxygen or carbon flux)



- 1.) Solve for carbon and oxygen balance
- 2.) Let local oxygen pressure correspond to oxygen potential of the fuel
- 3.) Assume the CO_2 , CO , and O_2 components are in thermodynamic equilibrium
- 4.) Know

$$\bar{x} = \frac{1}{L} \int_0^L x(z) dz$$

End Result

Hyper- fuel results in more oxygen at the hot end

Hypo-fuel results in more oxygen at the cold end

**See figures 11.19a (hyper)
11.19b (hypo)
11.20**

Explanation for hyper OK but the kinetics are wrong for Hypo

**possible that UO , UO_2 , UO_3
or PuO , PuO_2
or MoO_2 , MoO_3**

could account for transport

=====

11.6.2 Aitken Model

**Mainly aimed at Hypo case.
Assume,**

$$\ln x = \frac{Q^+}{RT} + \text{constant}$$

where Q^+ represents the combined effects of solid state diffusion and vapor migration and is negative (figure 11.21)

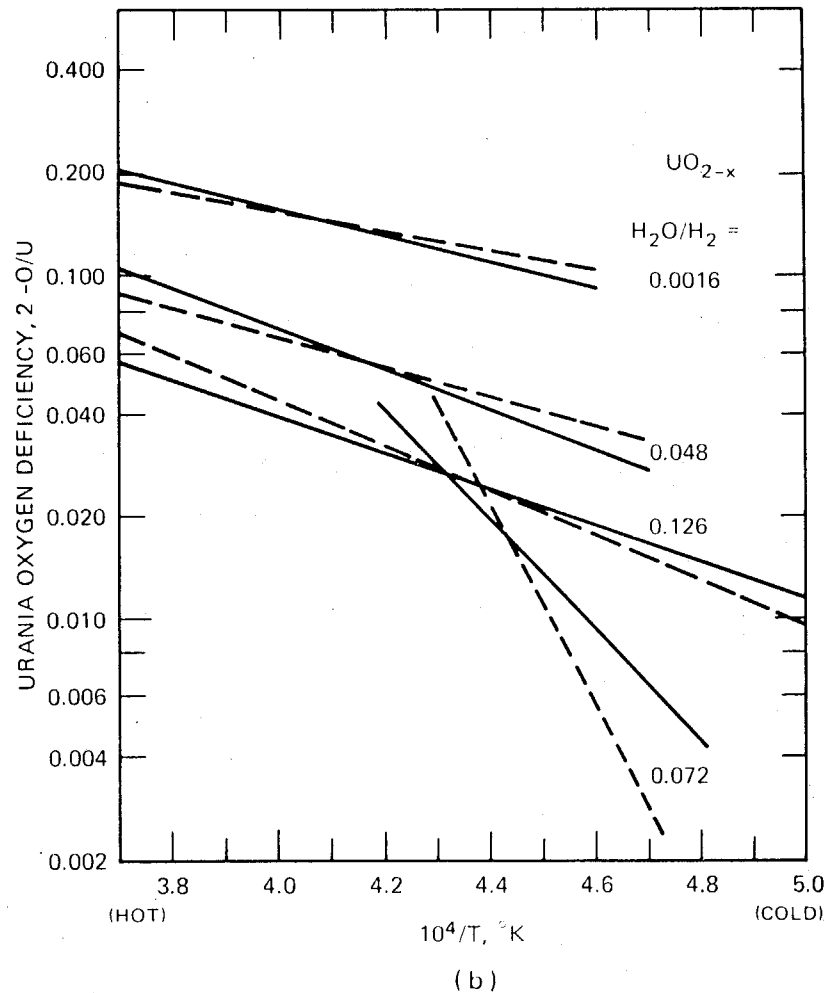
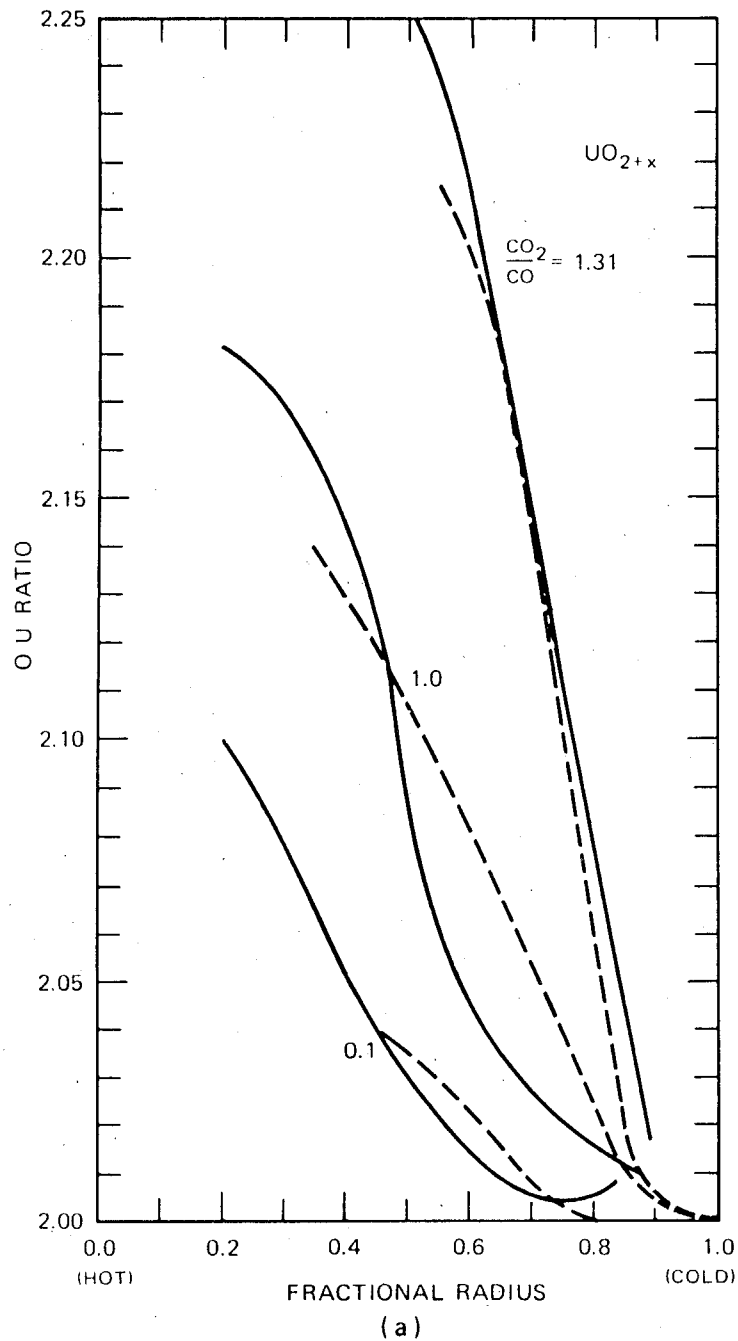


Fig. 11.19 Comparison of calculated and experimental O/U profiles in urania subject to a temperature gradient. [From P. O. Perron, *J. Nucl. Mater.*, 27: 237 (1968).] (a) —, after J. A. Christensen, USAEC Report BNWL-536, 1967. - - -, calculated. (b) —, after R. E. Fryxell, USAEC Report GEMP-516, 1967. - - -, calculated.

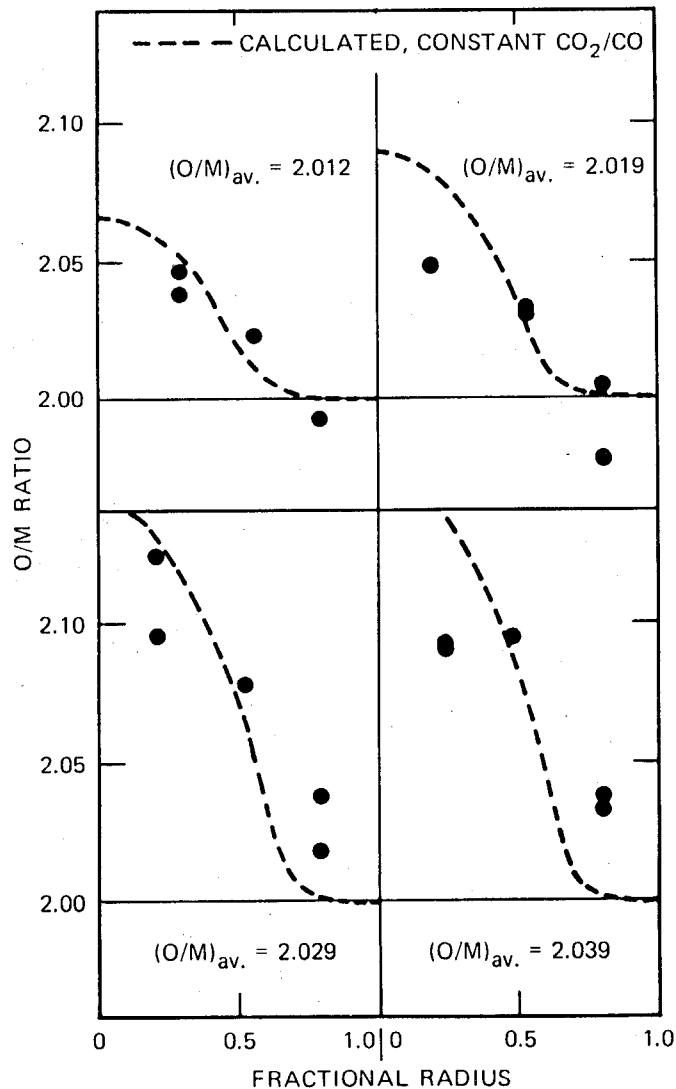


Fig. 11.20 Comparison of experimental oxygen redistribution results and the predictions of the Rand-Markin model for $(U,Pu)O_{2+x}$. (From A. T. Jeffs, Canadian Report AECL-3690, 1970.)

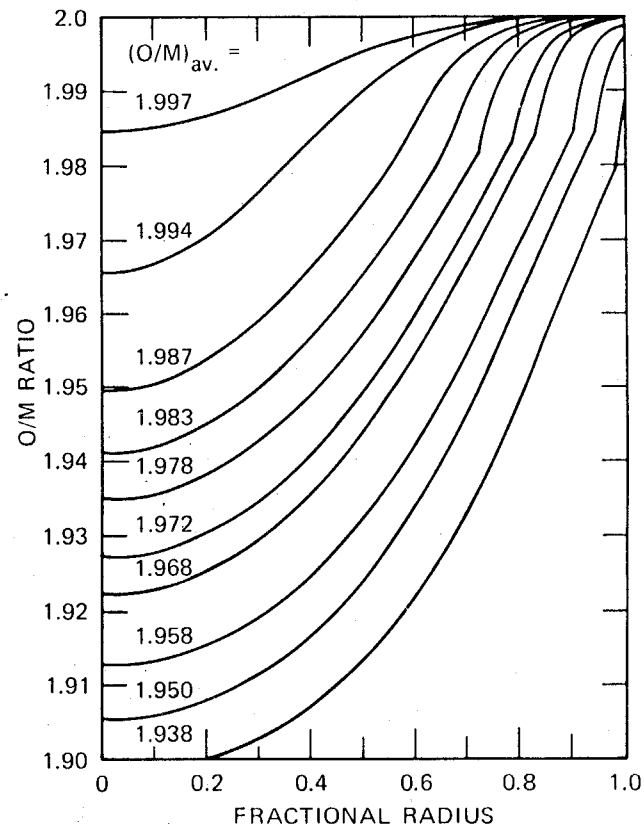


Fig. 11.21 Stoichiometry profiles for irradiation at a linear power of 500 W/cm with 700°C fuel surface temperature using heat of transport from experiments without artificial barriers. (From E. A. Aitken et al., USAEC Report GEAP-12254, General Electric Company, 1971.)

11.6.3 Bober-Schumacher Model

Observed that there must be solid state diffusion. It was postulated that oxygen vacancies migrate to the hottest part of the fuel which causes the $\frac{O}{M}$ ratio to drop.



Measured Q^+ and found that it was close to that in Aitkens Model.

11.7 Actinide Redistribution

Pu and U can redistribute in a fuel pellet to;

**1.) Cause Pu to increase at the hot zone
(Fig. 11.22) --> Thermal diffusion**

**2.) Cause U to increase at the pellet
surface ---> Vapor transport**

Both of these effects change the temperature profile, further aggravating the situation.

11.7.1 Thermal Diffusion of Pu

Check Chapter 7 for more details!

For small Pu concentrations

$$J_{\text{Pu}} = -D_{\text{Pu}} \frac{C_{\text{Pu}}}{r} + \frac{Q^* C_{\text{Pu}}}{RT^2} \frac{T}{r} \quad 1)$$

**where Q^* = heat of transport of Pu in
the fuel (empirical det'd)**

$$\text{and, } D_{\text{Pu}} = D_o \exp -\frac{E}{RT} \quad 2)$$

**Says that Pu
migrates down
conc. gradient**

**Says Pu will migrate
down a temp. gradient
if Q^* is positive and
up a temp. gradient if
 Q^* is negative**

Assume T/r , $T(r)$ are known or can be solved for.

**Assuming that steady state is not achieved
during normal fuel lifetime**

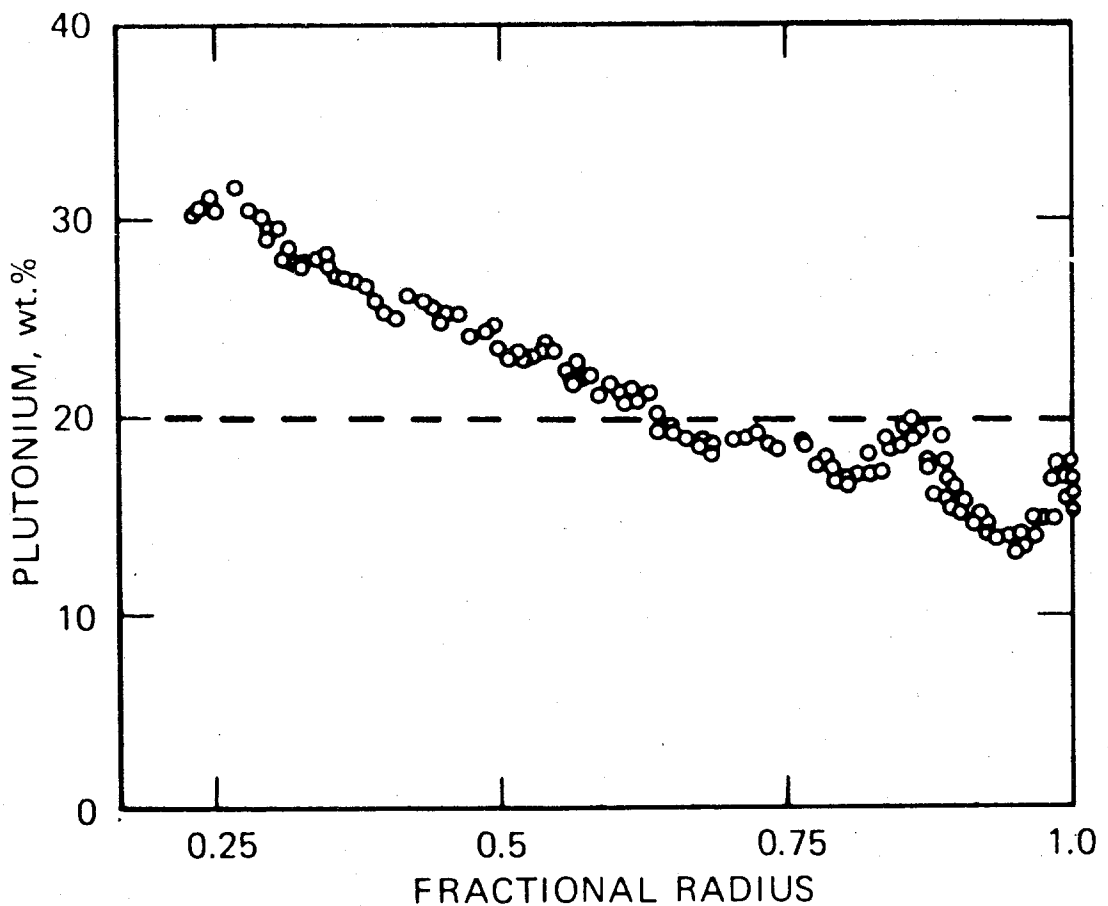


Fig. 11.22 Plutonium redistribution in a fuel element initially containing 20% plutonium uniformly distributed. The element was irradiated to a burnup of 5% at a linear power of 660 W/cm. (From R. Natesh and D. R. O'Boyle, USAEC Report ANL-7669, p. 107, Argonne National Laboratory, 1970.)

$$\frac{C_{Pu}}{t} = - \frac{1}{r} \frac{(rJ_{Pu})}{r} \quad 3)$$

(see Eq. 7.6)

 Substitute eq. 1) into 3) and solve for $\frac{C_{Pu}}{r}$

also, $C_{Pu}(r, 0) = C_{Pu0}^{\circ}$
 $C_{Pu}(r, t) = C_{Pu0}^{\circ}$

(This means that relative diffusion coefficient is so low that nothing changes)

and, $J_{Pu} = 0 @ r = r_0$ (central void)
 $J_{Pu} = 0 @ r = R$

and, $\frac{C_{Pu}}{r} = 0$

r_0
 See figures 11.23 a&b (note lack of equilibrium)

11.7.2 Vapor Transport

From before (fig. 11.17), we saw that in stoichiometric or hyperstoichiometric fuel, UO_3 is the dominant species.

When fuel pellet contains cracks, UO_3 goes from the hot end to cold end, thus enriching the surface with U.

However, when $\frac{O}{M} < 1.96$, Pu will also migrate down temp.gradients.

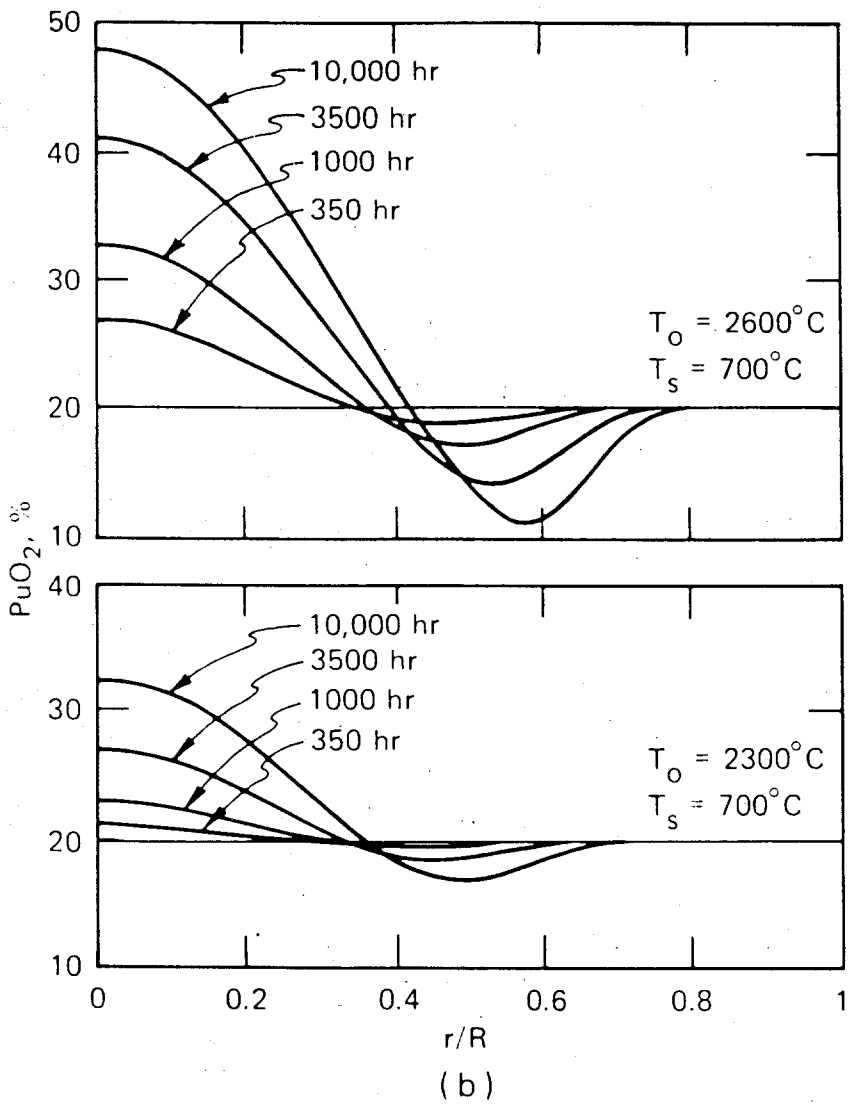


Fig. 11.23 Plutonium redistribution in mixed-oxide fuels due to a thermal gradient. (a) After 110 hr annealing in an axial temperature gradient. (b) Calculated for an LMFBR fuel rod with a parabolic temperature distribution (restructuring not considered). [From H. Beisswenger, M. Bober, and G. Schumacher, *Plutonium as a Reactor Fuel*, Symposium Proceedings, Brussels, 1967, pp. 273-282, International Atomic Energy Agency, Vienna, 1967 (STI/PUB/153).]