

## Problem 11.4

Calculate  $p_{O_2}$  in equilibrium with



@ 2241 °K (Use Rand Marlin Thermodynamics)

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Valences

$$\begin{aligned}V_U = 4, \quad V_{Pu} &= 4 - \frac{2x}{q} \\ &= 4 - (0.04/0.2) \\ &= 3.8\end{aligned}$$

From Figure 11.13 (using the higher temperature extrapolated data)

$$\overline{S}_{O_2} = -210 \text{ J/mole } ^\circ\text{K}$$

From Figure 11.14

$$\overline{H}_{O_2} = -840 \text{ kJ/mole}$$

and

$$\overline{G}_{O_2} = -840 + 0.21 \cdot (2241)$$

$$\overline{G}_{O_2} = -370 \text{ kJ/mole}$$

Also,

$$\overline{G}_{O_2} = RT \ln (p_{O_2})$$

But the problem wants the atomic partial pressure

**For atomic oxygen,**



**Equilibrium requires:**

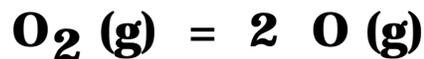
$$K_p = \frac{O}{\sqrt{O_2}}$$

$$\ln K_p = \ln O - \frac{1}{2} \ln O_2$$

**or,**

$$\ln O = \ln K_p + \frac{1}{2} \ln O_2$$

**From Table 11.2 we can calculate the equilibrium between atomic and molecular oxygen**



$$H^\circ = 514 \text{ kJ/mole}$$

$$S^\circ = 136 \text{ J/mole } ^\circ\text{K}$$

$$\text{Therefore } K = \frac{O^2}{O_2} = K_p^2 = \exp \frac{-G^\circ}{RT}$$

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$$G^\circ = H^\circ - T S^\circ$$

$$= 514 - 2241 \cdot 0.136$$

$$= 209 \text{ kJ/mole}$$

**Now**

$$K_p = \exp (-G^\circ/2RT)$$

$$= \exp (-209/2 \cdot 0.008314 \cdot 2241)$$

$$= \exp (-5.61)$$

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**Finally,**

$$\ln p_{O} = \ln K_p + \frac{1}{2} \ln p_{O_2}$$

$$= -5.61 + [ (-370)/2 \cdot (0.00813 \cdot 2241) ]$$

$$= -5.61 - 10.15$$

$$= -15.76$$

**or,**

$$p_{O} = 1.4 \cdot 10^{-7} \text{ atmospheres}$$

## 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**

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

- **Thermal Conductivity (hence temperature)**
- $\mu_{O_2}$  (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**

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**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**

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**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)**

### 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.***

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### 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**

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

(see Eq. 7.6)

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 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)

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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.