PROBLEM 11.1 **From reaction equation:**

$$H_2(g) + \frac{1}{2} O_2(g) \longleftrightarrow H_2O(g)$$

@ 1500°K (remember 1 cal = 4.18 J)

$$\Delta G^\circ_{H_2O} = -58.9 + 13.1 \bullet 1.5 = -39.2 \frac{kcal}{mole}$$

but, $\Delta G^\circ_{H_2O} = -RT \ln K_{H_2O}$

$$\Delta G^\circ_{H_2O} = -RT \ln \left[\frac{\Pi_{H_2O}}{\Pi_{H_2} \sqrt{\Pi_{O_2}}} \right]$$

$$\left[\frac{\Pi_{H_2O}}{\Pi_{H_2}} \right] = 1 \quad \text{equal partial pressures}$$

$$RT \ln \Pi_{O_2} = 2\Delta G^\circ_{H_2O} = -78.4 \text{ kcal/mole} \quad (1)$$

Now, above UO_{2+x} **at 1500°K**

$$\overline{\Delta G_{O_2}} = RT \ln \Pi_{O_2} = \overline{\overline{\Delta H_{O_2}}} - \overline{\overline{\Delta S_{O_2}}} \left(\frac{T}{1000} \right) \frac{kcal}{mole}$$

Using $RT \ln \Pi_{O_2}$ **from eq.1, and**
$\Delta H_{O_2}, \Delta S_{O_2}$ **from.problem**

-78.4 = -125+16,000x-1.5(-29+6,600x) = -81.5+6,100x

x=0.00051 and $UO_{2.0005}$

Problem 11.2

In General,

$$\Pi_{O_2} = \text{constant (with radius)}$$

$$\overline{\Delta G_{O_2}} = RT \ln \Pi_{O_2} = \overline{\Delta H_{O_2}} - T\overline{\Delta S_{O_2}}$$

$$= -65 + 120\ RTx \qquad \text{kcal/mole}$$

(T in units of 1000 °K)

$$\text{or,}\ x = \frac{1}{120}\left\{ \ln \Pi_{O_2} + \frac{65}{RT} \right\} \qquad 1.)$$

and

$$\left(\frac{T - T_s}{T_o - T_s}\right) = 1 - \left(\frac{r}{R}\right)^2$$

a.)

$$\bar{x} = \frac{1}{\pi R^2}\int_0^R 2\pi r \bullet x(r) \bullet dr$$

$$\eta = \left(\frac{r}{R}\right)^2, d\eta = \frac{2r}{R^2}\, dr$$

Then, $T = T_s - (T_o - T_s)(1 - \eta)$

$$\bar{x} = \int_0^1 x(\eta)\,d\eta$$

$$\bar{x} = \frac{1}{120}\int_0^1 \left[\ln \Pi_{O_2} + \frac{65}{RT_s\left[1 + \frac{T_0 - T_s}{T_s}(1-\eta)\right]}\right] d\eta$$

Solving;

$$\ln \Pi_{O_2} = 120\bar{x} - \frac{65}{R(T_O - T_s)} \ln\left(\frac{T_O}{T_s}\right)$$

or since $\bar{x} = 0.05$

$$\ln \Pi_{O_2} = 120 \bullet 0.05 - \frac{65}{1.98(1.5)} \ln(2.5)$$

$$= -14.1$$

$$\Pi_{O_2} = 7.5x10^{-7}\,\text{atm} \quad (6 \text{ x } 10^{-4} \text{ torr})$$

b.) to plot x(r), use eq. 1

$$x = \frac{1}{120}\left\{\ln \Pi_{O_2} + \frac{65 \bullet 1}{RT}\right\}$$

$$= -\frac{14.1}{120} + \frac{65}{1.98 \bullet 120 \bullet T}$$

$$= -0.1175 + 0.274\left(\frac{1}{T}\right)$$

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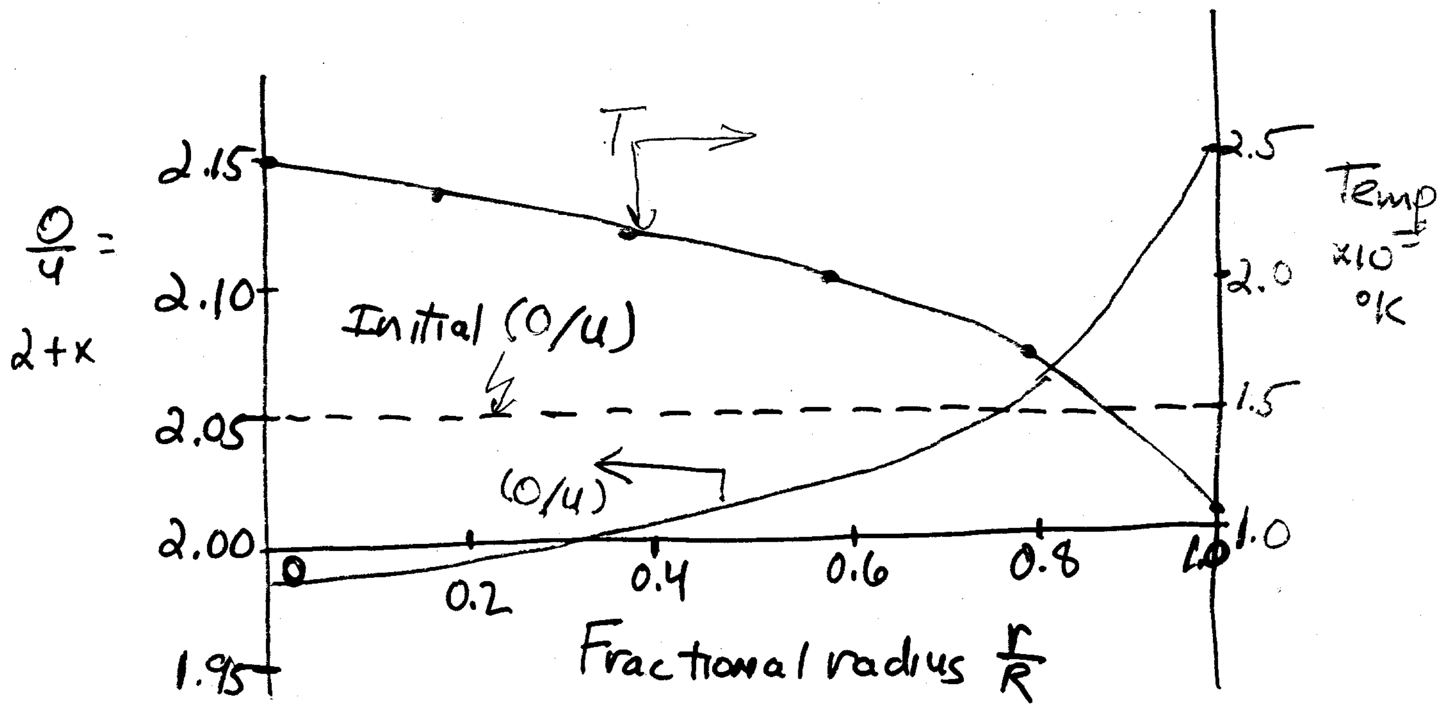
Use x from above with parabolic temperature Profile to get x(R)



$$\overline{\Delta G_{O_2}} = RT_s \ln \Pi_{O_2}$$

$$= 1.98 \cdot 1.00 \cdot (-14.1)$$

$$= -28 \text{ kcal}$$

in chapter 12 we will see that

$$Zr + O_2 (g) \rightarrow ZrO_2$$

$$1000°K \approx -220 \text{ kcal/mole}$$

$\overline{\Delta G^\circ_{O_2}} > \overline{\Delta G^\circ_{Zr}}$ **cladding oxidized. We shall see later that oxide layer prevents oxidation from occurring too fast.**