PROBLEM 11.1 From reaction equation:
\[ \text{H}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightleftharpoons \text{H}_2\text{O}(g) \]

@ 1500°K (remember 1 cal = 4.18 J)

\[ \Delta G_{\text{H}_2\text{O}}^\circ = -58.9 + 13.1 \cdot 1.5 = -39.2 \text{ kcal/mole} \]

but, \[ \Delta G_{\text{H}_2\text{O}}^\circ = -RT \ln K_{\text{H}_2\text{O}} \]

\[ \Delta G_{\text{H}_2\text{O}}^\circ = -RT \ln \left[ \frac{\Pi_{\text{H}_2\text{O}}}{\Pi_{\text{H}_2} \sqrt{\Pi_{\text{O}_2}}} \right] \]

\[ \left[ \frac{\Pi_{\text{H}_2\text{O}}}{\Pi_{\text{H}_2}} \right] = 1 \text{ equal partial pressures} \]

\[ RT \ln \Pi_{\text{O}_2} = 2 \Delta G_{\text{H}_2\text{O}}^\circ = -78.4 \text{ kcal/mole} \ (1) \]

Now, above UO_{2+x} at 1500°K

\[ \Delta G_{\text{O}_2} = RT \ln \Pi_{\text{O}_2} = \Delta H_{\text{O}_2} - \Delta S_{\text{O}_2} \left( \frac{T}{1000} \right) \text{ kcal/mole} \]

Using \( RT \ln \Pi_{\text{O}_2} \) from eq.1, and \( \Delta H_{\text{O}_2}, \Delta S_{\text{O}_2} \) from problem

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

\[ x = 0.00051 \text{ and UO}_2.0005 \]
Problem 11.2

In General,

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

\[ \Delta G_{O_2} = RT \ln \Pi_{O_2} = \Delta H_{O_2} - T \Delta S_{O_2} \]

\[ = -65 + 1200 \times R \times T \times x \quad \text{kcal/mole} \]  
\[ \text{(T in units of 1000 °K)} \]

or, \[ x = \frac{1}{120} \left\{ \ln \Pi_{O_2} + \frac{65}{R} \right\} \]

and

\[ \left( \frac{T - T_s}{T_0 - T_s} \right) = 1 - \left( \frac{r}{R} \right)^2 \]

\[ a.) \]

\[ \bar{x} = \frac{1}{\pi R^2} \int_{0}^{R} 2\pi r \cdot x(r) \cdot dr \]

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

Then, \[ T = T_s - (T_0 - T_s)(1 - \eta) \]
\[ \bar{x} = \int_{0}^{1} x(\eta) d\eta \]

\[ \bar{x} = \frac{1}{120} \int_{0}^{1} \left[ \ln \Pi_{O_2} + \frac{65}{RT_s} \left[ 1 + \frac{T_0 - T_s}{T_s} (1 - \eta) \right] \right] d\eta \]

Solving:

\[ \ln \Pi_{O_2} = 120 \bar{x} - \frac{65}{R(T_0 - T_s)} \ln \left( \frac{T_0}{T_s} \right) \]

or since \( \bar{x} = 0.05 \)

\[ \ln \Pi_{O_2} = 120 \cdot 0.05 - \frac{65}{1.98(1.5)} \ln(2.5) \]

\[ = -14.1 \]

\[ \therefore \Pi_{O_2} = 7.5 \times 10^{-7} \text{ atm} \quad (6 \times 10^{-4} \text{ torr}) \]

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

\[ x = \frac{1}{120} \left\{ \ln \Pi_{O_2} + \frac{65 \cdot 1}{RT} \right\} \]

\[ = -14.1 \cdot \frac{1}{120} + \frac{65}{1.98 \cdot 120 \cdot T} \]

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

Use \( x \) from above with parabolic temperature profile to get \( x(R) \)
\[
\Delta G_{O_2} = RT_s \ln \Pi_{O_2}
\]

\[
= 1.98 \cdot 1.00 \cdot (-14.1)
\]

\[
= -28 \text{ kcal}
\]

in chapter 12 we will see that

\[
\text{Zr} + \text{O}_2 (g) \rightarrow \text{ZrO}_2
\]

\[
1000^\circ \text{K} \approx -220 \text{ kcal/mole}
\]

\[
\Delta G_{O_2}^\circ > \Delta G_{Zr}^\circ \text{ cladding oxidized. We shall see later that oxide layer prevents oxidation from occurring too fast.}
\]