Problem 11.4

Calculate Π_O in equilibrium with

$$(U_{0.8}\ Pu_{0.2})\ O_{1.98}$$

@ 2241 °K (Use Rand Markin Thermodynamics)

Valences

$$V_U = 4 \quad , \quad V_{Pu} = 4 - \left(\frac{2x}{q}\right)$$

$$= 4 - (0.04/0.2)$$

$$= 3.8$$

From Figure 11.13 (using the higher temperature extrapolated data)

$$\overline{\Delta S_{O_2}} \approx -210 \text{ J/mole °K}$$

From Figure 11.14

$$\overline{\Delta H_{O_2}} \approx -840 \text{ kJ/mole}$$

and

$$\overline{\Delta G_{O_2}} = -840 + 0.21 \bullet (2241)$$

$$\overline{\Delta G_{O_2}} = -370 \text{ kJ/mole}$$

Also,

$$\overline{\Delta G_{O_2}} = RT \ln (\Pi_{O_2})$$

But the problem wants the atomic partial pressure

For atomic oxygen,

$$1/2\ O_2\ (g) = O\ (g)$$

Equilibrium requires:

$$K_p = \frac{\Pi_O}{\sqrt{\Pi_{O_2}}}$$

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

or,

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

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

$$O_2\ (g) = 2\ O\ (g)$$

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

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

Therefore $K = \frac{\Pi_O^2}{\Pi_{O_2}} = K_p^2 = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$

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

= 514 - 2241 • 0.136

= 209 kJ/mole

Now

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

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

$$= \exp(-5.61)$$

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Finally,

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

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

$$= -5.61 - 10.15$$

$$= -15.76$$

or,

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