

Problem 11.4

Calculate p_{O_2} in equilibrium with



@ 2241 °K (Use Rand Marlin Thermodynamics)

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:

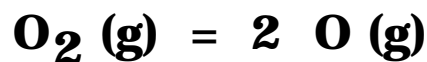
$$K_p = \frac{O}{\sqrt{O_2}}$$

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

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



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

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

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

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

$$= 514 - 2241 \cdot 0.136$$

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

Now

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

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

$$= \exp (-5.61)$$

Finally,

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

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

$$= -5.61 - 10.15$$

$$= -15.76$$

or,

$$p_{O_2} = 1.4 \cdot 10^{-7} \text{ atmospheres}$$

Problem 11.5

a.) $\overline{G}_{O_2} = \overline{H}_{O_2}(x) - T \overline{S}_{O_2}(x)$

From figure 11.10 for $x=0.2$

$$\overline{H}_{O_2} = -315 \text{ kJ/mole}$$

$$\overline{S}_{O_2} = -0.126 \text{ kJ/mole-}^\circ\text{K}$$

$$\begin{aligned}\overline{G}_{O_2} &= -315 + 1873 \cdot 0.126 \\ &= -79 \text{ kJ/mole}\end{aligned}$$

$$o_2 = \exp \frac{\overline{G}_{O_2}}{RT}$$

$$\begin{aligned}&= \exp -\frac{79}{8.31 \cdot 1.873} \\ &= 0.0062 \text{ atm}\end{aligned}$$

From figure 11.6

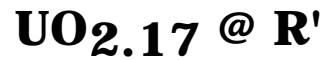
$$o_{2-} = 0.01 \text{ atm}$$

b.) Following the $o_{2-} = 0.01 \text{ atm}$ isobar, U_5O_{13} precipitates out at point Q, $T = 1350^\circ\text{K}$

The other phase is $UO_{2.25}$

c.) Cooling at constant $\frac{O}{U}$ to 800°C (point R) the

two phases present are;



Relative Amounts- (assuming 1 mole of $\text{UO}_{2.2}$ initially)

Let f = fraction of $\text{UO}_{2.17}$ in the mixture

Oxygen Balance:

$$2.17 f + 2.23(1-f) = 2.2$$

$$f=0.5$$

$$\text{o}_2 \quad 5 \times 10^{-10} \text{ atm @ T}$$