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)

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

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

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

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

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

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 11.5

a.) \[ \Delta G_{O_2} = \Delta H_{O_2}(x) - T \Delta S_{O_2}(x) \]

From figure 11.10 for \( x = 0.2 \)

\[ \Delta H_{O_2} = -315 \text{ kJ / mole} \]

\[ \Delta S_{O_2} = -0.126 \text{ kJ / mole} - ^oK \]

\[ \Delta G_{O_2} = -315 + 1873 \cdot 0.126 \]
\[ = -79 \text{ kJ / mole} \]

\[ \Pi_{O_2} = \exp \left( \frac{\Delta G_{O_2}}{RT} \right) \]
\[ = \exp \left( -\frac{79}{8.31 \cdot 1.873} \right) \]
\[ = 0.0062 \text{ atm} \]

From figure 11.6

\[ \Pi_{O_{2-}} = 0.01 \text{ atm} \]

b.) Following the \( \Pi_{O_{2-}} = 0.01 \text{ atm} \) isobar, \( U_5O_{13} \) precipitates out at point Q, \( T = 1350^oK \)

The other phase is \( UO_{2.25} \)

c.) Cooling at constant \( \frac{O}{U} \) to 800 °C (point R) the
two phases present are;

\[ \text{UO}_2.17 \ @ \ R' \]
\[ \text{UO}_2.23 \ @ \ R'' \]

Relative Amounts- (assuming 1 mole of \text{UO}_2.2 initially)

Let \( f \) = fraction of \text{UO}_2.17 in the mixture

Oxygen Balance:
\[ 2.17f + 2.23(1-f) = 2.2 \]
\[ f = 0.5 \]

\[ \Pi_{O_2} \approx 5 \times 10^{-10} \text{ atm @ T} \]
11.5 Thermochemistry of Fuel Vaporization

11.5.1 Gas-Solid Equilibria (Rand Markin)

Look at Other Components Besides Oxygen

**Hypostoichiometric Oxides**

Consider

\[
(U_{1-q}Pu_q)O_{2-x}
\]

\[
(1 - q)UO_{2.0} + qPuO_{2-m}
\]

where \( m = \frac{x}{q} \)

Raoult’s Law for partial pressure of \( UO_2 \) Over Solid

\[
\Pi_{UO_2} = (1 - q)P^o_{UO_2}
\]

\[
\Pi_{UO_2} = (1 - q) \exp \left\{ -\frac{\Delta G_{UO_2, vap}}{RT} \right\}
\]

\( \text{Vapor Pressure of pure solid } UO_2 \)

\[PuO_{2-m}(s) + \frac{m}{2}O_2 = PuO_2(g)\]

is the same as the sum of

\[PuO_{2-m}(s) + \frac{m}{2}O_2 = PuO_2(s)\]

and

\[PuO_2(s) = PuO_2(g)\]
\[ \Pi_{PuO_2} = q \left( \Pi_{O_2} \right)^{\frac{m}{2}} \exp \left\{ \frac{-\Delta G_{comp}^\circ}{RT} \right\} \]

\[ \Delta G_{comp}^\circ = \Delta G_{PuO_{2-m},PuO_2(s)}^\circ + \Delta G_{PuO_2,vap}^\circ \]

**Hyperstoichiometric Oxides**

\[(U_{1-q}Pu_q)O_{2+x}\]

\[(1-q)UO_{2+x} \quad qPuO_2\]

**note** \[UO_{2+m}(s) = UO_2(g) + \frac{m}{2}O_2(g)\]

\[\Pi_{UO_2} = \left[ \frac{(1-q)}{m} \left\{ \Pi_{O_2} \right\}^{\frac{m}{2}} \right] \exp \left\{ \frac{-\Delta G_{Comp}^\circ}{RT} \right\} \]

\[\Pi_{PuO_2} = q \exp \left\{ \frac{-\Delta G_{PuO_2,vap}^\circ}{RT} \right\} \]

**note that**

\[\Delta G_{comp}^\circ = \Delta G_{UO_{2+x}(s),UO_2(g)}^\circ + \Delta G_{UO_2,vap}^\circ\]
11.5.2 Equilibria in the Gas Phase
(Rand Markin Model)

There are 9 components in the gas phase above the fuel:

\[ O, O_2, U, UO, UO_2, UO_3, Pu, PuO, PuO_2 \]

(see equations)

To get the Composition of the Vapor

<table>
<thead>
<tr>
<th>Determine (O_2) from the oxygen potential of the fuel (section 11.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Get (UO_2, PuO_2) from earlier eqs</td>
</tr>
<tr>
<td>Get atomic oxygen from 11.56</td>
</tr>
<tr>
<td>Get (UO, PuO) from eqs. 11.58, 11.61</td>
</tr>
<tr>
<td>Use monoxide pressures to determine (U, Pu) (11.57, 11.60)</td>
</tr>
<tr>
<td>Get (UO_3) from (UO_2) (11.59)</td>
</tr>
</tbody>
</table>

11.5.3 Another method of determining heavy metal oxide vapor pressures--- Blackburn

Note that

\[ \Pi_{UO} \propto [U^{+2}] \quad K_{UO} = \frac{\Pi_{UO}}{[U^{+2}] \cdot [O^{-2}]} \]

\[ \Pi_{UO_2} \propto [U^{+4}] \quad K_{UO_2} = \frac{\Pi_{UO_2}}{[U^{+4}] \cdot 2[O^{-2}]} \]
and  $\ln K_i = \left\{ \frac{-A_i}{T} \right\} \left( \frac{T}{1000} \right) + B_i $

get $A_i, B_i$ from table 11.1

and  $[O^{-2}] \approx 2$

so,

$\Pi_{UO} \approx 2K_{UO}[U^2]$  
get from $U, O$ Eqs

$\Pi_{UO_2} \approx 4K_{UO_2}[U^4]$  

11.5.4 Knudsen Cell Mass Spectrometer Expts.

READ
See Figure 11.17
Also examine the results of partial Pressures over

\[(U_{0.85}Pu_{0.15})O_{2\pm x}\]

**Figure 11.17**

**Key Features**

**Hyper-**

1.) UO$_3$ is predominant

\[UO_2(g) + \frac{1}{2}O_2(g) = UO_3(g)\]

2.) $\frac{U}{Pu}$ is larger in vapor than in the solid ($\approx 10^6$ times)

3.) $\frac{O}{M}$ in vapor is higher than in solid which means the solid is losing oxygen.

**Hypo-**

1.) $\frac{U}{Pu}$ is smaller than in solid for $O/M < 1.96$ (means solid is losing Pu preferentially)