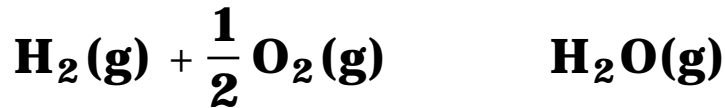


**PROBLEM 11.1 From reaction equation:**



**@ 1500°K (remember 1 cal = 4.18 J)**

$$G_{\text{H}_2\text{O}}^\circ = -58.9 + 13.1 \cdot 1.5 = -39.2 \frac{\text{kcal}}{\text{mole}}$$

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

$$G_{\text{H}_2\text{O}}^\circ = -RT \ln \frac{\text{H}_2\text{O}}{\text{H}_2 \sqrt{\text{O}_2}}$$

$$\frac{\text{H}_2\text{O}}{\text{H}_2} = 1 \text{ equal partial pressures}$$

$$RT \ln \text{O}_2 = 2 G_{\text{H}_2\text{O}}^\circ = -78.4 \text{ kcal/mole} \quad (1)$$

Now, above  $\text{UO}_{2+x}$  at 1500°K

$$\overline{G}_{\text{O}_2} = RT \ln \text{O}_2 = \overline{\overline{H}}_{\text{O}_2} - \overline{\overline{S}}_{\text{O}_2} \frac{T}{1000} \frac{\text{kcal}}{\text{mole}}$$

Using  $RT \ln \text{O}_2$  from eq. 1, and

$\overline{H}_{\text{O}_2}$ ,  $\overline{S}_{\text{O}_2}$  from problem

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

$$x = 0.00051 \text{ and } \text{UO}_{2.0005}$$

### 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

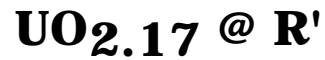
$$o_{2-} = 0.01 \text{ atm}$$

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  $800^\circ\text{C}$  (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:**

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

$$f=0.5$$

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

## 11.5 Thermochemistry of Fuel Vaporization

### 11.5.1 Gas-Solid Equilibria (Rand Markin)

*Look at Other Components Besides Oxygen*

#### Hypostoichiometric Oxides

Consider  $(U_{1-q}Pu_q)O_{2-x}$



$$\text{where } m = \frac{x}{q}$$

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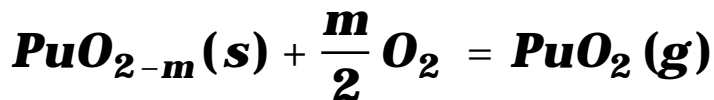
**Raoult's Law for partial pressure of  $UO_2$  Over Solid**

$$P_{UO_2} = (1 - q)P_{UO_2}^\circ$$

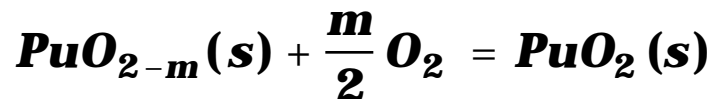
$$P_{UO_2} = (1 - q) \exp \frac{-G_{UO_2, \text{vap}}}{RT}$$

*Vapor Pressure, of, pure, solid,  $UO_2$*

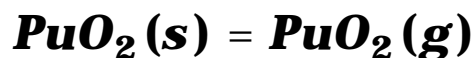
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is the same as the sum of



and



$$PuO_2 = q \left( O_2 \right)^{\frac{m}{2}} \exp \frac{-G_{comp}^\circ}{RT}$$

$$G_{comp}^\circ = G_{PuO_{2-m}, PuO_{2(s)}}^\circ + G_{PuO_{2,vap}}^\circ$$

### Hyperstoichiometric Oxides



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

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

$$PuO_2 = q \exp \frac{-G_{PuO_{2,vap}}^\circ}{RT}$$

note that

$$G_{comp}^\circ = G_{UO_{2+x}(s), UO_2(g)}^\circ + G_{UO_{2,vap}}^\circ$$

## **11.5.2 Equilibria in the Gas Phase**

*(Rand Markin Model)*

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



### **To get the Composition of the Vapor**

**Determine  $O_2$  from the oxygen potential of the fuel (section 11.4)**

**Get  $UO_2, PuO_2$  from earlier eqs**

**Get atomic oxygen from 11.56**

**Get  $UO, PuO$  from eqs. 11.58, 11.61**

**Use monoxide pressures to determine  $U, Pu$  (11.57, 11.60)**

**Get  $UO_3$  from  $UO_2$  (11.59)**

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

**Note that**

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

$$UO_2 \quad [U^{+4}] \quad K_{UO_2} = \frac{UO_2}{[U^{+4}] \cdot 2[O^{-2}]}$$

and  $\ln K_i = \frac{-A_i}{\frac{T}{1000}} + B_i$

get  $A_i, B_i$  from table 11.1

and  $[O^{-2}] = 2$

so,

$UO = 2K_{UO} [U^{+2}]$  get from U, O Eqs

$UO_2 = 4K_{UO_2} [U^{+4}]$

" " "

### 11.5.4 Knudsen Cell Mass Spectrometer Expts.

**READ**

See Figure 11.17

**Also examine the results of partial Pressures over**

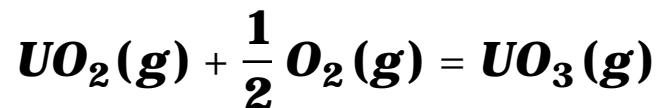


**Figure 11.17**

**Key Features**

**Hyper-**

**1.)  $UO_3$  is predominant**



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