

# Chapter 11 Fuel Chemistry

***One key question is what is in the atmosphere above the fuel pellet that could interact with the cladding ?***

-----

---

## 11.2 Phase Diagrams of $\text{UO}_2$ and $\text{PuO}_2$

**Figures [ Columnar (1800-2000 °C),  
Equiaxed (1600 °C),  
As Fabricated ( 1000 °C)]**

---

|                |               |                                   |                                      |                                   |                          |
|----------------|---------------|-----------------------------------|--------------------------------------|-----------------------------------|--------------------------|
| <b>Phase</b>   | $\text{UO}_2$ | $\text{---}>\text{U}_4\text{O}_9$ | $\text{---}>\text{U}_5\text{O}_{13}$ | $\text{---}>\text{U}_3\text{O}_8$ | $\text{---}>\text{UO}_3$ |
| <b>O/U</b>     | <b>2.00</b>   | <b>2.25</b>                       | <b>2.6</b>                           | <b>2.67</b>                       | <b>3.00</b>              |
| <b>Valence</b> | <b>+4</b>     | -----                             |                                      |                                   |                          |
| <b>&gt;+6</b>  |               |                                   |                                      |                                   |                          |

**From UO<sub>2</sub> Phase Diagram**

**at T < 1300- 1800 °C  
and O/U < 2.00**

**Then at low temperatures, UO<sub>2</sub> is a mixture of  
UO<sub>2.00</sub> +U (met)**

=====

**From PuO<sub>2</sub> Phase Diagram;**

**Phase    Pu<sub>2</sub>O<sub>3</sub>    PuO<sub>1.52</sub>    PuO<sub>1.61</sub>    PuO<sub>2</sub>**

**O/M    1.5    1.52    1.61    2.00**

**Valence   +3    ----->  
+4**

## 11.3 Defect Structure

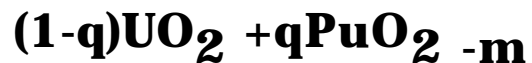
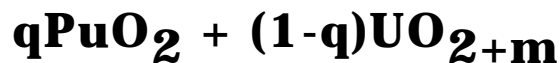


add x oxygen

subtract x oxygen

*Oxidize  $2xU^{+4}$  to  $2xU^{+5}$*

*Reduce  $2xPu^{+4}$  to  $2xPu^{+3}$*



$$m = \frac{x}{(1 - q)}$$

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

**Q: Where does the deficiency of oxygen come from?**

*Figure - Oxygen sublattice*

**Q: Where do the excess oxygen atoms go?**

*Figure - 2 types of interstitial positions*

**For example: What happens if we stick two excess oxygen atoms in the matrix?**

- 1.) Force 2 atoms off lattice site-> 2 vacancies**
- 2.) Form two type 1 and two type 2**
- 3.) Change four  $U^{+4}$  to four  $U^{+5}$**

# 11.4

## Oxygen Potentials

*How can we predict the partial pressure of oxygen around a hot pellet?*

- Use thermodynamics -- see chapter 5
- At equil. all chemical potentials are equal

$$\frac{1}{2} \mu_{O_2}(g) = \mu_O(g)$$

$$\mu_O(g) = \mu_O(\text{solution})$$

$$\mu_{O_2}(g) = G_{O_2}^\circ + RT \ln (p_{O_2})$$

***Gibbs Free Energy of Pure O<sub>2</sub> gas at Temp. T***

***Partial Pressure of O<sub>2</sub> (Figure 11.6)***

=  $\overline{G}_{O_2}$  = partial molar free energy of oxygen in the solid per mole of O<sub>2</sub>

---


$$\overline{G}_{O_2} = 2\mu_O(\text{solution}) - G_{O_2}^\circ \quad @ 1 \text{ atm.}$$

= a way of expressing equilibrium partial pressure over the material

---

**11.4.1 , 11.4.2 show ways to measure  $\overline{G}_{O_2}$**

### 11.4.3 Measured Oxygen Potentials

$$\overline{G}_{O_2} = \overline{H}_{O_2} - \overline{S}_{O_2} \left( \frac{T}{1000} \right)$$

partial molal (Enthalpy/entropy) of oxygen in solid oxide

---

#### 11.4.4 UO<sub>2</sub>

Can get oxygen partial pressure over hyperstoichiometric UO<sub>2</sub> from figure 11.10

A.) Knowing  $\overline{H}_{O_2}$ ,  $\overline{S}_{O_2}$ ,  $T \implies \overline{G}_{O_2}$

B.) Knowing  $\overline{G}_{O_2} \implies p_{O_2}$

---

Can get oxygen partial pressure over hypostoichiometric UO<sub>2</sub> from figure 11.11

<1300°C can get  $p_{O_2}$  over U(l) + UO<sub>2.00</sub>

>1300°C can have some UO<sub>2-x</sub> by  
converting some U<sup>+4</sup>  $\rightarrow$  U<sup>+2</sup>

---

Note - the higher the temperature,

the lower  $\overline{G}_{O_2}$ ,

the higher  $p_{O_2}$

i.e.,  $p_{O_2} = \exp \left( \overline{G}_{O_2} / RT \right)$

as  $x \rightarrow 0$ ,  $p_{O_2}$  increases