

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 UO_2 and PuO_2

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

Phase	UO_2	$\text{---}>\text{U}_4\text{O}_9$	$\text{---}>\text{U}_5\text{O}_{13}$	$\text{---}>\text{U}_3\text{O}_8$	$\text{---}>\text{UO}_3$
O/U	2.00	2.25	2.6	2.67	3.00
Valence	+4	-----			
>+6					

From UO₂ Phase Diagram

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

**Then at low temperatures, UO₂ is a mixture of
UO_{2.00} +U (met)**

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From PuO₂ Phase Diagram;

Phase Pu₂O₃ PuO_{1.52} PuO_{1.61} PuO₂

O/M 1.5 1.52 1.61 2.00

**Valence +3 ----->
+4**

11.3 Defect Structure

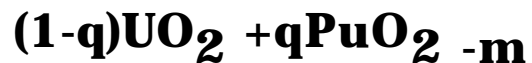
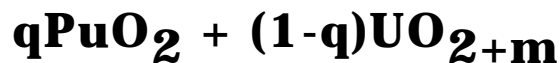


add x oxygen

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 O₂ gas at Temp. T

Partial Pressure of O₂ (Figure 11.6)

= \overline{G}_{O_2} = partial molar free energy of oxygen in the solid per mole of O₂

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

= 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 UO₂

Can get oxygen partial pressure over hyperstoichiometric UO₂ 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 UO₂ from figure 11.11

<1300°C can get p_{O_2} over U(l) + UO_{2.00}

>1300°C can have some UO_{2-x} by
converting some U⁺⁴ \rightarrow U⁺²

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