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-->U_4O_9--->U_5O_{13}-->U_3O_8->UO_3

O/U 2.00 2.25 2.6 2.67 3.00

Valence +4 ----------->+6

From UO_2 Phase Diagram

at T< 1300- 1800 °C
and O/U < 2.00

Then at low temperatures, UO_2 is a mixture of $UO_{2.00}$ +U (met)

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From PuO_2 Phase Diagram;

Phase	**Pu_2O_3**	**$PuO_{1.52}$**	**$PuO_{1.61}$**	**PuO_2**
O/M	**1.5**	**1.52**	**1.61**	**2.00**

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

11.3 Defect Structure

$(U_{1-q}Pu_q)O_{2.00}$

add x oxygen	subtract x oxygen
Oxidize $2xU^{+4}$ *to* $2xU^{+5}$	*Reduce* $2xPu^{+4}$ *to* $2xPu^{+3}$
$qPuO_2 + (1-q)UO_{2+m}$	$(1-q)UO_2 + qPuO_{2-m}$
$m = \frac{x}{(1-q)}$	$m = \frac{x}{q}$

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**

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

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

$$\mu_{O_2}(g) = G^{\circ}_{O_2} + RT \ln(\Pi_{O_2})$$

Gibbs Free Energy of Pure O_2 gas at Temp. T ***Partial Pressure of O_2*** ***(Figure 11.6)***

$= \overline{\Delta G_{O_2}}$ = **partial molar free energy of oxygen in the solid per mole of O_2**

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

= a way of expressing equilibrium partial pressure over the material

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11.4.1 , 11.4.2 show ways to measure $\overline{\Delta G_{O_2}}$

11.4.3 Measured Oxygen Potentials

$$\overline{\Delta G_{O_2}} = \overline{\Delta H_{O_2}} - \overline{\Delta S_{O_2}} \left(\frac{T}{1000} \right)$$

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

11.4.4 UO_2

Can get oxygen partial pressure over hyperstoichiometric UO_2 from figure 11.10

A.) Knowing $\overline{\Delta H_{O_2}}$, $\overline{\Delta S_{O_2}}$, T ==> $\overline{\Delta G_{O_2}}$

B.) Knowing $\overline{\Delta G_{O_2}}$ ==> Π_{O_2}

Can get oxygen partial pressure over hypostoichiometric UO_2 from figure 11.11

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

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

Note - the higher the temperature, the lower $-\overline{\Delta G_{O_2}}$, the higher Π_{O_2}

i.e., $\Pi_{O_2} = \exp(\overline{\Delta G_{O_2}}/RT)$

as x--> 0, Π_{O_2} increases