11.6 Oxygen Redistribution

Because:

$$\ln \Pi_{O_2} = \frac{\overline{\Delta G_{O_2}}}{RT} = \frac{\overline{\Delta H_{O_2}}}{RT} - \frac{\overline{\Delta S_{O_2}}}{R}$$

then

$\Pi_{O_2}(r)$ **and oxygen can move in the temperature gradient. If that happens, then the** $\frac{O}{M}$ **ratio is changed effecting;**

- **Thermal Conductivity (hence temperature)**
- μ_{O_2} **(hence cladding corrosion)**
- **creep strength of UO_2 (e.g., dimensional stability)**
- **Diffusion coefficients (e.g., bubble growth, solid element redistribution)**

11.6.1) Markin-Rand-Roberts Model

Assumes that carbon can transport oxygen through gas phase to one part of the fuel or another (H_2 diffuses out)

Note the type of data that comes out of the Knudsen Cell measurements ! (Table 11.2)

Hyperstoichiometric Fuel-Proposed Model

$$CO_2 \longleftrightarrow CO + \frac{1}{2} O_2(g)$$

Model
(Assume rectangular coordinates + no net oxygen or carbon flux)

1.) Solve for carbon and oxygen balance
2.) Let local oxygen pressure correspond to oxygen potential of the fuel
3.) Assume the CO_2, CO, and O_2 components are in thermodynamic equilibrium
4.) Know

$$\overline{x} = \frac{1}{L} \int_0^L x(z) dz$$

End Result

Hyper- fuel results in more oxygen at the hot end

Hypo-fuel results in more oxygen at the cold end

See figures 11.19a (hyper)
11.19b (hypo)
11.20

Explanation for hyper OK but the kinetics are wrong for Hypo

possible that UO, UO_2, UO_3
or PuO, PuO_2
or MoO_2, MoO_3

could account for transport

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11.6.2 Aitken Model

Mainly aimed at Hypo case.
Assume,

$$\ln x = \frac{Q^+}{RT} + constant$$

where Q^+ represents the combined effects of solid state diffusion and vapor migration and is negative (figure 11.21)

11.6.3 Bober-Schumacher Model

Observed that there must be solid state diffusion. It was postulated that oxygen vacancies migrate to the hottest part of the fuel which causes the $\frac{O}{M}$ ratio to drop.

$$T_{hot} \xleftarrow[\text{Oxygen}]{Oxygen.Vacancies} T_{cold}$$

Measured Q^+ and found that it was close to that in Aitkens Model.