11.4.5 Mixed Oxides

Note that the oxygen partial pressure is quite a bit higher for hyperstoichiometric oxide

Figure 11.12

$$P_{O_2} = \exp\left(\frac{\overline{\Delta G_{O_2}}}{RT}\right)$$

11.4.6 Rand-Markin Model

It was shown that $\overline{\Delta H_{O_2}}, \overline{\Delta S_{O_2}}$ depend mainly on the valence of the heavy metal ions.

	Hypo	Hyper
V_U	4	$4 + \left[\frac{2x}{1-q}\right]$
V_{Pu}	$4 - \left[\frac{2x}{q}\right]$	4

See Figures 11.13, 11.14

11.4.7 Blackburn's Model

Main Aim

1.) To examine the dependence of μ_{O_2} on V_U for hyper and V_{Pu} for mixed fuel hypo oxides

2.) To allow for some $\frac{U}{Pu}$ ratio effects.

Procedure:

1.) Set up rate for U, Pu, and U-Pu
2.) Solve for rate constants
3.) Use normalization and charge balances to obtain quantitative solutions.

Example- UO2

Hypo	Hyper
$U^{+4} + O^{-2} = U^{+2} + \frac{O_2(g)}{2}$	$U^{+6} + O^{-2} = U^{+4} + \frac{O_2(g)}{2}$
$K^U_{2,4} = \frac{\sqrt{\Pi_{O_2}} \bullet [U^{+2}]}{[U^{+4}] \bullet [O^{-2}]}$	$K^U_{4,6} = \frac{\sqrt{\Pi_{O_2}} \bullet [U^{+4}]}{[U^{+6}] \bullet [O^{-2}]}$

[ ] = ions per U atom

$$\ln K^U_{2,4} = \left(\frac{78,300}{T}\right) + 13.6$$

$$\ln K^U_{4,6} = -\left(\frac{16,400}{T}\right) + 5.0$$

Normalization,

$$[U^{+2}] + [U^{+4}] + [U^{+6}] = 1$$

Electric Neutrality,

$$[O^{-2}] = 2 \pm x$$

$$[U^{+2}] + 2[U^{+4}] + 3[U^{+6}] = [O^{-2}]$$

- **Can do the same for Pu oxide**

- **Can do the same for U-Pu oxide**

$[O^{-2}] = 2 \pm x = [U^{+2}] + [Pu^{+2}] + 3/2[Pu^{+3}] + 2[U^{+4}] + 2[Pu^{+4}] + 3[U^{+6}]$

Then
1.) **Solve equations for K's**
2.) **Express Π_{O_2} in terms of Conc. [ ], [ ], ..**
3.) **Sub. for conc. in last eq. above to get $\Pi_{O_2 - x}$ relationship**

Solves differences in figures 11.13 and 11.14