10.3.2
Stoichiometric Effect

When T is low enough to neglect thermal generation of defects;

$$k_s \propto \frac{1}{A(x,q) + B(x,q)T}$$

mainly	mainly
stoichiometry	Pu content

Coefficient A,

$$A = A_o + \Delta A(x)$$

from interactions with point defects

$$\Delta A = A^* \sum_i \left\{ Y_i \left(\frac{(r_i - r)}{r} \right)^2 \right\}$$

Const. **Conc. of Point defects**

r= radius of host lattice
r_i = radius of defect

Comment about r_i ;

in metals, $r_i < r$ for vacancies

in ceramics, $r_i > r$ for vacancies

(because of charge repulsion)

For hypostoichiometric UO_2, replace 2 Pu^{+4} with 2 Pu^{+3} when we lose an oxygen atom

$$\Delta A = A^* [\, 2(0.15)^2 + (0.15)^2 \,] x$$

$Pu^{+3} \rightarrow Pu^{+4}$
1.04 --> 0.93

$$= 0.068\, A^* x$$

or, $\Delta A/x \approx 400$

Finally,

$$k_s = \frac{1}{A_o + 400x + B(q)T}$$ See Figure

Effect of Pu Content

Generally, B increases with Pu content

$$B = B_o \left\{ \left[\frac{a_o}{(a_o)_{UO_2}} \right]^2 \bullet \left[\frac{(T_m)_{UO_2}}{T_m} \right]^{\frac{3}{2}} \right\}$$

- **No real good theory, but B depends on molar volume and Debye Temperature (a T_{mp})**

- **Note that stoichiometry is more effective than Pu content (see figure)**

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Burn Up Effects

Should lower k_s but no good experimental conformation of that