Outline of the solution to Problem 6: A shiver down the spine-l

10 marks

11 September, 2020

1. A^{2+} in Tetrahedral sites = xv
   B^{2+} in Tetrahedral sites = yv
   A^{2+} in Octahedral sites = (1-d-x)v
   A^{2+} in Octahedral sites = (d-y)v
   C^{3+} in Tetrahedral sites = (1-x-y)v
   C^{3+} in Octahedral sites = (1+x+y)v
   Thus,

$$W = \frac{[(1-d)v]!}{(xv)![(1-d-x)v]!} \times \frac{(dv)!}{(dv)![(d-y)v]!} \times \frac{(2v)!}{[(1-x-y)v]![(1+x+y)v]!}$$

2. (a) A + (B) $\rightleftharpoons (A) + B$
   $K = \dfrac{x}{(1-x)(2-x)}$

(b)

$$\begin{aligned}
\Delta G^\circ &= -RTlnK \\
lnK &= -\frac{\Delta G^\circ}{RT} \\
&= -\frac{(\Delta H^\circ - T\Delta S)}{RT} \\
lnK &= \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
\end{aligned}$$

From the graph, $\frac{\Delta S}{R} = 0$
Thus, entropy for non-configurational changes = 0

(c) $\Delta S = -R[xlnx + (1-x)ln(1-x) + xln(\frac{x}{2}) + (2-x)ln(\frac{1-x}{2})]$

3. Normal spinel structure
   $Co^{3+} \rightarrow$ Low spin in octahedral field and high spin in tetrahedral field. But low spin d^6 confers additional stabilization in octahedral site.

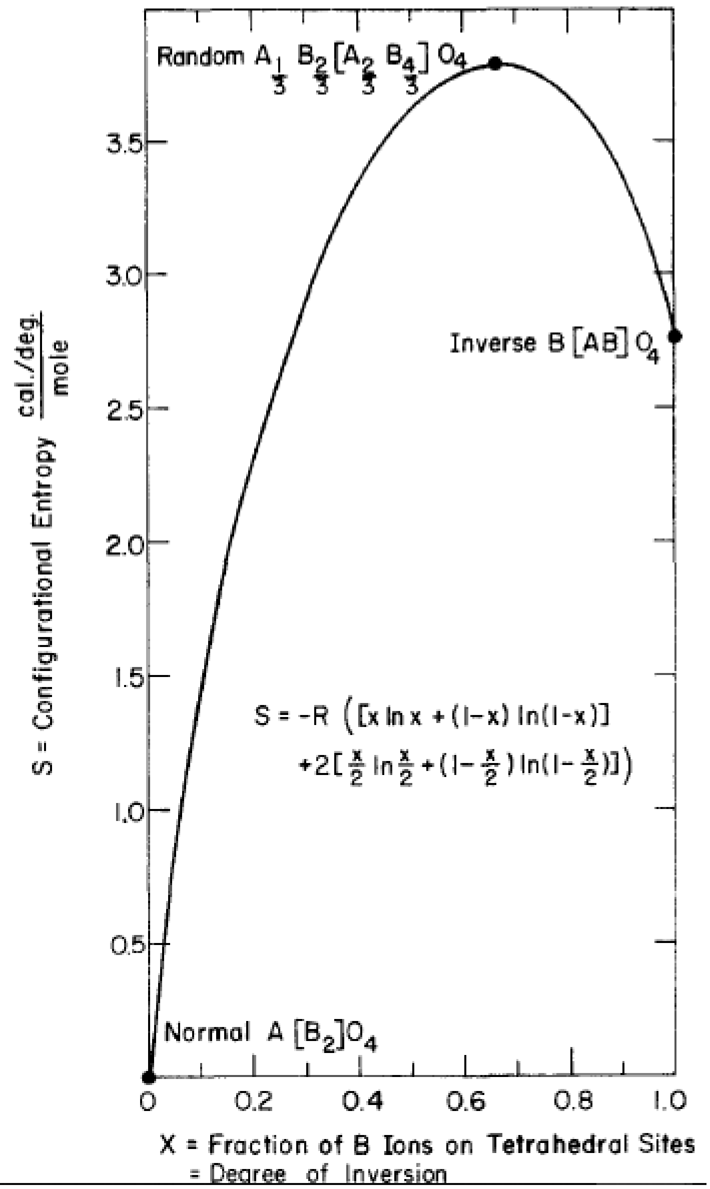

Figure 1: Entropy v/s degree of inversion