HW 5 Solutions

3.2) $U_{tot} = 2N\epsilon \sum_j{}' \left[\left(\frac{\sigma}{p_{ij} R} \right)^{12} - \left(\frac{\sigma}{p_{ij} R} \right)^{6} \right]$

$$U_{tot} = 2N\epsilon \left[A \left(\frac{\sigma}{R} \right)^{12} - B \left(\frac{\sigma}{R} \right)^{6} \right]$$

$$A = \sum_j{}' \frac{1}{p_{ij}^{12}} \qquad B = \sum_j{}' \frac{1}{p_{ij}^{6}}$$

$$= 9.114 \text{ (bcc)} \qquad = 12.253 \text{ (bcc)}$$

Equilibrium:

$$0 = \frac{dU_{tot}}{dR} = 2N\epsilon \left[-12A \frac{\sigma^{12}}{R^{13}} + 6B \frac{\sigma^{6}}{R^{7}} \right]$$

$$0 = -12A \left(\frac{\sigma}{R} \right)^{12} + 6B \left(\frac{\sigma}{R} \right)^{6}$$

$$2A \left(\frac{\sigma}{R} \right)^{6} = B \qquad \frac{2A}{B} = \left(\frac{R}{\sigma} \right)^{6}$$

$$R = \sigma \left(\frac{2A}{B} \right)^{1/6} = 1.068\,\sigma$$

$$\frac{U_{tot}(bcc)}{U_{tot}(fcc)} = \frac{A_{bcc}(1.068)^{-12} - B_{bcc}(1.068)^{-6}}{A_{fcc}(1.09)^{-12} - A_{fcc}(1.09)^{-6}}$$

$$= \frac{9.114\,(1.068)^{-12} - 12.253\,(1.068)^{-6}}{-4.30}$$

$$= \frac{4.118}{4.30} = 0.958$$

3.5) a) $U(R) = \frac{2NA}{R^n} + N \sum_{i \neq j} \frac{\pm q^2}{R_{ij}}$

$$U(R) = \frac{2NA}{R^n} - \frac{2Nq^2}{R}\underbrace{\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right)}_{\ln 2}$$

$$U(R) = 2N\left(\frac{A}{R^n} - \frac{q^2 \ln 2}{R}\right)$$

Equilibrium:

$$0 = \frac{1}{2N} U'(R_0) = \frac{-nA}{R_0^{n+1}} + \frac{q^2 \ln 2}{R_0^2}$$

$$R_0^{n-1} = \frac{nA}{q^2 \ln 2} \Rightarrow U(R_0) = -\frac{2Nq^2 \ln 2}{R_0}\left(1 - \frac{1}{n}\right)$$

3.5b) $U(R_0(1-\delta)) = U(R_0) + \frac{1}{2}U''(R_0)R_0^2\delta^2 + \cdots$

$$U''(R_0) = 2N\left(\frac{n(n+1)A}{R_0^{n+2}} - \frac{2q^2/n^2}{R_0^3}\right)$$

$$= \frac{2Nq^2/n^2(n-1)}{R_0^3}$$

$$W = \Delta U \simeq \frac{1}{2}U''(R_0)R_0^2\delta^2$$

$$= \frac{Nq^2/n^2(n-1)}{R_0}\delta^2$$

Total length: $L = 2NR_0$

$$\frac{W}{L} = \frac{1}{2}\left(\varepsilon\frac{q^2/n^2(n-1)}{R_0^2}\right)\delta^2$$

$\uparrow$

C

3.6) KCl in cubic ZnS structure

$z\lambda = 2.05 \times 10^{-8}$ erg $\rho = 0.326$ Å

$z = 6$

$\lambda = 3.42 \times 10^{-9}$ erg $= 3.42 \times 10^{-16}$ J

$\alpha = 1.6381$

$$R_0^2 e^{-R_0/\rho} = \frac{\rho \alpha e^2}{z\lambda} = \frac{\rho e^2}{\lambda}\frac{\alpha}{z}$$

$$= \frac{\rho e^2}{\lambda} \times \begin{cases} 0.4095 & ZnS \\ 0.2913 & NaCl \end{cases}$$

$$\left(\frac{R_0}{\rho}\right)^2 e^{-R_0/\rho} = \frac{e^2}{\rho\lambda}\frac{\alpha}{z}$$

$$\frac{R_0}{\rho}(NaCl) = \frac{3.147}{0.326} = 9.653 = x_{NaCl}$$

$$x^2 e^{-x}/_{NaCl} = 5.985 \times 10^{-3}$$

$$x^2 e^{-x}/_{ZnS} = 8.414 \times 10^{-3} \rightarrow x_{ZnS} \simeq 9.22$$

$$R_0|_{ZnS} = 9.22\rho = 3.01\ \text{Å}$$

$$U_{tot} = -\frac{N\alpha e^2}{R_0}\left(1-\frac{1}{x}\right) = -\frac{N\alpha e^2}{\rho}\,\frac{x-1}{x^2}$$

$$\frac{U_{tot}|_{ZnS}}{U_{tot}|_{NaCl}} = \frac{\alpha_{ZnS}}{\alpha_{NaCl}}\,\frac{\left(\frac{1}{x}-\frac{1}{x^2}\right)|_{ZnS}}{\left(\frac{1}{x}-\frac{1}{x^2}\right)|_{NaCl}}$$

$$= \frac{1.6381}{1.7476}\,\frac{0.1085-(0.1085)^2}{0.1036-(0.1036)^2}$$

$$= 0.976$$

$$\frac{1}{x}|_{ZnS} = 0.1085$$

$$\frac{1}{x}|_{NaCl} = 0.1036$$

$$U_{tot}|_{ZnS} = 158\ \frac{kcal}{mol}$$