Spring 1997 #5

A binary alloy is composed of N_A atoms of type A and N_B atoms of type B. Over the temperature range of interest the A type atoms can only be found in the ground state and in an excited state of energy E_0. Similarly the B-type atoms can only occupy the ground state and an excited state having energy $2E_0$. The entire mixture is in thermal equilibrium at temperature T.

a) Calculate the Helmholtz free energy F of this alloy.

→ Since the ground state energy is unspecified, assume it is zero for both A and B type atoms.

$$Z = \left(1 + e^{-\beta E_0}\right)^{N_A} \left(1 + e^{-2\beta E_0}\right)^{N_B}$$

$$\boxed{F = -kT \ln Z = -kT N_A \ln\left(1 + e^{-\beta E_0}\right) - kT N_B \left(1 + e^{-2\beta E_0}\right)}$$

b) Deduce the heat capacity of this system at temperature T.

find energy E

$$E = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta}\left[N_A \ln\left(1 + e^{-\beta E_0}\right) + N_B \ln\left(1 + e^{-2\beta E_0}\right)\right]$$

$$E = \frac{-N_A (-E_0) e^{-\beta E_0}}{\left(1 + e^{-\beta E_0}\right)} - \frac{N_B (-2E_0) e^{-2\beta E_0}}{\left(1 + e^{-2\beta E_0}\right)}$$

$$C = \left(\frac{\partial E}{\partial T}\right) = \left(\frac{\partial E}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right)$$

$$\boxed{C = \left[\frac{N_A E_0 e^{-\beta E_0}(-1)(-E_0) e^{-\beta E_0}}{\left(1 + e^{-\beta E_0}\right)^2} + \frac{N_A E_0 (-E_0) e^{-\beta E_0}}{\left(1 + e^{-\beta E_0}\right)} + \frac{2N_B E_0 e^{-2\beta E_0}(-1)(-2E_0) e^{-2\beta}}{\left(1 + e^{-2\beta E_0}\right)^2} + \frac{2E_0 (-2E_0) e^{-2\beta E_0}}{\left(1 + e^{-2\beta E_0}\right)}\right]\left(-\frac{1}{kT^2}\right)}$$