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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 type A 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.

let ground state energy be equal to ϵ. So, the partition function of the system is

$$Z = Z_A Z_B = \left[\frac{(e^{-\beta\epsilon} + e^{-\beta E_0})^{N_A}}{N_A!}\right]\left[\frac{(e^{-\beta\epsilon} + e^{-2\beta E_0})^{N_B}}{N_B!}\right]$$

i assume that the type A particles are indistinguishable from each other but distinguishable from type B particles and likewise for the type B particles.

So, the Helmholtz free energy is

$$F = -KT \ln Z$$

$$= -KT \ln\left[\frac{(e^{-\beta\epsilon} + e^{-\beta E_0})^{N_A}}{N_A!}\right] - KT \ln\left[\frac{(e^{-\beta\epsilon} + e^{-2\beta E_0})^{N}}{N_B!}\right]$$

$$\Rightarrow F = +KT(\ln N_A! + \ln N_B!) - KTN_A \ln(e^{-\beta\epsilon} + e^{-\beta E_0}) - KTN_B \ln(e^{-\beta\epsilon} + e^{-2\beta E_0})$$

where for $N_A \gg 1$, $N_B \gg 1$

$$\ln N_A! \simeq N_A \ln N_A - N_A$$

$$\ln N_B! \simeq N_B \ln N_B - N_B$$

Thus,

$$\boxed{F = KTN_A\left[\ln N_A - 1 - \ln(e^{-\beta\epsilon} + e^{-\beta E_0})\right] + KTN_B\left[\ln N_B - 1 - \ln(e^{-\beta\epsilon} + e^{-2\beta E_0})\right]}$$

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

we could do $C = T\left(\frac{\partial S}{\partial T}\right)$, $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$ ← but lot's of math

or do

$$\bar{E} = -\frac{\partial}{\partial \beta}\ln Z \quad \text{and} \quad C = \frac{\partial E}{\partial T} = \frac{\partial E}{\partial \beta}\frac{\partial \beta}{\partial T} = -\frac{1}{KT^2}\frac{\partial \bar{E}}{\partial \beta}$$

so,

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

$$= N_A \frac{\epsilon e^{-\beta\epsilon} + E_0 e^{-\beta E_0}}{e^{-\beta\epsilon} + e^{-\beta E_0}} + N_B \frac{\epsilon e^{-\beta\epsilon} + 2E_0 e^{-2\beta E_0}}{e^{-\beta E} + e^{-2\beta E_0}}$$

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

Then

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

$$-\frac{N_B}{KT^2}\left[\frac{-2E_0(2E_0+\epsilon)e^{-\beta(2E_0+\epsilon)}}{1+e^{-\beta(2E_0+\epsilon)}} + \frac{2E_0(2E_0+\epsilon)e^{-2\beta(2E_0+\epsilon)}}{\left(1+e^{-\beta(2E_0+\epsilon)}\right)^2}\right]$$

Thus

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