

1. (a) Consider a non-ideal gas that can be described by the equation of state  $PV = RT(1 + BP)$ , where  $B$  is a constant independent of temperature  $T$  and pressure  $P$ . Show that the work done by this non-ideal gas during isothermal expansion from pressure  $P_1$  to  $P_2$  is the same as that achieved by an ideal gas. (10%)

(b) Show that for a van der Waals gas that can be described by  $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ , the change in entropy can be expressed as  $\Delta S = \int \frac{c_v}{T} dT + R \ln(V - b)$ . (10%)

2. (a) Please briefly describe the second law of thermodynamics. (5%)

(b) Starting from Boltzmann's equation  $S = k \ln \Omega$ , show that when two closed systems  $A$  and  $B$  are in thermal contact, the condition for  $A$  to be in thermal equilibrium with  $B$  will lead to  $T_A = T_B$ . (5%)

(c) Generally speaking, the molar heat capacity of a metallic solid can be expressed as  $c_v = K \left(\frac{T}{\Theta}\right)^3 + \gamma T$  at low temperatures. What are the physical origins of these two temperature-dependent terms? What is  $\Theta$ ? (5%)

(d) While dealing with different thermodynamic processes, under what circumstances (conditions) will you use Helmholtz free energy and Gibbs free energy? (5%)

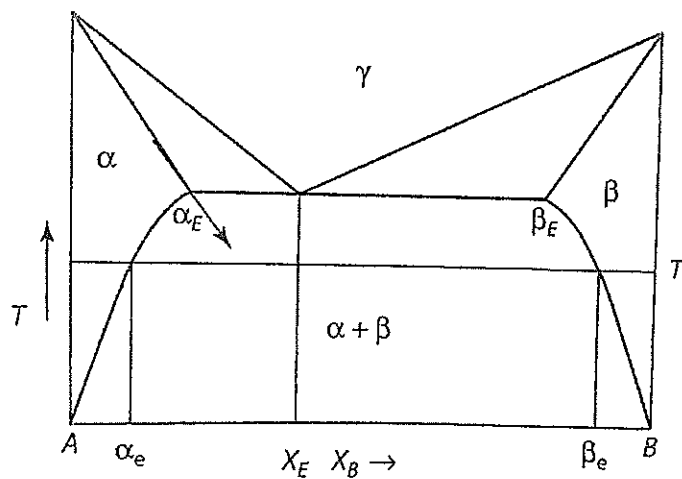
3. A piece of copper goes through a reversible isothermal compression process from  $P = 1$  atm to 1000 atm at  $T = 273$  K. Assume that the isobaric thermal expansivity  $\alpha$ , the isothermal compressibility  $\beta$ , and the mass density  $\rho$  are  $5 \times 10^{-5} \text{ K}^{-1}$ ,  $8 \times 10^{-12} \text{ N}^{-1} \text{ m}^2$ , and  $8.9 \times 10^3 \text{ kg m}^{-3}$ , respectively. Please calculate: (a) How much work (per kg) is done on the copper? (10%) (b) How much heat is absorbed or released? (10%)

4. Consider a system with  $N$  particles, and the system obeys Maxwell-Boltzmann distribution. Show that: (a) The expectation value of number of particles that occupy  $i^{\text{th}}$  energy level (with energy  $\varepsilon_i$ ) is  $n_i = -Nk_B T \left( \frac{\partial \ln Z}{\partial \varepsilon_i} \right)_T$ , where  $Z = \sum_i e^{-\varepsilon_i/k_B T}$  is the single particle partition function. (10%) (b) The internal energy  $U$  (expectation value of

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the total energy) of the system can be expressed as  $U = -(\partial \ln Z / \partial \beta)_v$ , where  $\beta = 1/k_B T$ . (5%) (c) The Helmholtz free energy  $A$  of the system can be expressed as  $A = -\beta^{-1} \ln Z$ . (5%)

5. The phase diagram of an alloy that possesses a eutectoid transformation is shown below. (a) Sketch the Gibbs free energy curves for this alloy at  $T = T'$ . (10%) (b) Show that the  $\alpha/\gamma$  solvus must enter the  $\alpha/\beta$  two-phase field as indicated by the arrow. (10%)



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