

Do all four questions. Each question is worth 25 points.

(1) (a) Derive the Helmholtz free energy,  $A$ , in terms of its proper variables starting with the internal energy. Calculate  $dA$ .

(b) Derive the relation

$$TdS = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dV$$

(Derive any Maxwell relations you need.)

(2) The Clausius-Clapeyron equation is

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v}$$

where  $s$  is the molar entropy,  $v$  the molar volume along a phase equilibrium line and  $\Delta$  implies the change in a quantity from one phase to another.

(a) Assuming latent heat is temperature independent, calculate the vapor pressure of a liquid as a function of temperature far from the critical point. Assume that

$$v_{\text{liquid}} \ll v_{\text{gas}}$$

(b) Draw a schematic P-T phase diagram appropriate for a typical substance. Label the triple point and critical point. How would the diagram differ for a substance like water that is less dense when solid than when liquid?

(3) NOTE: The following question does not require any special knowledge about electromagnetism, superconductivity, or any subject other than thermodynamics.

A piece of metal has the following properties:

- (i) The free energy of the normal state (at high  $T$ ),  $G_n$ , is independent of magnetic field
- (ii) At low  $T$ , the metal becomes a superconductor (a phase transition).
- (iii) The free energy of the superconducting state in a field,  $G_s(T, H)$ , is given by

$$G_s(T, H) = G_s(T, 0) + \frac{V}{8\pi} H^2$$

where  $G_s(T, 0) < G_n$  and  $V$  is the volume.

(a) Show that there is a critical field  $H_c$  (which is a function of temperature) at which the superconductor becomes normal.

(b) Calculate the change in entropy between the superconducting and normal states in zero field. Express your answer in terms of  $H_c$ .

(c) What is the latent heat at constant temperature as the metal goes superconducting, that is, as the field  $H$  falls below  $H_c$ ?

(d) What is the change in specific heat,  $\Delta C(T, H) = C_S(T, H) - C_N(T, H)$ , as you pass from the superconducting state into the normal state by varying  $H$ ? You may assume that  $C_V = C_P$ . What is  $\Delta C$  for  $T = T_c$ , the critical temperature?

- (4) Calculate the engine efficiency for the thermodynamic cycle shown on the left operating on an ideal gas. Paths  $2 \rightarrow 3$  and  $4 \rightarrow 1$  are constant pressure while  $1 \rightarrow 2$  and  $3 \rightarrow 4$  are adiabats. Express your answer in terms of the specific heats  $C_V$  and  $C_P$  and the temperatures  $T_1, T_2, T_3, T_4$ .

