1) The following equations of state each violate at least one basic principle of thermodynamics. Identify the violation in each case. R, θ, v₀ are all positive constants. (Hint: What does the Third Law say?)

a) \[ S = \left( \frac{R}{\theta^2} \right)^{1/3} \left( \frac{nE}{V} \right)^{3/4} \]

b) \[ S = \left( \frac{R}{\theta} \right)^{1/2} n \exp \left( -\frac{EV}{nR \theta v_0} \right) \]

c) \[ S = nR \ln \left( \frac{EV}{n^2 R \theta v_0} \right) \]

2) In Chapter 1 of Chandler’s text there is a discussion of the variational statement of the second law as the entropy maximization principle, i.e. \((\delta S)_{E,V,n} \leq 0\) and its corollary, the energy minimization principle, i.e. \((\delta E)_{S,V,n} \geq 0\) for all small variations from the stable equilibrium state. Prove the variational principle for Gibbs free energy, i.e. \((\delta G)_{T,p,n} \geq 0\).

3) Consider a rubber band under tension, f, with length per mole, \(l = L/n\). For this system it has been suggested that the entropy S is related to the energy (here \(E>0\)), and the length according to

\[ S = 2cn \sqrt{E/n} g(l/l_o) \]

where \(|l/l_o| \leq 1\), c>0, and

\[ g(x) = (1-x^2)^\gamma \], \(|x| \leq 1\)

a) Determine as a function of temperature and length per mole the constant length heat capacity per mole, \(C_l/n\).

b) For small tension \(f\), the length per mole is also small. Show that in this regime \(f = bT^2l\) and identify the positive constant b in terms of \(\gamma\), c, and \(l_o\).

c) In the regime where the result to part (b) is valid, an experimentalist changes the tension reversibly from \(f_1\) to \(f_2\). To maintain the system at a constant temperature, heat must flow between the rubber band and its surroundings. Determine the net heat flow as a function of \(f_1, f_2, T, b, \) and \(n\).
4) Which thermodynamic potential would be most convenient for making equilibrium calculations in each circumstance? Briefly justify your answers.

a) An isolated system.

b) An insulated system enclosed in a piston bearing a weight.

c) A liquid system contained in a beaker exposed to the atmosphere.

d) A closed system of fixed dimensions submerged in an ice bath.

e) A two component system contained by a flexible membrane permeable only by component 1.