1. Problem 22–24 in McQuarrie & Simon:

   We can derive the Gibbs-Helmholtz equation directly from Equation 22.31 (a) in the following way. Start with $(\partial G/\partial T)_p = -S$ and substitute fro S from $G = H - TS$ to obtain

   $$\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = -\frac{H}{T^2}$$

   Now show that the left side is equal to $(\partial[G/T]/\partial T)_P$ to get the Gibbs-Helmholtz equation.

2. The surface tension of water is observed to decrease linearly with temperature (in experiments at constant p and a): $\gamma(T) = b - cT$, where T = temperature (in °C), $b = 75.6\,\mathrm{erg\,cm^{-2}}$ (the surface tension at 0 °C) and $c = 0.1670\,\mathrm{erg\,cm^{-2}\,deg^{-1}}$.

   (a) If γ is defined by $dU = TdS - pdV + \gamma da$, where da is the area change of a pure material, give γ in terms of a derivative of the Gibbs free energy at constant T and p.

   (b) Using a Maxwell relation, determine the quantitative value of $(\partial S/\partial a)_{p,T}$ from the relationships above.

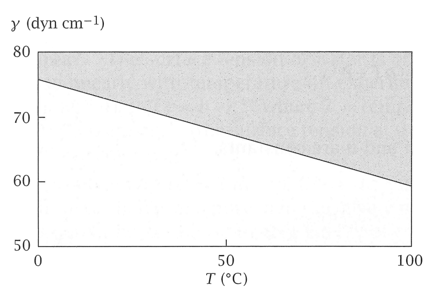
   (c) Estimate the entropy change ΔS from the results above if the area of the water/air interface increases by 4 Å^2 (about the size of a water molecule).

3. (a) Show that, in general, for quasi-static processes:

   $$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

   (b) Based on (a), show that $(\partial C_p/\partial p)_T = 0$ for an ideal gas.

4. The figure below shows the surface tension of water as a function of temperature.



   (a) From the figure, determine the numerical value of $(\partial\gamma/\partial T)_{p,N,A}$, where T = temperature, p = pressure, and A = surface area.

   (b) Find the Maxwell relation for the partial derivative equal to $(\partial\gamma/\partial T)_{p,N,A}$.

   (c) Write an expression for the enthalpic and entropic components of the surface tension γ.

(d) Combining the results from above, compute the numerical values of the enthalpic and entropic parts of γ at $T = 300\,\mathrm{K}$, and comment on which component dominates the surface tension.

5. (a) Start with Problem 22-54 in McQuarrie & Simon:

When a rubber band is stretched, it exerts a restoring force, f, which is a function of its length L and its temperature T. The work involved is given by

$$w = \int f(L,T)\,dL \tag{1}$$

Why is there no negative sign in front of the integral, as there is in Equation 19.2 for P-V work? Given that the volume change upon stretching a rubber band is negligible, show that

$$dU = T\,dS + f\,dL \tag{2}$$

and that

$$\left(\frac{\partial U}{\partial L}\right)_T = T\left(\frac{\partial S}{\partial L}\right)_T + f \tag{3}$$

Using the definition $A = U - TS$, show that Equation 2 becomes

$$dA = -S\,dT + f\,dL \tag{4}$$

and derive the Maxwell relation

$$\left(\frac{\partial f}{\partial T}\right)_L = -\left(\frac{\partial S}{\partial L}\right)_T \tag{5}$$

Substitute Equation 5 into Equation 3 to obtain the analog of Equation 22.22

$$\left(\frac{\partial U}{\partial L}\right)_T = f - T\left(\frac{\partial f}{\partial T}\right)_L$$

For many elastic systems, the observed temperature-dependence of the force is linear. We define an *ideal rubber band* by

$$f = T\phi(L) \qquad \text{(ideal rubber band)} \tag{6}$$

Show that $(\partial U/\partial L)_T = 0$ for an ideal rubber band. Compare this result with $(\partial U/\partial V)_T = 0$ for an ideal gas.

Now let's consider what happens when we stretch a rubber band quickly (and, hence, adiabatically). In this case, $dU = dw = f\,dL$. Use the fact that U depends upon only the temperature for an ideal rubber band to show that

$$dU = \left(\frac{\partial U}{\partial T}\right)_L dT = f\,dL \tag{7}$$

The quantity $({}^{\partial U}/_{\partial T})_L$ is a heat capacity, so Equation 7 becomes

$$C_L dT = f\,dL \tag{8}$$

Argue now that if a rubber band is suddenly stretched, then its temperature will rise. Verify this result by holding a rubber band against your upper lip and stretching it quickly.

(b) Given what you've derived, do you predict that a rubber band will stretch or shrink when you heat it?

(c) Can you think of a molecular explanation for this process? (Hint: what happens to the entropy, S, as you stretch the band?)

Numbered equations:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{22.31 (a)}$$

$$w = -\int_{V_i}^{V_f} P_{\text{ext}} dV \tag{19.2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \tag{22.22}$$