5.9: Chapter 5 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

5.1
Show that the enthalpy of a fixed amount of an ideal gas depends only on the temperature.

5.2
From concepts in this chapter, show that the heat capacities C_V and C_p of a fixed amount of an ideal gas are functions only of T.

5.3
During the reversible expansion of a fixed amount of an ideal gas, each increment of heat is given by the expression $đq = C_V\,\mathrm{d}T + (nRT/V)\,\mathrm{d}V$ (Eq. 4.3.4).

(a) A necessary and sufficient condition for this expression to be an exact differential is that the reciprocity relation must be satisfied for the independent variables T and V (see Appendix F). Apply this test to show that the expression is *not* an exact differential, and that heat therefore is not a state function.

(b) By the same method, show that the entropy increment during the reversible expansion, given by the expression $\mathrm{d}S = đq/T$, is an exact differential, so that entropy is a state function.

5.4

This problem illustrates how an expression for one of the thermodynamic potentials as a function of its natural variables contains the information needed to obtain expressions for the other thermodynamic potentials and many other state functions.

From statistical mechanical theory, a simple model for a hypothetical "hard-sphere" liquid (spherical molecules of finite size without attractive intermolecular forces) gives the following expression for the Helmholtz energy with its natural variables T, V, and n as the independent variables:

$$A = -nRT\ln\left[cT^{3/2}\left(\frac{V}{n} - b\right)\right] - nRT + na \tag{5.9.1}$$

Here a, b, and c are constants. Derive expressions for the following state functions of this hypothetical liquid as functions of T, V, and n.

(a) The entropy, S

(b) The pressure, p

(c) The chemical potential, μ

(d) The internal energy, U

(e) The enthalpy, H

(f) The Gibbs energy, G

(g) The heat capacity at constant volume, C_V

(h) The heat capacity at constant pressure, C_p (hint: use the expression for p to solve for V as a function of T, p, and n; then use $H = U + pV$)

5.6
Use the data in Table 5.1 to evaluate $(\partial S/\partial A_\mathrm{s})_{T,p}$ at $25\,^\circ\mathrm{C}$, which is the rate at which the entropy changes with the area of the air–water interface at this temperature.

5.7
When an ordinary rubber band is hung from a clamp and stretched with constant downward force F by a weight attached to the bottom end, gentle heating is observed to cause the rubber band to contract in length. To keep the length l of the rubber band constant during heating, F must be increased. The stretching work is given by $đw' = F\,\mathrm{d}l$. From this information, find the sign of the partial derivative $(\partial T/\partial l)_{S,p}$; then predict whether stretching of the rubber band will cause a heating or a cooling effect.

(Hint: make a Legendre transform of U whose total differential has the independent variables needed for the partial derivative, and write a reciprocity relation.)

You can check your prediction experimentally by touching a rubber band to the side of your face before and after you rapidly stretch it.