# Assignment 8

**1. (a)** The molar-specific energy equation for a monatomic van der Waals gas is given by

$$u = \frac{3}{2}RT - av \tag{1}$$

Show that the molar-specific enthalpy is given by

$$h = \frac{5}{2}RT + RT\frac{b}{v} - 2\frac{a}{v} \tag{2}$$

where $a$ and $b$ are constants as shown in the van der Waals equation.

**(b)** It can be shown that the Joule-Thomson coefficient for such a gas is given by

$$\mu \equiv \left.\frac{\partial T}{\partial P}\right|_h = \left(\frac{-1}{c_P}\right) \frac{\left[RTv^3b - 2av\left(v-b\right)^2\right]}{\left[RTv^3 - 2a\left(v-b\right)^2\right]} \tag{3}$$

where $c_P$ is the molar specific heat at constant pressure. Find an expression for the inversion temperature, $T_{inv}$, for this gas. The right hand side should include only $v$ and some constants.

**(c)** Calculate the inversion temperature for $N_2$ for a molar volume of $v = 1.27 \times 10^{-4}$ m$^3$/mol. [Note: $a = 0.1408$ Jm$^3$/mol$^2$ and $b = 3.913 \times 10^{-5}$ m$^3$/mol]

**(d)** What pressure does the result of part (c) correspond to?

**(e)** Suppose $b << v$. Find a simplified expression for $T_{inv}$ for that case and re-evaluate it for $N_2$. Is this result similar to the result of part (c) or is it very different? Comment on the result.

**2.** Do Prob. 5.5 in the text.

**3.** (This question is a modified version of Prob. 5.14 in the text.)

**(a)** Expand $S$ in terms of $T$ and $V$, and expand $V$ in terms of $T$ and $P$.

**(b)** Insert $dV$ from the second expansion into the first, let $P$ be constant, and simplify the result.

**(c)** It can be shown that

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V \qquad C_P = T\left.\frac{\partial S}{\partial T}\right|_P \tag{4}$$

Write the result of part (b) in terms of $C_P$ and $C_V$ using Eqns. 4 and arrange the result so that only $C_P$ is on the left hand side of the equation.

**(d)** Use a Maxwell relation, the cyclic relation, and the definitions of $\beta$ and $\kappa$ to reproduce the result

$$C_P = C_V + \frac{TV\beta^2}{\kappa} \tag{5}$$

Notice that, for a liquid or solid, this equation provides a simple relation between $T$ and $V$ since all other quantities are likely constants. [Also note that when $\kappa$ is written without a subscript, it means $\kappa_T$.]

**4.** Suppose that the molar-specific Gibbs free energy function is

$$g = RT\,ln\left(\frac{P}{P_0}\right) - AP \tag{6}$$

where $P$ is the pressure, $P_0$ is a reference pressure, and $A$ is a function which depends only on temperature, $T$. For the following, express all extensive quantities in molar specific form, express all results in terms of *known* quantities and constants, and express the results as simply as possible. Find expressions for

**(a)** the equation of state
**(b)** the entropy, $s$
**(c)** the remaining thermodynamic potentials, $h$, $f$, and $u$
**(d)** the specific heats, $c_v$ and $c_P$
**(e)** $\beta$ and $\kappa$
**(f)** the Joule-Thomson coefficient, $\mu$