ECHE 363 – Thermodynamics of Chemical Systems
Homework #6

100 points total. Complete the following problems and upload your solutions to the Canvas assignment dropbox by the due date/time.

You are strongly encouraged to collaborate with your classmates on the homework, but each student is required to come up with a unique solution to the homework problems. For full credit, you must show all work. This includes showing all steps involving algebra and/or calculus. Your calculator can only be used for the final evaluation of numerical answers and may not be used for solving algebraic equations and/or integrals.

1. Verify that

   a. $\left(\dfrac{\partial P}{\partial T}\right)_{v_\mathrm{m}} = \dfrac{\beta}{\kappa}$

   b. $c_{\mathrm{p,m}} - c_{\mathrm{v,m}} = \dfrac{v_\mathrm{m} T \beta^2}{\kappa}$

2. Consider the following equation of state: $Z = \dfrac{Pv_\mathrm{m}}{RT} = 1 + B'P + C'P^2$, where B' and C' are constant parameters with no temperature dependence. In terms of B', C', R, P, T, and $c_{\mathrm{p,m}}$ find the following expressions

$$\left(\frac{\partial h_\mathrm{m}}{\partial P}\right)_T, \left(\frac{\partial h_\mathrm{m}}{\partial P}\right)_{s_\mathrm{m}}, \left(\frac{\partial h_\mathrm{m}}{\partial T}\right)_P, \left(\frac{\partial h_\mathrm{m}}{\partial T}\right)_{s_\mathrm{m}}$$

3. The PVT behavior of a certain gas is described by the equation of state: $P(v_\mathrm{m}-b)=RT$, where b is a constant. If in addition $c_{\mathrm{v,m}}$ is constant, show that:
   (a) u_m is a function of T only
   (b) $c_{\mathrm{p,m}}/c_{\mathrm{v,m}}$=constant

4. Starting with $s_\mathrm{m}(P, v_\mathrm{m})$, derive an expression for ds_m in terms of measurable properties (P, T, v_m, $c_{\mathrm{p,m}}$, $c_{\mathrm{v,m}}$).

5. We are interested in the thermodynamic properties of a strip of rubber as it is stretched. Consider n moles of pure ethylene propylene rubber (EPR) that has an unstretched length z_0. If it is stretched by applying a force F, it will obtain an equilibrium length z given by $F = kT(z - z_0)$, where k is a positive constant.

   The heat capacity of unstretched EPR is given by: $c_{z,\mathrm{m}} = \left(\frac{\partial u_{\mathrm{m}}}{\partial T}\right)_z = a + bT$, where a and b are both constants.

   a. Come up with fundamental property relations for dU and dA for this system, where A is the Hemholtz free energy. Recall from mechanics that the work required for a reversible elastic extension is given by $dW_{\mathrm{rev}} = Fdz$.

   b. Develop an expression that relates the change in entropy to the changes in temperature and length, that is, the independent variables z and T (and constants a, b, k, n, and z_0). In other words, for $S = S(T,z)$, find dS. Hint: you will need to derive an expression for $\left(\frac{\partial S}{\partial z}\right)_T$. This can be done with the appropriate Maxwell relationship.

   c. Develop an expression that relates the change in internal energy to changes in temperature and length. For $U = U(T,z)$ find dU.

   d. Consider the relative energetic and entropic contributions to the isothermal extension of EPR. The energetic force (the component of the force that, upon isothermal extension of the rubber, increases the internal energy) is given by

   $$F_U = \left(\frac{\partial U}{\partial z}\right)_T$$

   while the entropic force is given by

   $$F_S = -T\left(\frac{\partial S}{\partial z}\right)_T$$

   Come up with expressions for F_U and F_S for EPR.

   e. If the change from the unstretched state to the stretched state above occurred adiabatically, would the temperature of the EPR go up, stay the same, or go down? Explain.

6. Answer the following reflection questions (5 points):

    a. What about the way this class is taught is helping your learning?

    b. What about the way this class is taught is inhibiting your learning?