Problem Set PS08

ISSUED: 3/21/02 **Due: 4/4/02**

Prof. Darin J. Ulness Name ______________________

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Exercises

1. Use Eq. (18.46) of the notes to calculate the ratio of the thermal expansion to the isothermal compressibility for a Dieterici and Redlich–Kwang gas

2. Use Eqs. (18.52) and (18.55) to find the relation between C_{Pm} and C_{Vm} for a Deterici and a Redlich–Kwang gas. (You can use MATHEMATICA to help you with the derivatives.)

3. Each degree of freedom a molecule has contributes $\frac{1}{2}R$ to the molar heat capacity. Knowing this, what is $\frac{C_{Pm}}{C_{Vm}}$ for argon, nitrogen, carbon dioxide and water vapor. Assume the ideal gas law applies. Quantum mechanics comes into play here because at room temperature there is not enough thermal energy to exicte vibrations so the vibrational degrees of freedom are shut down and do not contribute to the heat capacity.

4. Calculate the work done during reversible isothermal expansion of a van der Waals, Berthelot and Redlich-Kwang gas.

5. It can be shown that for an ideal gas

$$\frac{\partial G}{\partial P} = V.$$

   Replace V on the right hand side using the ideal gas law. Then solve the resulting differential equation to show that for an ideal gas the free energy is

$$G = nRT \ln P + f(T),$$

   where $f(T)$ is at most a function of T. What is $\triangle G$ for an isothermal pressure change?

6. Repeat the previous problem for a gas described be the equation of state: $PV = nRT + \alpha P$

7. A simple model for particles in a centrifuge tube is to treat the particles of interest as an ideal "gas" (here empty space between particles is replaced by solution). The "centrifugal pressure," P, is a function of the position (or height, h) of the particle in the test tube:

$$\frac{dP}{dh} = \frac{-Mg}{V_m},$$

where M is the mass of the particle and g is the centrifugal force. The free energy of the particles is given by the results of the previous question but with the addition of a potential energy term based on the height in the test tube,

$$G = RT \ln P + f(T) + Mgh,$$

If the centrifugal pressure at the bottom of the tube (at $h = 0$) is P_0 and the tube is at a constant temperature show that the centrifugal pressure at any height h is

$$P = P_0 e^{-\frac{Mgh}{RT}}.$$

Solve the problem two different ways. First, solve the differential equation for P. Second use the free energy functions.

Conceptual Problems

8. Explain how the Joule expansion experiment differs from the Joule–Tomson experiment (See legacy projects by Cara Hagen and Stephanie Collins (fall99)).

9. How do you think the ratio $\frac{C_{Pm}}{C_{Vm}}$ compares between gases liquids and solids?

Computer Problems

10. Use MATHEMATICA to derive the virial series for the van der Waals, Berthelot, Dieterici and Redlich–Kwang gases. Find an expression for the Boyle temperature of each type of gas.