

## PROBLEM SET 4

1) **(20 pts)** A closed cylinder of total volume  $V$  is divided into three sections. The first section contains 1000 moles of helium, the second section 2000 moles of neon, and the third section 3000 moles of argon (all monatomic gases). The volumes of the three sections are chosen so that the pressures in each section are the same and equal to 2.0 atm. The temperatures in the three sections are also the same and equal to 300 K.

- a) Express the volume of each section as a fraction of  $V$ .
- b) The partitions dividing the sections are now removed allowing all three gases to occupy the full volume  $V$ . Calculate the resulting change in the entropy of the system. Keep in mind that the temperature stays constant during the expansion of the three gases.
- c) Determine the resulting change in the Helmholtz free energy of the system. *Hint:* recall that the work done by an expanding gas is equal to the negative of its free energy change.

2) **(20 pts)** The Gibbs free energy of a non-ideal gas is given by the equation  $G = n[RT \ln(P/P_0) - f(T)P]$

where  $n$  is the number of moles of the gas,  $P_0$  is a constant, and  $f(T)$  is some function of the temperature.

- a) Using the relation between  $V$  and  $G$ , show that  $PV = n[RT - f(T)P]$
- b) Using the relation between  $S$  and  $G$ , find the entropy of the gas.
- c) Determine the Helmholtz free energy (the function  $F$ ) of the gas.

3) **(20 pts)** Recall that the equation of state for a van der Waals gas is given by

$$\left(P + \frac{aN^2}{V^2}\right)(V - bN) = NkT$$

where  $a$  and  $b$  are constants and  $N$  is the number of molecules of the gas.

a) Solve for the pressure in terms of  $V$  and  $T$ .

b) Suppose that  $N$  molecules of a van der Waals gas expand *isothermally* from volume  $V_1$  to volume  $V_2$ . Calculate the change in the Helmholtz free energy.

c) By integrating the expression connecting  $P$  and  $F$ , derive an expression for  $F$  in terms of  $T$  and  $V$ . Note that the integration over  $V$  yields an integration constant that is a function of  $T$ . Now differentiate the result to find the entropy  $S$  as a function of  $V$  and  $T$ .

d) Using the results of the previous parts, show that the change in the internal energy of the gas during the isothermal expansion is given by

$$\Delta U = aN^2(1/V_1 - 1/V_2)$$

4) **(10 pts) Text Problem 5.5**

5) **(5 pts) Text Problem 5.10** – assume here that neither the entropy nor the volume per mole of liquid water depend on the temperature within the range considered.

6) **(15 pts) Text Problem 5.32** – in part b, use the value  $L=334$  kJ/kg for the latent heat of fusion of water. In part d, use the value  $m=60$  kg for the mass of the skater and assume that only one skate is in contact with the ice and that the part of the blade in contact with the ice is a rectangle with dimensions 30 cm x 0.5 cm.

7) **(10 pts) Text problem 5.35** – note that the quantity  $L$  is here is the latent heat per mole rather than per kg, so in the Clausius-Clapeyron equation, you should replace  $m$  by  $n$ .

**(Optional) Extra Credit Problem** (to count towards Exam II) — due Oct 26  
(20 points undergraduates, 15 points graduates)

8) **Text problem 5.52** - To clarify what is asked in the problem, I've broken down the problem into multiple parts, and added an additional part c) as well.

- a) For the requested isotherm of  $T/T_c = 0.95$  :, plot the Van der Waals pressure as a function of volume in terms of the reduced quantities. This is similar to your extra credit problem (HW Set 2). From this plot, you can use Maxwell Construction to determine which reduced vapor pressure (horizontal line) can get approximately equal areas under the curves, as described in Fig. 5.21 of the text as well as described / to be described in lecture. **Hint:** re-write the van der Waals as a cubic equation and solve for the 3 solutions of  $v$ . Then use these 3 roots as integration limits to get the areas under the curves.
- b) Plot the Gibbs free energy (in units of  $NkT_c$ ) versus pressure and check that the graph predicts the same vapor pressure, as in part a), i.e., check the vertical crossing within the triangle corresponds to the vapor pressure you determine from part a) (as an example, see Fig. 5.21 (left))

When plotting Gibbs free energy versus pressure, it must be done in terms of the reduced variables discussed in Text Problem 5.51, and then factor out  $NkT_c$ , and express the Gibbs free energy as :  $G / NkT_c$  , which should only be a function of reduced variables,  $t$  and  $v$  and an arbitrary constant  $C(T)$ .

The constant  $C(T)$  can be omitted in the plot.

**Hint:** Starting with Eq. 5.56, express Gibbs free energy  $G$  in terms of only reduced variables, and critical constants (Text Problem 5.48), which should end up either cancelling out or being absorbed by the arbitrary constant  $C(T)$

- c) Since now you have the machinery (programming code) to determine the vapor pressure from Maxwell construction for a single isotherm, perform the same operation for different isotherms ( $T/T_c = 0.85, 0.9, 0.95, 1.0$ ) to determine the corresponding vapor pressures (from Maxwell construction) at which the gas-liquid transition occurs. Make a plot the vapor pressure determined,  $P/P_c$  versus the  $T/T_c$ . You should be able to reconstruct the phase boundary, similarly to Fig. 5.23 (right). Also, provide the plot of the overlayed different isotherms in the PV diagram.