Homework 4 Due Friday, February 18

The problems in this homework will be the last for our study of thermodynamics. Reminder: Exam 1 will be on Monday, 2/21/22.

Warm-up exercises: Do not pass in solutions. Practice until you can go through all four exercises in just a few minutes.

1) A process takes place at constant T and V. For this process, $\Delta S_{univ} = 5\,\text{J/K}$. What is the change in the Helmholz free energy if T=300 K? What is the maximum work that could be extracted from this process?

2) A process takes place at constant T and P. The temperature is 300 K. For this process, $\Delta S_{univ} = 3\,\text{J/K}$. What is the change in the Gibbs free energy? What is the maximum work that could be extracted from this process (besides any PV work)?

3) An endothermic chemical reaction is proposed to take place at constant T and P. For 300 K and 1 atm, $\Delta H = 10\,kJ$. If $\Delta S = 40\,\text{J/K}$, what is ΔG ? Will this reaction take place spontaneously?

4) Consider 10 moles of monatomic ideal gas at T=300 K and V=20 liters. The volume doubles and the temperature remains the same. Calculate ΔS . What is ΔA ? What is the maximum work that could be performed by the gas for this change in state?

Problems: <u>Do</u> pass in solutions.

1) Consider the system shown in the figure. When the pins fall away, the gas expands against a constant external pressure to 1 atm. How much work was performed on the surroundings? Calculate ΔS_{univ} for this irreversible process, and determine the <u>additional</u> work $T\Delta S_{univ}$ that could have been extracted had the expansion to the same final pressure been carried out reversibly. (Alternatively, think of a way to carry out a reversible expansion and calculate the reversible work. The difference between the reversible work and the work you calculated for the irreversible process above is the <u>additional</u> work.)
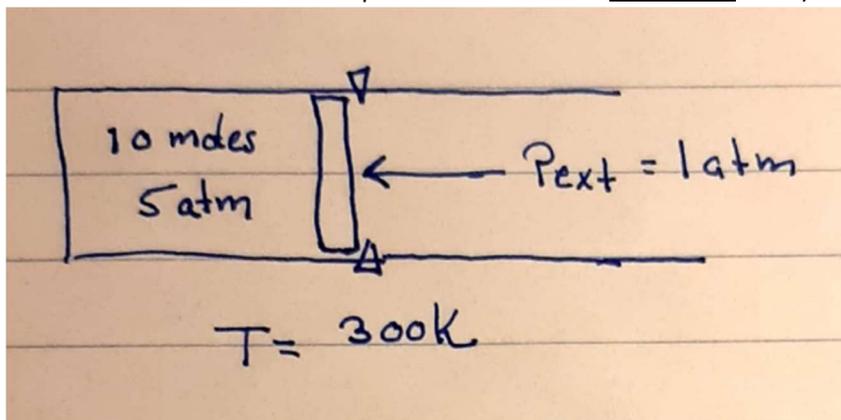
2) Two glass bulbs, one on the left with a volume of 2 liters and the other on the right with a volume of 6 liters, are connected to one another by a thin tube that is initially closed by a stopcock. The bulb on the left has 0.1 moles of ideal gas, and the bulb on the right is

evacuated. The system is in thermal equilibrium with the surroundings at 300K. When the stopcock is opened, the gas flows out to fill both bulbs. Calculate ΔA for this process. If we were to insert a propeller to extract work as the gas flows from left to right, what is the maximum amount of work that we could possibly extract?
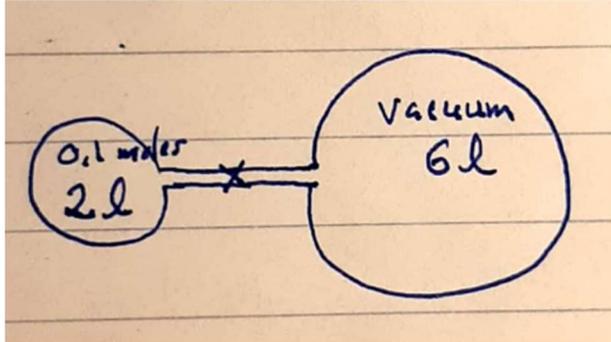
3) An ideal gas consisting of one mole of molecules of type A is in contact with the surroundings at T=300 K, and under a constant pressure of 1 atm. The gas undergoes a spontaneous isomeric chemical reaction, wherein some fraction x of molecules of type A change shape, become isomers of type B. This results in an equilibrium mixture of 1-x moles of A and x moles of B. The enthalpy of B is lower than the enthalpy of A by 3 kJ/mole, such that $\Delta H = -x\varepsilon; \quad \varepsilon = 3\,\text{kJ/mole}$. The change in entropy is given by

$$\Delta S = -R\left(x \ln x + (1-x)\ln(1-x)\right)$$

Use the computer to graph the change in Gibbs free energy as a function of x. Determine, by inspection of your graph, or otherwise, the concentration of A and the concentration of B when equilibrium is obtained. What is the maximum work that could be extracted from this process (aside from PV work)?
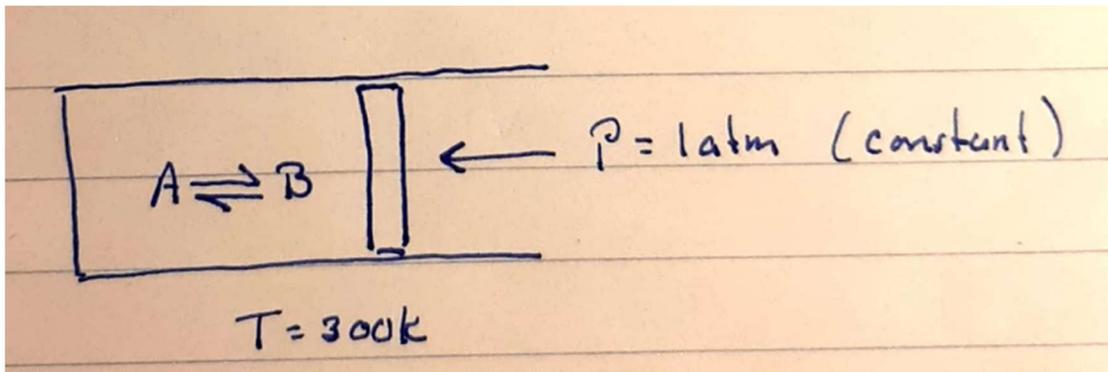
4) Calculate the RMS velocity of an I_2 molecule (diatomic iodine) at 300 K. Calculate the RMS velocity of a He atom at 300 K. Compare these two.

5) Consider a vessel of diatomic nitrogen gas at room temperature. (a) What is the most likely speed of a molecule? (b) How fast does a molecule have to be traveling to be in the top 5%? (Hint: For (a), use DESMOS to make a graph of the Maxwell-Boltzmann velocity distribution and locate the maximum on the graph. For (b), integrate the Maxwell-Boltzmann distribution numerically. See planetcalc.com/5494)

6) Calculate the absolute entropy for 1 mole of Ar gas (monatomic) with 22.4 liter volume at 273 K using Boltzmann's formula. What is the change in entropy if the temperature doubles while V is constant? What is the change in entropy if the volume doubles while T is constant? What is the change in entropy if both T and V double? (Note: To evaluate $\ln(N!)$ use Stirling's asymptotic formula $\ln(N!) \sim N \ln N - N$)

7) When water initially at a temperature T1 is mixed with the same amount of water at a different temperature T2 in an insulated container at constant pressure, the final temperature of the mixture is the average of the two. Show that the change in entropy for the adiabatic mixing process is given by

$$\Delta S = C_p \ln \frac{(T_1 + T_2)^2}{4 T_1 T_2}$$

Prove that ΔS is always positive for any values of the two initial temperatures provided that they are not the same.