

Homework Assignment 5

PHYSICS 314 - THERMODYNAMICS & STATISTICAL PHYSICS (Spring 2018)

Due Friday, March 9th, by noon, Noyce 1135

I cannot award full credit for work that I am unable to read or follow. For my benefit and for yours, please:

- *Write neatly*
- *Show and EXPLAIN all steps*
- *Make diagrams large and clearly-labeled*

You are welcome to collaborate with others on this assignment. However, the work you turn in should be your own. Please cite collaborators and outside sources. See the syllabus for details.

Regardless of the number of parts, all homework problems are weighted equally. Regardless of the number of questions, all homework assignments are weighted equally.

- 1) Two identical blocks of copper A and B initially at temperatures T_A and T_B , respectively, are placed in thermal contact with one another. Each block has mass m and specific heat capacity c . Assume that the combined system of the two copper blocks is isolated.
- a) Derive an expression for the total change in energy of the system, ΔU , as the system goes from its initial state to equilibrium. Express your answer in terms of c , m , T_A , T_B , and T_f , the equilibrium temperature of the system.

Start with the definition of heat capacity.

$$c = \frac{Q}{m\Delta T}$$

Since no work is being done, by the first law, the heat is equal to the change in energy.

$$c = \frac{\Delta U}{m\Delta T}$$

$$\Delta U = cm\Delta T$$

The change in the total energy is the sum of the changes in energy for A and B.

$$\Delta U = \Delta U_A + \Delta U_B$$

Use the expression above. c and m are the same for both systems.

$$\Delta U = cm\Delta T_A + cm\Delta T_B$$

Write the change in energy as the difference between the final and initial temperatures. Note that they will have the same final temperature at equilibrium.

$$\Delta U = cm(T_f - T_A) + cm(T_f - T_B)$$

$$\Delta U = cm(2T_f - T_A - T_B)$$

- b) Use your expression from a) to find the final temperature of the system. *I know you probably know the answer without doing any calculations. I want you to follow this method anyway.*

Since the system is isolated, the total change in energy is zero.

$$\Delta U = 0$$

Plug this in above and solve for T_f .

$$\Delta U = 0 = cm(2T_f - T_A - T_B)$$

$$0 = 2T_f - T_A - T_B$$

$$2T_f = T_A + T_B$$

$$T_f = \frac{T_A + T_B}{2}$$

- c) Find the change in entropy of each block (ΔS_A and ΔS_B) and the total variation in entropy of the system (ΔS). Express your answer in terms of c , m , T_A , and T_B .

Start with the expression for change in entropy at constant volume from class - Schroeder (3.18).

$$dS = \frac{C_V dT}{T}$$

Replace the heat capacity with the specific heat capacity (Schroeder (1.42)).

$$dS = \frac{cmdT}{T}$$

Integrate to get the total change in entropy for block A.

$$\Delta S_A = \int dS = \int_{T_A}^{T_f} \frac{cmdT}{T}$$

$$\Delta S_A = cm \int_{T_A}^{T_f} \frac{dT}{T}$$

Integrate.

$$\Delta S_A = cm \ln[T] \Big|_{T_A}^{T_f}$$

$$\Delta S_A = cm(\ln[T_f] - \ln[T_A])$$

$$\Delta S_A = cm \ln \left[\frac{T_f}{T_A} \right]$$

Sub in the expression for the final temperature from above.

$$\Delta S_A = cm \ln \left[\frac{T_A + T_B}{2T_A} \right]$$

The process for B is identical.

$$\Delta S_B = cm \ln \left[\frac{T_A + T_B}{2T_B} \right]$$

The sum of these two expressions is the total change in entropy.

$$\Delta S = \Delta S_A + \Delta S_B$$

$$\Delta S = cm \ln \left[\frac{T_A + T_B}{2T_A} \right] + cm \ln \left[\frac{T_A + T_B}{2T_B} \right]$$

$$\Delta S = cm \left(\ln \left[\frac{T_A + T_B}{2T_A} \right] + \ln \left[\frac{T_A + T_B}{2T_B} \right] \right)$$

Simplify using the log rule about sums.

$$\Delta S = cm \ln \left[\frac{(T_A + T_B)^2}{4T_A T_B} \right]$$

d) Show that the second law of thermodynamics holds for the system.

This is equivalent to showing that the change in entropy is greater than zero.

$$\Delta S = cm \ln \left[\frac{(T_A + T_B)^2}{4T_A T_B} \right]$$

The specific heat capacity and the mass are positive definite. Thus, the change in entropy is greater than zero if the log term is greater than zero. Examine to see if the following inequality holds.

$$\ln \left[\frac{(T_A + T_B)^2}{4T_A T_B} \right] > 0$$

Exponentiate.

$$\frac{(T_A + T_B)^2}{4T_A T_B} > e^0 = 1$$

$$(T_A + T_B)^2 > 4T_A T_B$$

Expand.

$$T_A^2 + T_B^2 + 2T_A T_B > 4T_A T_B$$

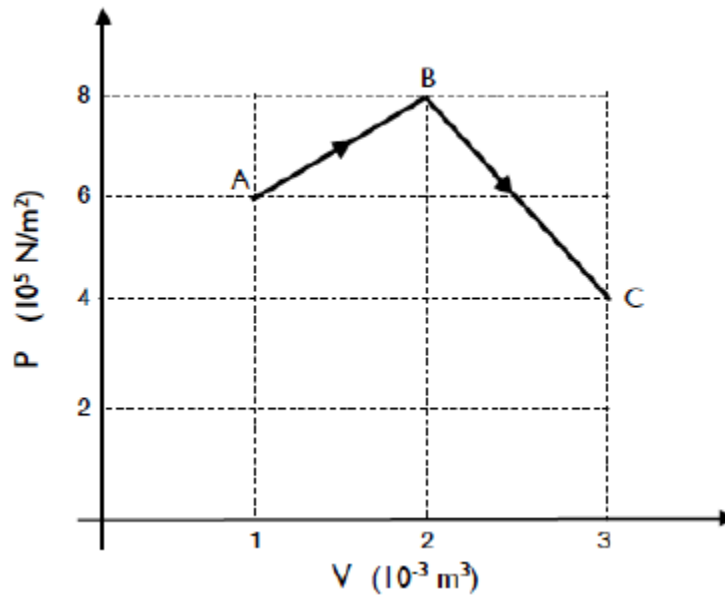
$$T_A^2 + T_B^2 - 2T_A T_B > 0$$

Note that we can rewrite this expression as a difference squared.

$$(T_A - T_B)^2 > 0$$

This is definitely true, so our original supposition was true, and the total change in entropy is positive.

- 2) Assume there is one mole of an ideal diatomic gas. This gas is taken quasistatically first from state **A** to state **B**, and then from state **B** to state **C** along the straight-line paths shown in the pressure vs. volume diagram.



- a) What is the heat capacity at constant volume of the gas, C_V ?

One mole of an ideal diatomic gas has an internal energy given by the equipartition theorem. $f = 5$ for a diatomic ideal gas.

$$U = \frac{5}{2} (1 \text{ mol}) RT$$

Differentiate to find the heat capacity.

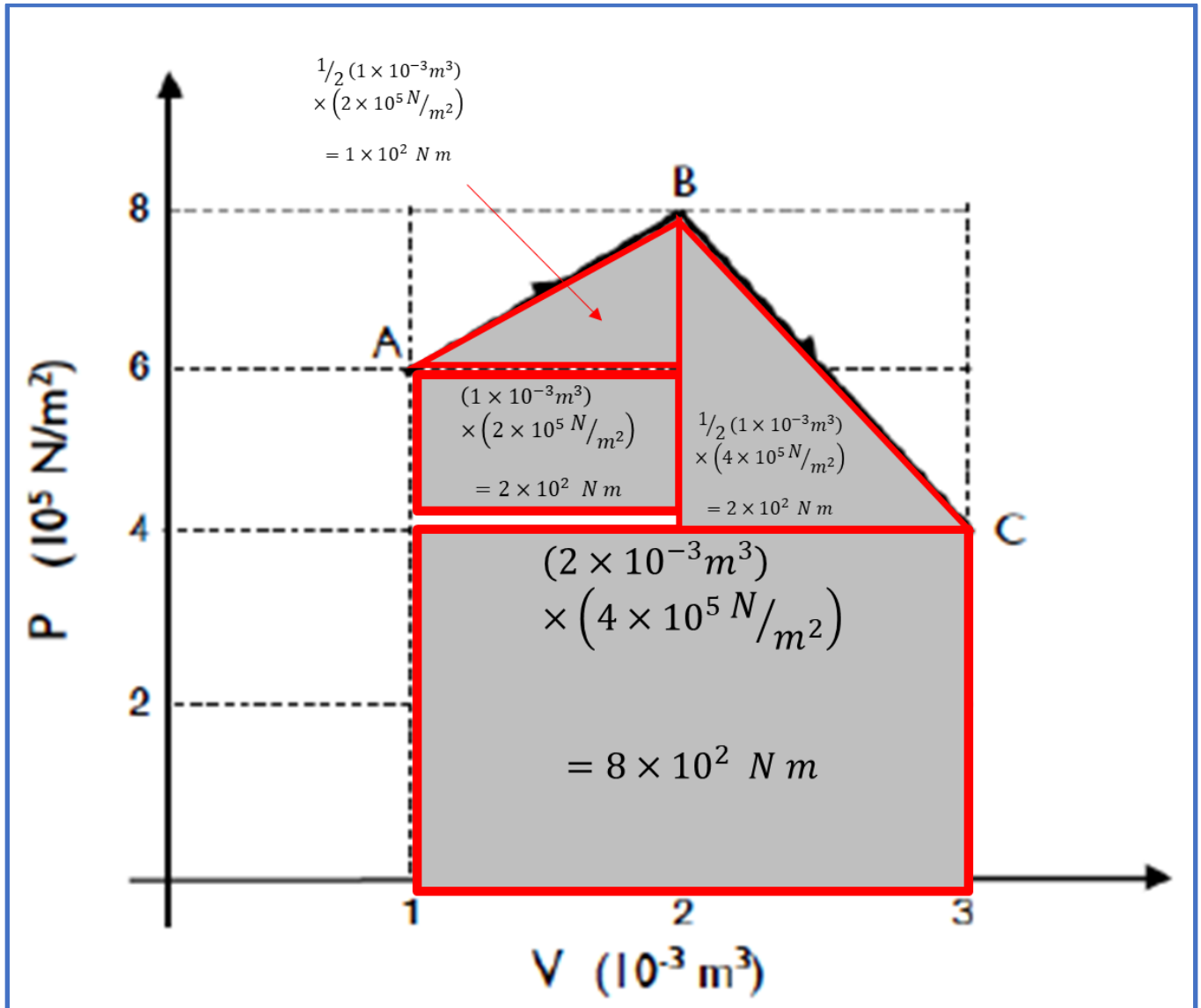
$$C_V = \left. \frac{\partial U}{\partial T} \right|_V$$

$$C_V = \left. \frac{\partial}{\partial T} \left(\frac{5}{2} (1 \text{ mol}) RT \right) \right|_V$$

$$C_V = \frac{5}{2} (1 \text{ mol}) R \approx 20.79 \text{ J/K}$$

b) What is the work done on the gas in the process **A** → **B** → **C**?

The work done on the gas is the negative of the area under the curve.



Adding up the areas of the four shapes shown gives a total area.

$$8 \times 10^2 \text{ N m} + 2 \times 10^2 \text{ N m} + 1 \times 10^2 \text{ N m} + 1 \times 10^2 \text{ N m} = 13 \times 10^2 \text{ N m}$$

$$1.3 \times 10^3 \text{ N m} = 1300 \text{ J}$$

The work done on the gas is the negative of this.

$$-1300 \text{ J}$$

c) What is the heat absorbed by the gas in this process?

Use the First Law to find the heat from the work done on the gas and the change in the internal energy.

$$Q = \Delta U - W$$

Find the energy using the equipartition theorem for one mole of gas.

$$\Delta U = \frac{5}{2} R \Delta T$$

$$\Delta U = \frac{5}{2} R (T_C - T_A)$$

Replace the temperature using the ideal gas law for one mole of gas.

$$\Delta U = \frac{5}{2} R \left(\frac{P_C V_C}{R} - \frac{P_A V_A}{R} \right)$$

$$\Delta U = \frac{5}{2} (P_C V_C - P_A V_A)$$

Plug in the pressure and volume values from the plot.

$$\Delta U = \frac{5}{2} \left(\left[4 \times 10^5 \text{ N/m}^2 \right] \left[3 \times 10^{-3} \text{ m}^3 \right] - \left[6 \times 10^5 \text{ N/m}^2 \right] \left[1 \times 10^{-3} \text{ m}^3 \right] \right)$$

$$\Delta U = 1500 \text{ J}$$

Plug in this and the work done on the system from b).

$$Q = 1500 \text{ J} - (-1300 \text{ J})$$

$$Q = 2800 \text{ J}$$

d) What is the change of entropy in this process?

Begin with the expression for entropy change on Schroeder page 93 (below (3.17)).

$$dS = \frac{Q}{T}$$

Replace heat with energy and work using the First Law.

$$dS = \frac{\Delta U - W}{T}$$

Plug in the expression for change in energy from the equipartition theorem above and the standard expression for work in terms of pressure and change in volume. (Note the negative signs cancel in the work expression.)

$$dS = \frac{\frac{5}{2} R dT + P dV}{T}$$

$$dS = \frac{5}{2} \frac{R}{T} dT + \frac{P}{T} dV$$

To facilitate integration, rewrite the second expression in terms of volume using the ideal gas law for one mole.

$$\frac{P}{T} = \frac{R}{V}$$

$$dS = \frac{5/2 R}{T} dT + \frac{R}{V} dV$$

$$dS = 5/2 R \frac{dT}{T} + R \frac{dV}{V}$$

To find the total change in entropy, integrate.

$$dS = 5/2 R \frac{dT}{T} + R \frac{dV}{V}$$

$$\Delta S = \int dS = 5/2 R \int_{T_A}^{T_C} \frac{dT}{T} + R \int_{V_A}^{V_C} \frac{dV}{V}$$

$$\Delta S = 5/2 R \ln[T] \Big|_{T_A}^{T_C} + R \ln[V] \Big|_{V_A}^{V_C}$$

$$\Delta S = 5/2 R (\ln[T_C] - \ln[T_A]) + R (\ln[V_C] - \ln[V_A])$$

$$\Delta S = 5/2 R \ln \left[\frac{T_C}{T_A} \right] + R \ln \left[\frac{V_C}{V_A} \right]$$

Replace the temperatures with (known) pressures and volumes using the ideal gas law for one mole.

$$T = \frac{PV}{R}$$

$$\Delta S = 5/2 R \ln \left[\frac{\frac{P_C V_C}{R}}{\frac{P_A V_A}{R}} \right] + R \ln \left[\frac{V_C}{V_A} \right]$$

$$\Delta S = 5/2 R \ln \left[\frac{P_C V_C}{P_A V_A} \right] + R \ln \left[\frac{V_C}{V_A} \right]$$

Plug in the values from the plot.

$$\Delta S = 5/2 R \ln \left[\frac{\left[4 \times 10^5 \text{ N/m}^2 \right] \left[3 \times 10^{-3} \text{ m}^3 \right]}{\left[6 \times 10^5 \text{ N/m}^2 \right] \left[1 \times 10^{-3} \text{ m}^3 \right]} \right] + R \ln \left[\frac{\left[3 \times 10^{-3} \text{ m}^3 \right]}{\left[1 \times 10^{-3} \text{ m}^3 \right]} \right]$$

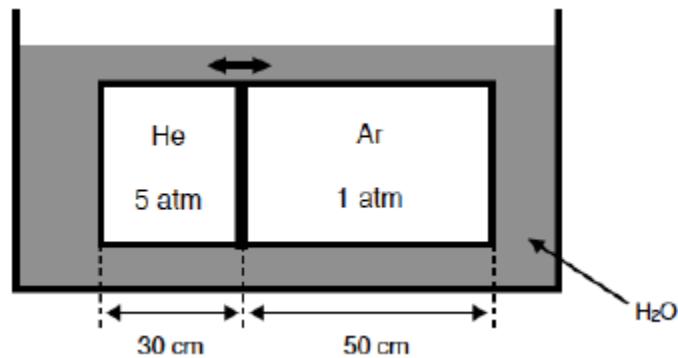
$$\Delta S = 5/2 R \ln[2] + R \ln[3]$$

$$\Delta S = R \left(\frac{5}{2} \ln[2] + \ln[3] \right)$$

$$\Delta S \approx 2.83 R$$

$$\Delta S \approx 23.54 \text{ J/K}$$

- 3) An 80-cm-long cylindrical container is separated into two compartments by a thin piston. The piston is originally clamped in position 30 cm from the left end. The left compartment is filled with one mole of helium gas at a pressure of 5 atmospheres. The right compartment is filled with argon gas at 1 atmosphere of pressure. Consider the gases to be ideal. The cylinder is submerged in 1 liter of water, and the entire system is initially at a uniform temperature of 25° C. The heat capacities of the cylinder and of the piston may be neglected. When the piston is unclamped, it moves until a new equilibrium situation is ultimately reached. Assume the system as a whole is isolated, that is, assume that the water can exchange energy with the helium and the argon, but not with anything else.



- a) What is the increase in temperature of the water?

By conservation of energy, the net change in energy of the isolated system must be zero.

$$\Delta U_{system} = 0$$

The change in energy of the system is equal to the sum of the change of energy of its constituents.

$$\Delta U_{system} = 0 = \Delta U_{He} + \Delta U_{Ar} + \Delta U_{water}$$

Use the equipartition theorem for the monatomic gases ($f=3$) to write the change in energies in terms of temperatures. For the water, use the same expression for the change in energy in terms of the specific heat capacity as in problem 1. Note that the initial and final temperatures are the same for all three materials; it is given that they are the same at the beginning, and at the final (thermal) equilibrium, they are the same.

$$0 = \frac{3}{2} n_{He} R \Delta T + \frac{3}{2} n_{Ar} R \Delta T + c_{water} m_{water} \Delta T$$

$$0 = \left(\frac{3}{2} n_{He} R + \frac{3}{2} n_{Ar} R + c_{water} m_{water} \right) \Delta T$$

The term in the parentheses is positive and constant. It must be the second term that is zero.

$$\Delta T = 0$$

The final temperature is the same as the initial.

$$T_f = T_i = 25^\circ\text{C}$$

$$T_f \approx 298\text{ K}$$

- b) How far from the left end of the cylinder will the piston come to rest? *Hint: First find the number of moles of argon.*

To solve for the number of moles, use the ideal gas law for the both sides with the initial conditions. Let T be the temperature, which is the same for all gases, both before and after.

$$P_i^{\text{He}} V_i^{\text{He}} = n_i^{\text{He}} RT$$

$$P_i^{\text{Ar}} V_i^{\text{Ar}} = n_i^{\text{Ar}} RT$$

Solve both for the common RT , and set them equal to one another.

$$RT = \frac{P_i^{\text{He}} V_i^{\text{He}}}{n_i^{\text{He}}} = \frac{P_i^{\text{Ar}} V_i^{\text{Ar}}}{n_i^{\text{Ar}}}$$

Solve for the number of moles of argon.

$$n_i^{\text{Ar}} = \frac{P_i^{\text{Ar}} V_i^{\text{Ar}} n_i^{\text{He}}}{P_i^{\text{He}} V_i^{\text{He}}}$$

The volume is unknown. The volume is the known length (L) multiplied by an unknown cross-sectional area (A), which is the same for both gases, and thus cancels.

$$n_i^{\text{Ar}} = \frac{P_i^{\text{Ar}} L_i^{\text{Ar}} A n_i^{\text{He}}}{P_i^{\text{He}} L_i^{\text{He}} A}$$

$$n_i^{\text{Ar}} = \frac{P_i^{\text{Ar}} L_i^{\text{Ar}} n_i^{\text{He}}}{P_i^{\text{He}} L_i^{\text{He}}}$$

Plug the known values in.

$$n_i^{\text{Ar}} = \frac{(1\text{ atm})(50\text{ cm})(1\text{ mol})}{(5\text{ atm})(30\text{ cm})}$$

$$n_i^{\text{Ar}} = \frac{1}{3}\text{ mol}$$

Now examine the final equilibrium condition. Since we again have thermal equilibrium, start with the same expression from above.

$$n_f^{Ar} = \frac{P_f^{Ar} L_f^{Ar} n_f^{He}}{P_f^{He} L_f^{He}}$$

At equilibrium, we also have mechanical equilibrium, so the pressures are the same, and thus cancel.

$$n_f^{Ar} = \frac{P_f L_f^{Ar} n_f^{He}}{P_f L_f^{He}}$$

$$n_f^{Ar} = \frac{L_f^{Ar} n_f^{He}}{L_f^{He}}$$

$$\frac{n_f^{Ar}}{n_f^{He}} = \frac{L_f^{Ar}}{L_f^{He}}$$

Rewrite using the fact that the total length, L , is constrained.

$$L_f^{Ar} + L_f^{He} = L$$

$$L_f^{He} = L - L_f^{Ar}$$

$$\frac{n_f^{Ar}}{n_f^{He}} = \frac{L_f^{Ar}}{L - L_f^{Ar}}$$

Solve for L_f^{Ar} .

$$(L - L_f^{Ar})n_f^{Ar} = L_f^{Ar} n_f^{He}$$

$$Ln_f^{Ar} - L_f^{Ar} n_f^{Ar} = L_f^{Ar} n_f^{He}$$

$$Ln_f^{Ar} = L_f^{Ar} n_f^{He} + L_f^{Ar} n_f^{Ar}$$

$$Ln_f^{Ar} = L_f^{Ar} (n_f^{He} + n_f^{Ar})$$

$$L_f^{Ar} = \frac{Ln_f^{Ar}}{n_f^{He} + n_f^{Ar}}$$

Plug in the known values. (Note the number of moles does not change.)

$$L_f^{Ar} = \frac{(80 \text{ cm}) \left(\frac{1}{3} \text{ mol}\right)}{1 \text{ mol} + \frac{1}{3} \text{ mol}}$$

$$L_f^{Ar} = \frac{(80 \text{ cm}) \left(\frac{1}{3} \text{ mol}\right)}{1 \text{ mol} + \frac{1}{3} \text{ mol}}$$

$$L_f^{Ar} = 20 \text{ cm}$$

The cylinder stops 20 cm from the right side, or 60 cm from the left side of the cylinder.

c) What is the increase in total entropy of the system?

Begin with the expression for entropy change on Schroeder page 93 (below (3.17)).

$$\Delta S = \frac{Q}{T}$$

Use the First Law to replace heat with energy and work.

$$\Delta S = \frac{\Delta U - W}{T}$$

As discussed above, the overall energy does not change.

$$\Delta S = \frac{-W}{T}$$

Break the work up into work done on the helium and the work done on the argon.

$$\Delta S = \frac{-W_{He}}{T} + \frac{-W_{Ar}}{T}$$

(Note: Unlike the HW2 problem, these work terms are not necessarily equal and opposite. This is because, unlike the HW2 problem, the process is not adiabatic, so there can be heat exchanged as well. Thus it is the total of work and heat that have to balance, not just work.)

Sub in the usual expression for work in terms of pressure and volume.

$$\Delta S = \frac{-(-\int P_{He} dV_{He})}{T} + \frac{-(-\int P_{Ar} dV_{Ar})}{T}$$

$$\Delta S = \frac{\int P_{He} dV_{He}}{T} + \frac{\int P_{Ar} dV_{Ar}}{T}$$

The volume is the length (L) multiplied by an unknown cross-sectional area (A). A does not change, so the change in volume is all from the change in length.

$$\Delta S = \frac{\int P_{He} A dL_{He}}{T} + \frac{\int P_{Ar} A dL_{Ar}}{T}$$

The pressure is going to change as we integrate over L . Rewrite the pressure in terms of the length using the ideal gas law.

$$\Delta S = \frac{\int \frac{n_{He}RT}{V_{He}} AdL_{He}}{T} + \frac{\int \frac{n_{Ar}RT}{V_{Ar}} AdL_{Ar}}{T}$$

$$\Delta S = \int \frac{n_{He}R}{V_{He}} AdL_{He} + \int \frac{n_{Ar}R}{V_{Ar}} AdL_{Ar}$$

Use the same technique as above to rewrite the volume in terms of area and length.

$$\Delta S = \int \frac{n_{He}R}{AL_{He}} AdL_{He} + \int \frac{n_{Ar}R}{AL_{Ar}} AdL_{Ar}$$

$$\Delta S = \int \frac{n_{He}R}{L_{He}} dL_{He} + \int \frac{n_{Ar}R}{L_{Ar}} dL_{Ar}$$

The number of moles of each gas is fixed. Pull that out front with the gas constants.

$$\Delta S = n_{He}R \int \frac{dL_{He}}{L_{He}} + n_{Ar}R \int \frac{dL_{Ar}}{L_{Ar}}$$

The bounds of integration can be found from the initial and final piston positions.

$$\Delta S = n_{He}R \int_{L_{Hei}}^{L_{He f}} \frac{dL_{He}}{L_{He}} + n_{Ar}R \int_{L_{Ari}}^{L_{Ar f}} \frac{dL_{Ar}}{L_{Ar}}$$

Integrate.

$$\Delta S = n_{He}R \ln(L_{He}) \Big|_{L_{Hei}}^{L_{He f}} + n_{Ar}R \ln(L_{Ar}) \Big|_{L_{Ari}}^{L_{Ar f}}$$

$$\Delta S = n_{He}R \left(\ln(L_{He f}) - \ln(L_{He i}) \right) + n_{Ar}R \left(\ln(L_{Ar f}) - \ln(L_{Ar i}) \right)$$

Use log properties for differences.

$$\Delta S = n_{He}R \ln \left(\frac{L_{He f}}{L_{He i}} \right) + n_{Ar}R \ln \left(\frac{L_{Ar f}}{L_{Ar i}} \right)$$

$$\Delta S = R \left[n_{He} \ln \left(\frac{L_{He f}}{L_{He i}} \right) + n_{Ar} \ln \left(\frac{L_{Ar f}}{L_{Ar i}} \right) \right]$$

Plug in the known values. The initial and final piston positions yield the lengths. The entire piston is 80 cm long. The piston starts 30 cm from the left ($L_{He} = 30 \text{ cm}$, $L_{Ar} = 50 \text{ cm}$) and ends 20 cm from the right ($L_{He} = 60 \text{ cm}$, $L_{Ar} = 20 \text{ cm}$).

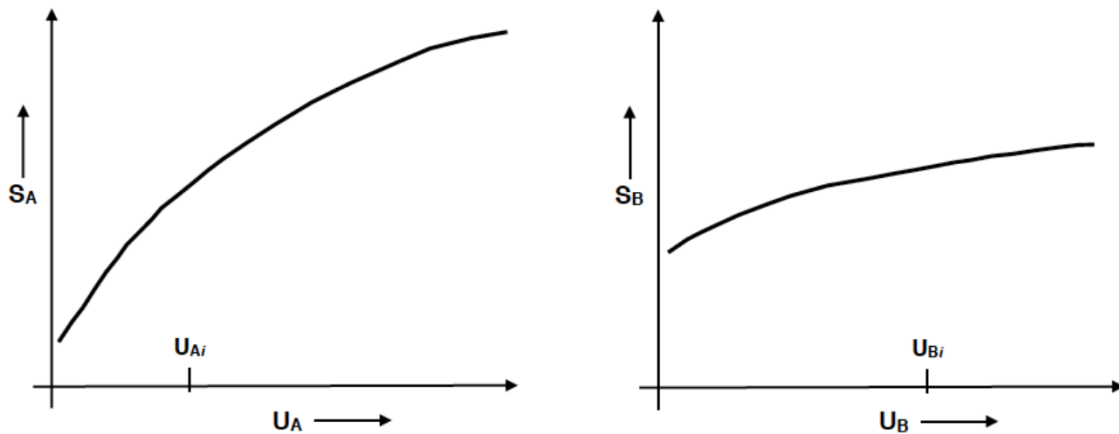
$$\Delta S = (8.314 \text{ J/mol K}) \left[(1 \text{ mol}) \ln \left(\frac{60 \text{ cm}}{30 \text{ cm}} \right) + \left(\frac{1}{3} \text{ mol} \right) \ln \left(\frac{20 \text{ cm}}{50 \text{ cm}} \right) \right]$$

$$\Delta S = \left(8.314 \text{ J/mol K}\right) \left[(1 \text{ mol}) \ln(2) + \left(\frac{1}{3} \text{ mol}\right) \ln\left(\frac{2}{5}\right) \right]$$

$$\Delta S = \left(8.314 \text{ J/mol K}\right) \left[(1 \text{ mol}) \ln(2) + \left(\frac{1}{3} \text{ mol}\right) \ln\left(\frac{2}{5}\right) \right]$$

$$\Delta S \approx 3.22 \text{ J/K}$$

4) Entropy versus energy plots for two objects, A and B, are shown below.



Both graphs use the same horizontal and vertical scales. The initial energies of the two objects are U_{Ai} and U_{Bi} at the values shown.

- a) Explain what happens initially when objects A and B are brought into thermal contact, and explain *why*.
You may NOT use the word “temperature” in your answer.

At the initial points, the slope of the plot of A is steeper than that of B. Thus, a transfer of energy from B to A results in gain in entropy for A that is larger in magnitude than the loss in entropy for B. Thus, the net entropy of the two objects increases. Thus, energy will spontaneously flow from B to A. B loses energy, and A gains energy.

- b) Now you can use “temperature” again. Which object was initially at a higher temperature? How do you know?

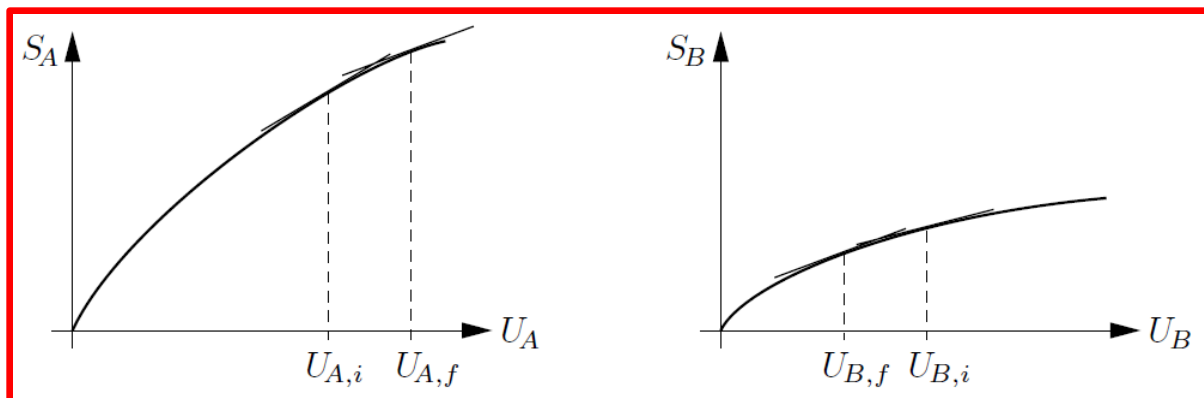
Temperature is inversely related to the slope of the plots.

$$\frac{1}{T} = \left. \frac{\partial S}{\partial U} \right|_{N,V}$$

B initially has a smaller slope, and therefore has a higher temperature.

- c) Sketch the two plots above and indicate on each plot the equilibrium energy of the object. *Explain.*

The systems will exchange energy until the slopes are the same. At that point, there is no gain in entropy to be had from further energy transfer. At this point the temperatures are equal. The final energies with equal slopes are shown below.



- 5) Assume your kitchen is 25°C. A 30.0-g ice cube at 0°C is left in the sink, where it eventually melts.
- a) Calculate the change in entropy for the phase change of the ice cube as it melts into water at 0°C. Ignore the small change in volume that happens with the phase change. *Hint: You will probably have to look up a value to complete this problem.*

The entropy can be calculated from the heat and temperature using Schroeder (3.17).

$$\Delta S = \frac{Q}{T}$$

The heat is the latent heat of the phase change.

$$\Delta S = \frac{mL}{T}$$

Substitute in values. For the latent heat of water, use the value from page 33 of Schroeder. Remember to convert temperature to K.

$$\Delta S \approx \frac{(30.0 \text{ g})(333 \text{ J/g})}{273 \text{ K}}$$

$$\Delta S \approx 36.6 \text{ J/K}$$

- b) Calculate the change in entropy of the resulting water as its temperature rises from 0°C to 25°C. *You can assume that the heat capacity of water is constant over this range, which is a pretty good assumption. Hint: You will probably need to look up a value again.*

To calculate the entropy increase from the heat capacity and the temperature change, use Schroeder (3.19).

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT$$

Pull out the nearly constant C_V and then integrate.

$$\Delta S \approx C_V \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\Delta S \approx C_V \ln T \Big|_{T_i}^{T_f}$$

$$\Delta S \approx C_V (\ln T_f - \ln T_i)$$

Use log rule for differences.

$$\Delta S \approx C_V \ln \left(\frac{T_f}{T_i} \right)$$

Replace the heat capacity with the specific heat times the mass. Do so in order to use the value for specific heat of water from Schroeder page 28.

$$\Delta S \approx cm \ln \left(\frac{T_f}{T_i} \right)$$

Plug in values, again remembering to convert to kelvin. The specific heat capacity of water is from Schroeder page 28.

$$\Delta S \approx \left(4.2 \frac{J}{g K} \right) (30 g) \ln \left(\frac{298 K}{273 K} \right)$$

$$\Delta S \approx 11 J/K$$

- c) Calculate the change in entropy *of the kitchen* as it gives up heat to the melt ice and warm the water to room temperature.

The heat lost by the kitchen must be the same as the heat gained by the melting ice and warming water. This is true by conservation of energy and the First Law with zero work.

$$\Delta U_{total} = 0 \rightarrow \Delta U_{H_2O} = -\Delta U_{kitchen}$$

$$\Delta U_{H_2O} = -\Delta U_{kitchen} \rightarrow Q_{H_2O} = -Q_{kitchen}$$

Calculate the change in entropy as in part a).

$$\Delta S = \frac{Q_{kitchen}}{T} = \frac{-Q_{H_2O}}{T}$$

The heat for melting is from part a). The heat for warming the water is given by the expressions for specific heat and heat capacity (Schroeder (1.41) and (1.42)). Plug in these heat expressions

$$\Delta S = \frac{-[mL + mc\Delta T]}{T}$$

$$\Delta S = \frac{-m[L + c\Delta T]}{T}$$

Plug in the values.

$$\Delta S \approx \frac{-(30 \text{ g}) \left[(333 \text{ J/g}) + (4.2 \text{ J/g K}) (25 \text{ K}) \right]}{298 \text{ K}}$$

$$\Delta S \approx -44.1 \text{ J/K}$$

- d) Calculate the net change in entropy of the universe during the process. Comment on the meaning of the sign of your answer.

The net change in entropy is the sum of the change in entropies from a), b), and c).

$$\Delta S = \Delta S_{\text{kitchen}} + \Delta S_{\text{melting}} + \Delta S_{\text{raise temperature}}$$

Plug in the values.

$$\Delta S \approx -44.1 \text{ J/K} + 36.6 \text{ J/K} + 11 \text{ J/K}$$

$$\Delta S \approx 3.5 \text{ J/K}$$

The net change is positive, which is what we expect for an irreversible process.

- 6) Fill in some of the gaps from our discussion of paramagnetism.
- a) Start with the expression for the multiplicity of a two-state paramagnet with N dipoles. Assume N is large. Derive an expression for the entropy in terms of N_{\uparrow} and N . Manipulate your expression so that it does not have any factorials, fractions, or exponents. You can use the form of Sterling's approximation that ignores large terms.

$$\Omega = \frac{N!}{N_{\uparrow}! N_{\downarrow}!}$$

Start with the definition of entropy.

$$S = k \ln \Omega = k \ln \left[\frac{N!}{N_{\uparrow}! N_{\downarrow}!} \right]$$

Rewrite using log rules for products and quotients.

$$S = k \ln \Omega = k(\ln[N!] - \ln[N_{\uparrow}!] - \ln[N_{\downarrow}!])$$

Since large terms can be ignored, use the Schroeder (2.16) version of Sterling's approximation.

$$S \approx k([N \ln N - N] - [N_{\uparrow} \ln N_{\uparrow} - N_{\uparrow}] - [N_{\downarrow} \ln N_{\downarrow} - N_{\downarrow}])$$

$$S \approx k(N \ln N - N_{\uparrow} \ln N_{\uparrow} - N_{\downarrow} \ln N_{\downarrow} - N + N_{\uparrow} + N_{\downarrow})$$

Use the fact that the total number of dipoles is fixed.

$$N = N_{\uparrow} + N_{\downarrow}$$

This leads to the non-log terms canceling.

$$S \approx k(N \ln N - N_{\uparrow} \ln N_{\uparrow} - N_{\downarrow} \ln N_{\downarrow})$$

Also use the fixed number to eliminate N_{\downarrow} .

$$N - N_{\uparrow} = N_{\downarrow}$$

$$S \approx k(N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln[N - N_{\uparrow}])$$

- b) Use your expression from part a) to calculate $\frac{\partial S}{\partial N_{\uparrow}}$, the partial derivative of entropy with respect to the number of spin-up dipoles.

Plug in your expression from part a).

$$\frac{\partial S}{\partial N_{\uparrow}} \approx \frac{\partial}{\partial N_{\uparrow}} [k(N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln[N - N_{\uparrow}])]$$

The first term is constant.

$$\frac{\partial S}{\partial N_{\uparrow}} \approx \frac{\partial}{\partial N_{\uparrow}} [k(-N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln[N - N_{\uparrow}])]$$

Use the chain rule to differentiate the other two terms.

$$\frac{\partial S}{\partial N_{\uparrow}} \approx k \left(\left[-N_{\uparrow} \left(\frac{1}{N_{\uparrow}} \right) - \ln N_{\uparrow} \right] - \left[(N - N_{\uparrow}) \left(\frac{-1}{N - N_{\uparrow}} \right) - \ln[N - N_{\uparrow}] \right] \right)$$

$$\frac{\partial S}{\partial N_{\uparrow}} \approx k(-1 - \ln N_{\uparrow} + 1 + \ln[N - N_{\uparrow}])$$

$$\frac{\partial S}{\partial N_{\uparrow}} \approx k(\ln[N - N_{\uparrow}] - \ln N_{\uparrow})$$

Use the log rule for differences.

$$\frac{\partial S}{\partial N_{\uparrow}} \approx k \ln \left[\frac{N - N_{\uparrow}}{N_{\uparrow}} \right]$$

- c) In class, we found an expression for energy as a function of spin-up dipoles. Differentiate to find $\frac{\partial U}{\partial N_{\uparrow}}$.

$$U = \mu B(N_{\downarrow} - N_{\uparrow})$$

Since N_{\downarrow} is dependent on N_{\uparrow} , write N_{\downarrow} in terms of N_{\uparrow} before differentiating.

$$N - N_{\uparrow} = N_{\downarrow}$$

$$U = \mu B(N - N_{\uparrow} - N_{\uparrow})$$

$$U = \mu B(N - 2N_{\uparrow})$$

Differentiate.

$$\frac{\partial U}{\partial N_{\uparrow}} = \frac{\partial}{\partial N_{\uparrow}} [\mu B(N - 2N_{\uparrow})]$$

$$\frac{\partial U}{\partial N_{\uparrow}} = -2\mu B$$

- d) Combine your previous results to find an expression for temperature as a function of N_{\uparrow} . *Hint: Use the chain rule and the fact that $\frac{\partial N_{\uparrow}}{\partial U} = \left(\frac{\partial U}{\partial N_{\uparrow}}\right)^{-1}$.*

Start with the definition of temperature, assuming B is held constant.

$$\frac{1}{T} = \frac{\partial S}{\partial U} \Big|_{N,V,B}$$

Rewrite the derivative using the chain rule.

$$\frac{1}{T} = \frac{\partial S}{\partial U} \Big|_{N,V,B} = \frac{\partial S}{\partial N_{\uparrow}} \frac{\partial N_{\uparrow}}{\partial U} \Big|_{N,V,B}$$

Substitute for the second derivative using the hint.

$$\frac{1}{T} = \frac{\partial S}{\partial N_{\uparrow}} \left(\frac{\partial U}{\partial N_{\uparrow}} \right)^{-1} \Big|_{N,V,B}$$

Substitute in for the derivatives using the expressions from parts b) and c).

$$\frac{1}{T} = \left(k \ln \left[\frac{N - N_{\uparrow}}{N_{\uparrow}} \right] \right) (-2\mu B)^{-1}$$

$$\frac{1}{T} = \frac{-k}{2\mu B} \ln \left[\frac{N - N_{\uparrow}}{N_{\uparrow}} \right]$$

Absorb the negative sign in the log term using the log rule for exponents.

$$\frac{1}{T} = \frac{k}{2\mu B} \ln \left[\frac{N_{\uparrow}}{N - N_{\uparrow}} \right]$$

$$T = \frac{2\mu B}{k \ln \left[\frac{N_{\uparrow}}{N - N_{\uparrow}} \right]}$$

- 7) There are three partial derivative of *entropy* formulas in Schroeder Table 3.3: one for temperature, one for pressure, and one for chemical potential. Use the thermodynamic identity to derive three similar formulas for temperature, pressure, and chemical potential that involve only partial derivatives of *energy*.

Hint: This is fairly straightforward. I just want you to spend a little time thinking about all of the information contained in this one formula.

$$dU = TdS - PdV + \mu dN$$

For the temperature formula, hold the volume and the number of particles constant.

$$dV = 0, dN = 0$$

Consider the thermodynamic identity in this case.

$$dU = TdS$$

Rearrange to get a partial derivative of energy. Indicate the values held constant.

$$T = \frac{dU}{dS}$$

$$T = \left. \frac{\partial U}{\partial S} \right|_{V,N}$$

For the pressure formula, hold the entropy and the number of particles constant.

$$dS = 0, dN = 0$$

Consider the thermodynamic identity in this case.

$$dU = -PdV$$

Rearrange to get a partial derivative of energy. Indicate the values held constant.

$$P = -\frac{dU}{dV}$$

$$P = -\left. \frac{\partial U}{\partial V} \right|_{S,N}$$

For the chemical potential formula, hold the entropy and the volume constant.

$$dS = 0, dV = 0$$

Consider the thermodynamic identity in this case.

$$dU = \mu dN$$

Rearrange to get a partial derivative of energy. Indicate the values held constant.

$$\mu = \frac{dU}{dN}$$

$$\mu = \left. \frac{\partial U}{\partial N} \right|_{S,V}$$

- 8) List three main ideas from this homework assignment. For example, you could write a few-sentence explanation of a concept, or list an equation and explain the variables and in what circumstances the equation applies.

The goal is for you to review and to reflect on the big picture. Think about what you might want to remember when you look back at this homework before the test. I hope that this will be useful for your studying. I am not looking for anything specific here; you will be graded on effort and completion.