Physics 114 Statistical Mechanics Spring 2021

Week 2 Reading and Problem Assignment

Overview:

This week, the new idea is entropy, S, a function which fully characterizes an equilibrium state. (So does the energy E; they have equivalent information content.) The partial derivatives of S define functions of state. Postulates about S (stated carefully in the optional Callen reading) give mathematical rigor to thermodynamics. The second and third laws of thermo are both about entropy: that S must increase in any real process, and at zero temperature, $S = 0$.

Also equal to zero at $T = 0$ are the partial derivatives of S with respect to functions of state. This makes it impossible to bring a thermodynamic system to $T = 0$ in any real process. Recently, a temperatures of only $0.006K$ was reached for a chunk of solid copper, and gas atoms have been cooled to within a billionth of a degree above $T = 0$. But $T = 0$ is not obtainable. (Or is it? See `https://www.quantum-munich.de/119947/Negative-Absolute-Temperatures`.) Practical consequences of the second and third laws are that we can envision heat engines which turn some heat into work, and refrigerators which work to pump heat against the "natural" thermodynamic direction. Both of these can be made optimally efficient, which means that input heat or work are used with as little waste as possible. However, it is impossible for any machine to convert heat entirely into work, without some heat being shed to increase the entropy of the universe.

Suggested Reading:

G&T Sections

- 2.12 - 2.20, 2.23.1

B&B sections

- Chapter 13,
- 14.1-14.4
- Chapter 18

Optional Reading:

Callen's "Thermodynamics and an introduction to thermostatics" Chapters 1, 2 &4 are linked to our Moodle site. You'll find superb discussions of the basic ideas of thermo; the kind that motivated Einstein's statement that thermo is the only theory in physics that will "never be overthrown". Particularly relevant for this week are Callen sections 1.9 - 2.7 and 4.1-4.5. (Though other sections in these chapters are relevant to our first two weeks of seminar, they are a repetition of material you'll find in G&T or B&B.)

Warmup Problems:

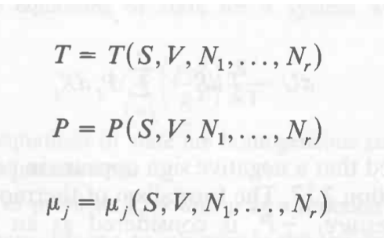
1. **entropy of an ideal gas** G&T 2.24
2. **heat pump: possible or impossible?** B&B 13.1

Problems to discuss in our meeting

Note: The * means that these problems are to be handed in They are due the day after we meet.

1: Ideal refrigerator G&T problem 2.19

2*: Equations of state
a) Write the van der Waals equations of state in the form $P = f(T, \rho)$, and thus show that this is an equation which is homogeneous and zero order in the extensive state variables.
b) Callen Ch. 2.2 opens our eyes to the definition that an "equation of state" is an expression in which any intensive parameter is expressed as a function of the extensive parameters of the system. For a system with r different types of particles, you can write $r+2$ equations of state:



$$T = T(S, V, N_1, \ldots, N_r)$$

$$P = P(S, V, N_1, \ldots, N_r)$$

$$\mu_j = \mu_j(S, V, N_1, \ldots, N_r)$$

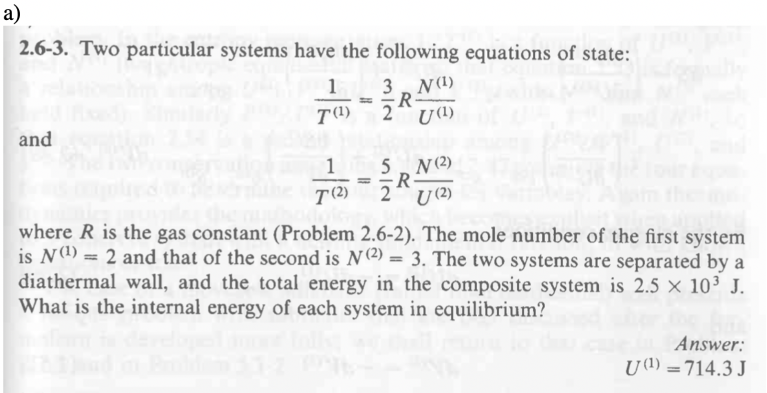
Suppose we just have our usual case where $r = 1$. Suppose the energy equation of state is:

$$U = \frac{aS^3}{R^2NV} \tag{1}$$

a) In Eq. (1) a is a constant. What are its units in SI?
b) What are the three equations of state for this system?

3: Establishing equilibrium (two problems, with answers provided :-)

a)



2.6-3. Two particular systems have the following equations of state:

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{U^{(1)}}$$

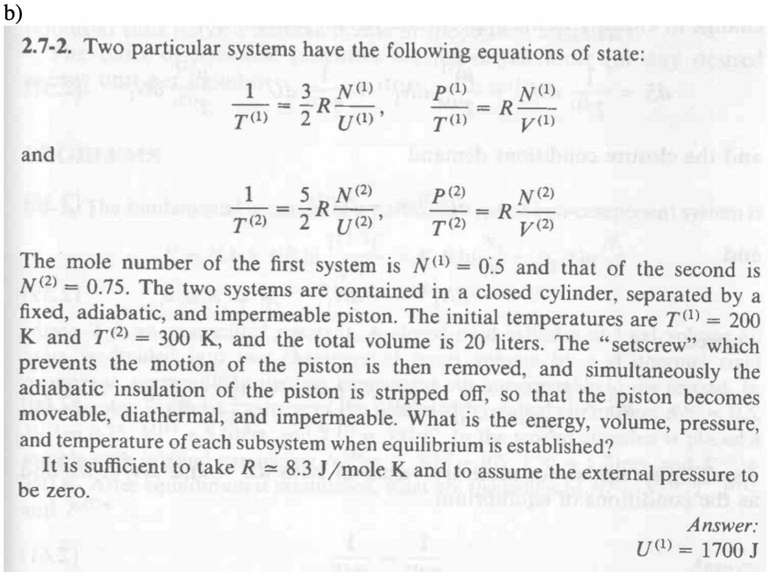
and

$$\frac{1}{T^{(2)}} = \frac{5}{2} R \frac{N^{(2)}}{U^{(2)}}$$

where R is the gas constant (Problem 2.6-2). The mole number of the first system is $N^{(1)} = 2$ and that of the second is $N^{(2)} = 3$. The two systems are separated by a diathermal wall, and the total energy in the composite system is 2.5×10^3 J. What is the internal energy of each system in equilibrium?

Answer:
$U^{(1)} = 714.3$ J

b)



2.7-2. Two particular systems have the following equations of state:

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{U^{(1)}}, \qquad \frac{P^{(1)}}{T^{(1)}} = R \frac{N^{(1)}}{V^{(1)}}$$

and

$$\frac{1}{T^{(2)}} = \frac{5}{2} R \frac{N^{(2)}}{U^{(2)}}, \qquad \frac{P^{(2)}}{T^{(2)}} = R \frac{N^{(2)}}{V^{(2)}}$$

The mole number of the first system is $N^{(1)} = 0.5$ and that of the second is $N^{(2)} = 0.75$. The two systems are contained in a closed cylinder, separated by a fixed, adiabatic, and impermeable piston. The initial temperatures are $T^{(1)} = 200$ K and $T^{(2)} = 300$ K, and the total volume is 20 liters. The "setscrew" which prevents the motion of the piston is then removed, and simultaneously the adiabatic insulation of the piston is stripped off, so that the piston becomes moveable, diathermal, and impermeable. What is the energy, volume, pressure, and temperature of each subsystem when equilibrium is established?

It is sufficient to take $R = 8.3$ J/mole K and to assume the external pressure to be zero.

Answer:
$U^{(1)} = 1700$ J

4: Free expansion of a non-ideal gas G&T Problem 2.29

5*: Realistic refrigerator B&B Problem 13.6

6: What's the change in entropy for the system? For the system plus its surroundings?

Hint: Reference data can be found on the Web and pp. 404-405 of Schroder's book.

a) when solid copper is slowly cooled from 42^oC to 20^oC by a mechanism of

your choice
b) when 100 g of ice at 0^oC melts into 100 g of water at 0^oC by a mechanism of your choice
c) when a magician goes "poof" and turns the crystal kyanite into a different crystal, andalusite; taking place at $T = 298K$ and atmospheric pressure.
d) when one mole of ideal gas at 0^oC does an isothermal expansion to twice its original volume.
e) when one mole of ideal gas at 0^oC does an adiabatic expansion (i.e. $Q = 0$, but happens quasi statically) to twice its original volume.
f) when one mole of ideal gas at 0^oC undergoes a free expansion (i.e. $Q = 0$, but happens quickly, and irreversibly), also known as a "Joule expansion", to twice its original volume.

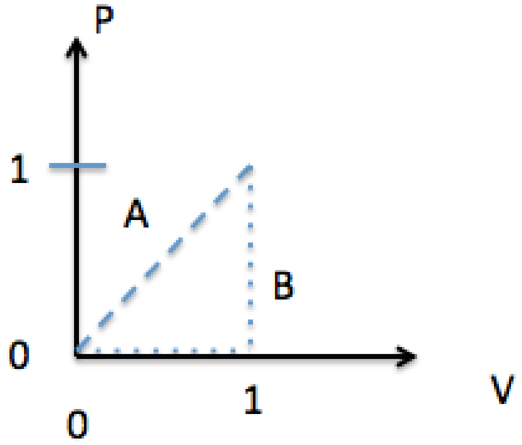
7: I think I just broke thermodynamics

a) I think I just found a cool new state function f(P,V) such that $df = F(P,V)dP + G(P,V)dV$ where $F = PV$ and $G = P^2$. Please show that it fails the test because df is not an exact differential.

b) Despite this, I still care about $\text{đ}f$ and wonder how f varies in different processes. So please find

$$\int_{0,0}^{1,1} df$$

on the two paths, A (dashed) and B (dotted) shown below.



c) I think I've found a system for which $S = NR\ ln(c\frac{UV}{N^2})$ where c is a constant. But wah, this violates the 3rd law. Why?

8: Positive change of entropy G&T Problem 2.61

9: The Otto cycle B&B problem 13.5. Is an Otto engine really less efficient than a Carnot engine? How so?

10*: Exploring the manifold of constrained equilibrium states
Suppose our system is a box of particles. At equilibrium, the particles obey the equation:

$$S = (NVU)^{1/3} \tag{2}$$

Suppose that this box could be divided in two by a diathermal wall ... one that permits energy to be exchanged, but not particles. Lets initially assume that there is no wall in place and that $N = 50, V = 13$ and $U = 80$. (Assume quantities in Eq. (2) are dimensionless, so don't worry about units; which are J/K for entropy.)

a) Find the entropy, S, for this system.

b) Suppose we now divide the box into A and B sides with a diathermal wall. Let $V_A = 9,\ N_A = 30$ and $V_B = 4,\ N_B = 20$. Use Eq. (2) and the additivity of entropy: $S(U_A) = S_A(U_A) + S_B(U - U_A)$ to create a graph of $S(U_A)$. Find which value of U_A maximizes $S(U_A)$ and find this maximum entropy.

c) Before doing part d) ... Why do you think the system picks that value of U_A for its entropy to be maximal? What's special about it?
d) What are the temperatures of the A side and the B side when U_A takes on its maximal value? Hint: $\frac{1}{T_i} \equiv \left(\frac{\partial S_i}{\partial E_i}\right)_{V_i,N_i}$ for $i = A,\ B$.
e) The maximal entropy you found in part b) is not quite as high as the entropy you found in a) . Say you are allowed to move the wall so that V_A and V_B take on new values. How might you relocate the wall to make the maximum value of $S(U_A)$ even higher? Can you find a place to put the wall where $S_A + S_B$ is equal to the value of S you found in part a)? If so, what would the temperatures of the two sides be, and how would they compare to the temperature you'd find for part a)?
f) Callen makes a rather fancy statement that "the values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states." After doing this problem, can you break that statement down into plainer language, using what you've found as an illustration of this principle?