HW 2

2.8

Problem 2.8. Consider a system of two Einstein solids, A and B, each containing 10 oscillators, sharing a total of 20 units of energy. Assume that the solids are weakly coupled, and that the total energy is fixed.

(a) How many different *macrostates* are available to this system?

(b) How many different *microstates* are available to this system?

(c) Assuming that this system is in thermal equilibrium, what is the probability of finding all the energy in solid A?

(d) What is the probability of finding exactly half of the energy in solid A?

(e) Under what circumstances would this system exhibit irreversible behavior?

2.34

Problem 2.34. Show that during the quasistatic isothermal expansion of a monatomic ideal gas, the change in entropy is related to the heat input Q by the simple formula

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

In the following chapter I'll prove that this formula is valid for *any* quasistatic process. Show, however, that it is *not* valid for the free expansion process described above.

3.10

Problem 3.10. An ice cube (mass 30 g) at $0°C$ is left sitting on the kitchen table, where it gradually melts. The temperature in the kitchen is $25°C$.

(a) Calculate the change in the entropy of the ice cube as it melts into water at $0°C$. (Don't worry about the fact that the volume changes somewhat.)

(b) Calculate the change in the entropy of the water (from the melted ice) as its temperature rises from $0°C$ to $25°C$.

(c) Calculate the change in the entropy of the kitchen as it gives up heat to the melting ice/water.

(d) Calculate the net change in the entropy of the universe during this process. Is the net change positive, negative, or zero? Is this what you would expect?

3.16

Problem 3.16. A **bit** of computer memory is some physical object that can be in two different states, often interpreted as 0 and 1. A **byte** is eight bits, a **kilobyte** is 1024 ($= 2^{10}$) bytes, a **megabyte** is 1024 kilobytes, and a **gigabyte** is 1024 megabytes.

(a) Suppose that your computer erases or overwrites one gigabyte of memory, keeping no record of the information that was stored. Explain why this process must create a certain minimum amount of entropy, and calculate how much.

(b) If this entropy is dumped into an environment at room temperature, how much heat must come along with it? Is this amount of heat significant?

3.30

Problem 3.30. As shown in Figure 1.14, the heat capacity of diamond near room temperature is approximately linear in T. Extrapolate this function up to 500 K, and estimate the change in entropy of a mole of diamond as its temperature is raised from 298 K to 500 K. Add on the tabulated value at 298 K (from the back of this book) to obtain $S(500 \text{ K})$.

4.13

Problem 4.13. Under many conditions, the rate at which heat enters an air conditioned building on a hot summer day is proportional to the difference in temperature between inside and outside, $T_h - T_c$. (If the heat enters entirely by conduction, this statement will certainly be true. Radiation from direct sunlight would be an exception.) Show that, under these conditions, the cost of air conditioning should be roughly proportional to the *square* of the temperature difference. Discuss the implications, giving a numerical example.

4.14

Problem 4.14. A **heat pump** is an electrical device that heats a building by pumping heat in from the cold outside. In other words, it's the same as a refrigerator, but its purpose is to warm the hot reservoir rather than to cool the cold reservoir (even though it does both). Let us define the following standard symbols, all taken to be positive by convention:

T_h = temperature inside building

T_c = temperature outside

Q_h = heat pumped into building in 1 day

Q_c = heat taken from outdoors in 1 day

W = electrical energy used by heat pump in 1 day

(a) Explain why the "coefficient of performance" (COP) for a heat pump should be defined as Q_h/W.

(b) What relation among Q_h, Q_c, and W is implied by energy conservation alone? Will energy conservation permit the COP to be greater than 1?

(c) Use the second law of thermodynamics to derive an upper limit on the COP, in terms of the temperatures T_h and T_c alone.

(d) Explain why a heat pump is better than an electric furnace, which simply converts electrical work directly into heat. (Include some numerical estimates.)

4.20

Problem 4.20. Derive a formula for the efficiency of the Diesel cycle, in terms of the compression ratio V_1/V_2 and the cutoff ratio V_3/V_2. Show that for a given compression ratio, the Diesel cycle is less efficient than the Otto cycle. Evaluate the theoretical efficiency of a Diesel engine with a compression ratio of 18 and a cutoff ratio of 2.

4.26

Problem 4.26. A coal-fired power plant, with parameters similar to those used in the text above, is to deliver 1 GW (10^9 watts) of power. Estimate the amount of steam (in kilograms) that must pass through the turbine(s) each second.

4.30

Problem 4.30. Consider a household refrigerator that uses HFC-134a as the refrigerant, operating between the pressures of 1.0 bar and 10 bars.

 (a) The compression stage of the cycle begins with saturated vapor at 1 bar and ends at 10 bars. Assuming that the entropy is constant during compression, find the approximate temperature of the vapor after it is compressed. (You'll have to do an interpolation between the values given in Table 4.4.)

 (b) Determine the enthalpy at each of the points 1, 2, 3, and 4, and calculate the coefficient of performance. Compare to the COP of a Carnot refrigerator operating between the same extreme temperatures. Does this temperature range seem reasonable for a household refrigerator? Explain briefly.

 (c) What fraction of the liquid vaporizes during the throttling step?

5.6

Problem 5.6. A muscle can be thought of as a fuel cell, producing work from the metabolism of glucose:

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O.$$

 (a) Use the data at the back of this book to determine the values of ΔH and ΔG for this reaction, for one mole of glucose. Assume that the reaction takes place at room temperature and atmospheric pressure.

 (b) What is the maximum amount of work that a muscle can perform, for each mole of glucose consumed, assuming ideal operation?

 (c) Still assuming ideal operation, how much heat is absorbed or expelled by the chemicals during the metabolism of a mole of glucose? (Be sure to say which direction the heat flows.)

 (d) Use the concept of entropy to explain why the heat flows in the direction it does.

 (e) How would your answers to parts (a) and (b) change, if the operation of the muscle is not ideal?

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5.11

Problem 5.11. Suppose that a hydrogen fuel cell, as described in the text, is to be operated at $75°C$ and atmospheric pressure. We wish to estimate the maximum electrical work done by the cell, using only the room-temperature data at the back of this book. It is convenient to first establish a zero-point for each of the three substances, H_2, O_2, and H_2O. Let us take G for both H_2 and O_2 to be zero at $25°C$, so that G for a mole of H_2O is -237 kJ at $25°C$.

  (a) Using these conventions, estimate the Gibbs free energy of a mole of H_2 at $75°C$. Repeat for O_2 and H_2O.

  (b) Using the results of part (a), calculate the maximum electrical work done by the cell at $75°C$, for one mole of hydrogen fuel. Compare to the ideal performance of the cell at $25°C$.

5.14

Problem 5.14. The partial-derivative relations derived in Problems 1.46, 3.33, and 5.12, plus a bit more partial-derivative trickery, can be used to derive a completely general relation between C_P and C_V.

  (a) With the heat capacity expressions from Problem 3.33 in mind, first consider S to be a function of T and V. Expand dS in terms of the partial derivatives $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$. Note that one of these derivatives is related to C_V.

  (b) To bring in C_P, consider V to be a function of T and P and expand dV in terms of partial derivatives in a similar way. Plug this expression for dV into the result of part (a), then set $dP = 0$ and note that you have derived a nontrivial expression for $(\partial S/\partial T)_P$. This derivative is related to C_P, so you now have a formula for the difference $C_P - C_V$.

  (c) Write the remaining partial derivatives in terms of measurable quantities using a Maxwell relation and the result of Problem 1.46. Your final result should be

$$C_P = C_V + \frac{TV\beta^2}{\kappa_T}.$$

  (d) Check that this formula gives the correct value of $C_P - C_V$ for an ideal gas.

  (e) Use this formula to argue that C_P cannot be less than C_V.

  (f) Use the data in Problem 1.46 to evaluate $C_P - C_V$ for water and for mercury at room temperature. By what percentage do the two heat capacities differ?

  (g) Figure 1.14 shows measured values of C_P for three elemental solids, compared to predicted values of C_V. It turns out that a graph of β vs. T for a solid has same general appearance as a graph of heat capacity. Use this fact to explain why C_P and C_V agree at low temperatures but diverge in the way they do at higher temperatures.

5.23

Problem 5.23. By subtracting μN from U, H, F, or G, one can obtain four new thermodynamic potentials. Of the four, the most useful is the **grand free energy** (or **grand potential**),

$$\Phi \equiv U - TS - \mu N.$$

- (a) Derive the thermodynamic identity for Φ, and the related formulas for the partial derivatives of Φ with respect to T, V, and μ.
- (b) Prove that, for a system in thermal and diffusive equilibrium (with a reservoir that can supply both energy and particles), Φ tends to decrease.
- (c) Prove that $\Phi = -PV$.

5.35

Problem 5.35. The Clausius-Clapeyron relation 5.47 is a differential equation that can, in principle, be solved to find the shape of the entire phase-boundary curve. To solve it, however, you have to know how both L and ΔV depend on temperature and pressure. Often, over a reasonably small section of the curve, you can take L to be constant. Moreover, if one of the phases is a gas, you can usually neglect the volume of the condensed phase and just take ΔV to be the volume of the gas, expressed in terms of temperature and pressure using the ideal gas law. Making all these assumptions, solve the differential equation explicitly to obtain the following formula for the phase boundary curve:

$$P = (\text{constant}) \times e^{-L/RT}.$$

This result is called the **vapor pressure equation**. Caution: Be sure to use this formula only when all the assumptions just listed are valid.

5.42

Problem 5.42. Ordinarily, the partial pressure of water vapor in the air is less than the equilibrium vapor pressure at the ambient temperature; this is why a cup of water will spontaneously evaporate. The ratio of the partial pressure of water vapor to the equilibrium vapor pressure is called the **relative humidity**. When the relative humidity is 100%, so that water vapor in the atmosphere would be in diffusive equilibrium with a cup of liquid water, we say that the air is **saturated.**[*] The **dew point** is the temperature at which the relative humidity would be 100%, for a given partial pressure of water vapor.

(a) Use the vapor pressure equation (Problem 5.35) and the data in Figure 5.11 to plot a graph of the vapor pressure of water from 0°C to 40°C. Notice that the vapor pressure approximately doubles for every 10° increase in temperature.

(b) Suppose that the temperature on a certain summer day is 30°C. What is the dew point if the relative humidity is 90%? What if the relative humidity is 40%?

5.48

Problem 5.48. As you can see from Figure 5.20, the critical point is the unique point on the original van der Walls isotherms (before the Maxwell construction) where both the first and second derivatives of P with respect to V (at fixed T) are zero. Use this fact to show that

$$V_c = 3Nb, \qquad P_c = \frac{1}{27}\frac{a}{b^2}, \qquad \text{and} \qquad kT_c = \frac{8}{27}\frac{a}{b}.$$

5.51

Problem 5.51. When plotting graphs and performing numerical calculations, it is convenient to work in terms of **reduced variables**,

$$t \equiv T/T_c, \qquad p \equiv P/P_c, \qquad v \equiv V/V_c.$$

Rewrite the van der Waals equation in terms of these variables, and notice that the constants a and b disappear.

6.6

Estimate the probability that a hydrogen atom at room temperature is in one of its first excited states (relative to the probability of being in the ground state). Don't forget to take degeneracy into account. Then repeat the calculation for a hydrogen atom in the atmosphere of the starγ UMa, whose surface temperature is approximately 9500 K.

> **Short Answer** ⊘ Expert verified
>
> As a result, no Hydrogen atoms can be found in the first excited state.
>
> On this star, there is one atom in the first excited state out of 64500 hydrogen atoms.

6.12

Cold interstellar molecular clouds often contain the molecule cyanogen (CN), whose first rotational excited states have an energy of 4.7×10^{-4} eV (above the ground state). There are actually three such excited states, all with the same energy. In 1941, studies of the absorption spectrum of starlight that passes | through these molecular clouds showed that for every ten CN molecules that are in the ground state, approximately three others are in the three first excited states (that is, an average of one in each of these states). To account for this data, astronomers suggested that the molecules might be in thermal equilibrium with some "reservoir" with a well-defined temperature. What is that temperature?

> **Short Answer** ⊘ Expert verified
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> Therefore, the temperature is 2.369K