Statistical and Thermal Physics: Homework 5

Due: 20 February 2018

1 Heat capacity in terms of entropy

a) Starting with the fundamental thermodynamic identity, show that MODERTATE

$$c_V = T \left(\frac{\partial S}{\partial T} \right)_{V,N}.$$

b) Rewrite the fundamental thermodynamic identity in terms of enthalpy rather than energy and use the result to show that (hint, write dH in terms of T, P, N then equate the dT parts)

$$c_P = T \left(\frac{\partial S}{\partial T} \right)_{P,N}.$$

2 Gould and Tobochnik, *Statistical and Thermal Physics*, 2.59, page 105. EASY

3 Gould and Tobochnik, *Statistical and Thermal Physics*, 2.63, page 106.HARD Extra credit. Ignore the 1-5 leg as it is the same as the 5-1 leg but with a minus sign. Also, there is an easy way to do this and a hard way. Don't forget the definition of $Q = C_v \Delta T$ for constant volume processes. Take as given, show for extra credit, $\frac{T_4 - T_1}{T_3 - T_2} = \frac{T_4}{T_3}$. Also $W_{total} = Q_1 - |Q_2|$. Don't forget that legs 4-1 and 2-3 are adiabatic.

4 Heat engine with a finite reservoir

HARD Consider a heat engine that absorbs heat Q_h from a reservoir that is initially at temperature T_{hi} and ejects heat Q_c to a reservoir that is initially at temperature T_{ci}. In class we analyzed the efficiency of such an engine with reservoirs which remained at a constant temperature. Now suppose that the reservoirs each have a finite but constant heat capacity and that these are the same. Thus the temperatures of the reservoirs will change. In one cycle the high temperature reservoir will drop to temperature T_{hf} and the low temperature reservoir will rise to T_{cf}. If c is the heat capacity of the higher temperature reservoir, then

$$Q_h = -c(T_{hf} - T_{hi})$$

and similarly, if the low temperature reservoir has the same heat capacity,

$$Q_c = c(T_{cf} - T_{ci}).$$

a) Starting with

$$\mathrm{d}S_h = \frac{c\,\mathrm{d}T}{T}$$

determine an expression for the change in entropy for the hot reservoir in terms of T_{hi}, T_{hf} and c. Rewrite T_{hf} in terms of Q_h and c to obtain expressions for the change in entropy in terms of T_{hi}, c and Q_h. Repeat this for the cold reservoir.

b) Use the second law to show that this implies that

$$\frac{Q_c}{Q_h} \geqslant \frac{T_{ci}}{T_{hi}} + \frac{Q_c}{cT_{hi}} = \frac{T_{cf}}{T_{hi}}$$

and use this to determine a bound on the efficiency of the heat engine.

c) Check that when the heat capacity becomes infinite, that one obtains the original efficiency that we obtained in class. How does this compare to the efficiency when the heat capacity is finite? Use the relations determined in part a to rewrite $\frac{T_{cf}}{T_{hi}}$ into two terms, one which includes the specific heat capacity and one which reads $\frac{T_{ci}}{T_{hi}}$. This should reduce to the form derived in class.

d) As time passes and the engine runs through many cycles, what will happen to its efficiency?

5 Carnot engine efficiency

EASY Consider a Carnot engine using an ideal gas and operating between heat baths at temperatures T_{high} and T_{low}. Assume either the lower or higher temperature is fixed.

a) Which of the following is true?

   i) The efficiency of the engine increases as the temperature difference between the baths increases.

   ii) The efficiency of the engine decreases as the temperature difference between the baths increases.

   iii) The efficiency of the engine stays the same as the temperature difference between the baths increases.

   Explain your answer.

b) Consider two Carnot engines, denoted A and B. The temperatures of the heat baths which they access are different but they are such that for each heat engine the temperature *difference* for the baths is the same. Which of the following is true?

   i) The efficiency of the engine A will be the same as that of engine B regardless of any other facts.

   ii) The efficiency of the engine A might be larger than that of engine B depending on the circumstances.

   Explain your answer.

c) Describe whether the efficiency of a Carnot engine depends on the number of molecules of gas present or the volumes and pressures that are accessed during the cycle.

6 Carnot engine and entropy

EASY During the Carnot cycle, the engine extracts heat from a high temperature bath and loses heat to a low temperature bath. How does the entropy change of the high temperature bath compare to that of the low temperature bath?

7 Entropy and equations of state

MODERATE For a particular gas the entropy is

$$S = S(E, V, N) = \frac{3}{2} Nk \ln\left(E + \frac{N^2 a}{V}\right) + Nk \ln(V - Nb) + f(N)$$

where a and b are constants and $f(N)$ is some function of N only.

a) Determine an expression for T in terms of E, V, N.

b) Use the previous result to show that

$$S = S(T, V, N) = \frac{3}{2} Nk \ln T + Nk \ln(V - Nb) + g(N)$$

where $g(N)$ is a function of N only.

c) Determine an expression for P in terms of T, V, N. Show that this reduces to a Van der Waals equation of state.

8 Helmholtz free energy and thermal energy

EASY Suppose that a system undergoes a process such that it's initial and final temperatures are the same.

a) For what type of process is $\Delta F = \Delta E$?

b) What is the requirement in terms of heat flow such that $\Delta F > \Delta E$?

c) What is the requirement in terms of heat flow such that $\Delta F < \Delta E$?

d) If the entropy of the system decreases during a process, will the work done by the system be equal to, less than or more than the decrease in thermal energy of the system? Explain why.

9 Helmholtz free energy in a free expansion of a gas

MODERATE During a free expansion of any gas, the pressure, volume and temperature of the gas are all ill-defined. However, at the beginning and end of the free expansion of the gas, they are well-defined and thus there are exact values for $\Delta E, \Delta S, \ldots$. The aim of this exercise is to determine ΔF for a free expansion and to check whether $\Delta F = W$ where W is the work done on the gas.

a) In general the work done on a gas is $W = -\int P_{\text{ext}} \mathrm{d}V$ where P_{ext} is the external pressure on the gas. Consider a cylinder of gas which is thermally insulted from its surroundings. Initially the gas is confined by a barrier to the left half of the cylinder and there is a vacuum in the right half of the cylinder. The barrier is removed and the gas eventually doubles its volume. Determine the work done on the gas in this process. Use this and the first law to determine an expression for the change in energy of the gas. Use this to show that

$$\Delta F = -\Delta(TS).$$

b) Consider an ideal gas. How does the temperature at the beginning of the process compare to the temperature at the end of the process? Use this and the expression for the entropy of an ideal gas to determine an expression for ΔF. Check whether $\Delta F = W$ or $\Delta F < W$ in this case.

10 Methane combustion

MODERATE When methane (CH_4) undergoes combustion according to

$$CH_4(\text{gas}) + 2O_2(\text{gas}) \rightarrow CO_2(\text{gas}) + 2H_2O(\text{liquid}),$$

at 298 K, the change in enthalpy is $-890\,\text{kJ mol}^{-1}$. The entropy of the constituents is $186.3\,\text{JK}^{-1}\text{mol}^{-1}$ (CH_4(gas)), $205.1\,\text{JK}^{-1}\text{mol}^{-1}$ (O_2(gas)), $213.74\,\text{JK}^{-1}\text{mol}^{-1}$ (CO_2(gas)) and $69.91\,\text{JK}^{-1}\text{mol}^{-1}$ (H_2O(liquid)). Suppose that 1.00 mol of methane undergoes combustion and that this occurs in such a way that the pressure at the beginning and end of the process is the same and that the temperatures are also the same.

a) Show that

$$\Delta H = \Delta E + P\Delta V$$

and assuming that the gases involved are ideal show that this gives

$$\Delta H = \Delta E + kT\Delta N.$$

Determine the change in energy for the process. ΔN in this process is minus two moles.

b) Determine the maximum work that can be done by the gas in this process.

c) If one generated energy by burning methane, what would be the minimum rate at which methane would have to be burnt (in terms of mols/hour) in order to produce 1.0 kW of power?