PROBLEM SETS ON THERMODYNAMICS
Merton College
Michaelmas Term 2024

Problem Set 1 *(due Sunday 10 November @23:59)*

- Andrew Steane's Problem Set 0:
  Section A Questions 3, 5, 6 (these should only take a few minutes each)
  Section B is optional: these are maths exercises that are essentially revision of first-year material that you should know, do them if they look challenging

- Andrew Steane's Problem Set 1:
  Section A Questions 2 (bookwork), 6, 7
  Section B Questions 1, 2 (bookwork)

- Andrew Boothroyd's Problem Set 1: do all of it (Questions 1-6)

- Andrew Steane's Problem Set 2:
  Section A Question 4 (if you are pressed for time, you may drop this question)

Problem Set 2 *(due Sunday 17 November @23:59)*

Entropy changes

- Andrew Steane's Problem Set 1:
  Section B Question 8

- Andrew Boothroyd's Problem Set 2: Questions 1-6

- Andrew Steane's Problem Set 2:
  Section A Question 3

Thermodynamic calculus

- Andrew Steane's Problem Set 2:
  Section B: Questions 2, 4, 5 (these should only take a few minutes each)

- Andrew Boothroyd's Problem Set 2: Questions 7 (bookwork), 8, 9

Thermodynamics of non-pV systems

- Andrew Steane's Problem Set 2:
  Section B: Question 6
  Section C: Questions 1, 3, 4

- Andrew Boothroyd's Problem Set 2: Questions 10, 11, 12

If you are pressed for time, you may drop Steane's Questions B6, C1 and C4; you may also drop either Steane's Question C3 or Boothroyd's Question 12.

Thermodynamics Problem sets

Andrew Steane

October 14, 2024

Many (not all) of the exercises are taken from *Steane, Thermodynamics* (OUP); the numbers in brackets state which they are. Most questions test a single concept and are brief. If you are spending a lot of time on such a question, it suggests you may have missed the concept. Longer question are indicated by an (L) after the question number. This signals merely that a larger amount of work is needed to solve the problem.

No problem set is easy, but set 0 here is easier than the others. This is to allow students to get started on the problems before they have had many lectures. Possible teaching arrangements could be:
{0, 1, 2} (3 sessions, gives the students more time);
or {0–1, 2} (2 sessions). With this arrangement, students could do set 0 over the first two weeks of term based on their reading and previous study, without the need for any lectures. Then set 1 is completed after lecture 5, and set 2 after lecture 7;
or {0–1.1, 1.2–2.2, 2.3 } In this version the first teaching session can take place after lecture 4, and part 2.3 (of problem set 2) is combined with some kinetic theory.

0   Problem set 0. Basic concepts

state, equilibrium, response function, temperature, function of state, reciprocity theorem, introduction to fundamental relation. (chapter 2, 3, 4, 5, 6)

0.1   Section A. Terminology and some concepts

(Exercises 3.1–3.7)

1. The relaxation time of an ideal of given density and temperature, in a container with all dimensions approximately equal, scales with volume as $V^{2/3}$. Given that a litre of gas at STP has a relaxation time of about 10 seconds, find the relaxation time of a cubic region of diameter 10 microns in such a gas. (Such a region has approximately 2×10^{10} molecules in it; we will see later that this implies concepts such as pressure and temperature can be defined to a fractional precision of order 10^{-5}.)

2. Define the terms *reversible* and *quasistatic* (as they are used in thermodynamics). Among the many processes going on inside the body of a living animal such as a cat, there are: breathing, circulation of blood, digestion, mietosis (cell division), osmosis. Briefly discuss which aspects, if any, of these processes are quasistatic to reasonable approximation.

3. Let the letters Q,R,I,T denote the terms *quasistatic*, *reversible*, *irreversible* and *isothermal*, respectively. State which of Q,R,I,T apply to each of the following processes (in each case list all appropriate terms):
(a) a gas slowly expanding in a thermally isolated cylinder fitted with a frictionless piston
(b) a volcanic eruption
(c) a steel nail oxidising (rusting) while immersed in a bucket of water
(d) ice forming over a pool of water on a still winter evening
(e) a force pushes an ordinary book across an ordinary table.

4. (i) Which has the higher bulk modulus, a gas or a solid?
(ii) Show that, in the limit $V \gg Nb$, the isothermal compressibility of a van der Waals gas is $(p - N^2 a/V^2)^{-1}$.

5. **Function of state**. Water can enter a lake by two routes: either by flowing down a river into the lake, or by falling as rain. It can leave by evaporation, or by flowing out into the outlet stream. Assume there is no difference between rain water and river water (e.g. both are pure).
Let the physical system under discussion be the lake of water. Which of the following quantities are functions of state?:

   (a) The depth of the water,

   (b) The total amount of water in the lake,

   (c) The mass of river water in the lake,

   (d) The temperature of the water,

   (e) The mass of water that has left the lake by evaporation,

   (f) The volume of rain water in the lake,

   (g) The rate of evaporation.

6. Suppose that the lake in the previous question empties completely during a dry spell, and then later fills up with water from the river during a period in which there is no rainfall. Does this change the answers to any parts of the previous question?

7. One mole of a certain gas at low pressure obeys the equation of state

$$\left(p + \frac{a}{V^2} + \frac{d}{V^3} \right) \left(V - b + \frac{f}{V} \right) = RT$$

where a, b, d, f are constants. Find the equation of state for n moles of this gas. [Hint: it is easy enough if you reason precisely; do not guess!]

0.2   Section B. Partial math

(Exercises 5.1–5.4)

1. (i) Consider the following small quantity: $y^2 dx + xy dy$. Find the integral of this quantity from $(x, y) = (0, 0)$ to $(x, y) = (1, 1)$, first along the path consisting of two straight line portions (0,0) to (0,1) to (1,1), and then along the diagonal line $x = y$. Comment.
   (ii) Now consider the small quantity $y^2 dx + 2xy dy$. Find (by trial and error or any other method) a function f of which this is the total differential.

2. A certain small quantity is given by

$$C_V dT + \frac{RT}{V} dV$$

   where C_V and R are constants and T and V are functions of state. (i) Show that this small quantity is an improper differential. (ii) Let $đQ = C_V dT + \frac{RT}{V} dV$. Show that $đQ/T$ is a proper differential.

3. Derive the reciprocity theorem.

4. If x, y are functions of state, give an argument to prove that

$$\frac{đQ_{(p)}}{dx} = \frac{đQ_{(p)}}{dy} \frac{\partial y}{\partial x}\bigg|_{(p)} \tag{1}$$

   where the subscript (p) indicates the path along which the changes are evaluated.

5. If $f(x, y, z)$ is a function of the variables x, y, z, under what circumstances, in general, is $(\partial f / \partial x)_{y,z}$ equal to f/x?

6. A and B are both functions of two variables x and y, and $A/B = C$. Show that

$$\frac{\partial x}{\partial y}\bigg|_C = \frac{\frac{\partial \ln B}{\partial y}\big|_x - \frac{\partial \ln A}{\partial y}\big|_x}{\frac{\partial \ln A}{\partial x}\big|_y - \frac{\partial \ln B}{\partial x}\big|_y}$$

   [Hint: develop the left hand side, and don't forget that for any function f, $(d/dx)(\ln f) = (1/f)df/dx$].

0.3   Section C. Temperature

(Exercises 6.1–6.5)

1. A constant volume gas thermometer contains a gas whose equation of state is the van der Waals equation. Another contains an ideal gas. Each thermometer is calibrated at the ice and steam points (the melting and boiling point of water at standard pressure), and thereafter the pressure is used as a linear indicator of temperature. Show that with such calibration the temperature measurements provided by these two thermometers will agree at all temperatures, with no requirement to extrapolate to zero pressure.

2. The equation of state of a certain solid is well approximated by

$$V = V_0(1 + \alpha T - \kappa p).$$

where V_0, α and κ are constants. Sketch the isotherms on a pV diagram. Explain briefly whether you expect the slopes of these isotherms to be large or small compared to those of a gas.

3. Prove from the Zeroth Law that two different isotherms cannot intersect.

1 Problem set 1. First and second law; associated reasoning

empirical temperature and equation of state; work and internal energy; heat engine, Carnot and Clausius theorems, entropy; diffusion equation (chapter 7, 8, 9, 10)

1.1 Section A. Energy

(7.1–7.5, 7.11, 7.19, 7.20)

1. (L) A mole of ideal gas is taken from a state p_1, V_1 to a state p_2, V_2 along a path forming a straight line on an indicator diagram. Find an expression for the work W done on the gas. Assuming the constant-volume heat capacity C_V is independent of temperature, find also the internal energy change ΔU and the heat Q entering the system. Apply your results to find ΔU, W and Q when the initial state is at volume $21 \times 10^{-3} \, \text{m}^3$ and temperature $290 \, \text{K}$, and the final state is at $22 \times 10^{-3} \, \text{m}^3$, $330 \, \text{K}$, for a gas with $\gamma = 1.4$.
   [*Ans.* $W = -120$ J; $\Delta U = 831$ J; $Q = 951$ J.]

2. (i) Prove that in an adiabatic expansion of an ideal gas with constant heat capacities, pV^γ is constant, where $\gamma = C_p/C_V$ is the ratio of the heat capacities (also called adiabatic index). (ii) Show that in such an expansion $TV^{\gamma-1}$ and $T^\gamma p^{1-\gamma}$ are also constant.

3. An ideal gas at initial pressure p_1 undergoes an adiabatic expansion from volume V_1 to volume V_2. Assuming γ is constant, find the final pressure and show that the work done is
$$W = \frac{p_1 V_1}{\gamma - 1} \left(\left(\frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right).$$

4. An ideal gas is taken between the same initial and final states as in question 1, by an adiabatic expansion followed by heating at constant volume. Calculate the work done and heat absorbed.
   [*Ans.* $W = -111$ J; $Q = 943$ J.]

5. An ideal elastic rod of length L and tension f has the equation of state
$$f = KT \left(\frac{L}{L_0} - \frac{L_0^2}{L^2} \right)$$
   where K, L_0 are constants. Show that the isothermal *Young's modulus* E (defined as the ratio of stress to strain: $E = (\delta f/A)/(\delta L/L_0)$ where A is a cross-sectional area) is given by
$$E = \frac{KT}{A} \left(1 + 2\frac{L_0^3}{L^3} \right)$$
   Calculate the work required to stretch the substance isothermally from $L = L_0$ to $L = 2L_0$.

6. (L) A thermally insulated chamber contains some hot gas and a lump of metal. Initially the gas and the lump at the same temperature T_i. The volume of the chamber can be changed by moving a frictionless piston. Assuming the heat capacities of the gas and the metal lump are comparable, sketch on one diagram the pressure-volume relation for the system

    (a) if the pressure is reduced to atmospheric pressure p_0 slowly enough for the temperature of the metal lump to be equal to that of the gas at all stages.

    (b) if the pressure is reduced to p_0 fast enough for the metal lump not to cool at first (but the process is still quasistatic for the gas) after which the piston is further moved so as to maintain the pressure at p_0 until the metal lump and the gas attain the same temperature.

    Use the first law to explain whether or not the final volume will be the same in these two processes. Explain which process finishes at the lower temperature. [Hint: consider the work done and use the fact that internal energy is a function of state for any given system.]

7. (L) A thermally insulated and evacuated chamber is placed in a room where the pressure and temperature T_0 are maintained constant. Gas leaks slowly into the chamber through a small hole. Show that when the pressures are equalised, the temperature of the air in the chamber is γT_0, where $\gamma = C_p/C_v$ and you may assume the heat capacities are independent of temperature. [Hint: imagine placing a bag around the chamber, just large enough to enclose the chamber and all the gas that finally ends up inside the chamber, and calculate the work done by the rest of the atmosphere as this bag collapses.] Consider the case of argon gas ($\gamma = 5/3$) at $50°$ C leaking into a flask made of tin. What happens to the flask?

1.2 Section B. Second law and entropy

(8.1, 8.2, 9.3–9.5, 9.9, 9.10)

1. Starting in some given state, a certain physical system absorbs some heat Q_1 and emits some heat Q_2. The difference between these two energies, $Q = Q_1 - Q_2$ is used to perform some work W while the system returns to its starting state. Is it physically possible to have $W = Q$, or is this ruled out by Kelvin's statement of the Second Law of thermodynamics? If this is not ruled out, then what, precisely, is ruled out?

2. By the use of heat engine diagrams, or otherwise, prove that the Clausius statement of the 2nd law is true *if and only if* the Kelvin statement is true.

3. A building is maintained at a temperature T by means of an ideal heat pump which uses a river at temperature T_0 as a source of heat. The heat pump consumes power W, and the building loses heat to its surroundings at a rate $\alpha(T - T_0)$. Show that T is given by

$$T = T_0 + \frac{W}{2\alpha}\left(1 + \sqrt{1 + 4\alpha T_0/W}\right)$$

4. A possible ideal-gas cycle operates as follows.
   (i) from an initial state (p_1, V_1) the gas is cooled at constant pressure to (p_1, V_2).
   (ii) the gas is heated at constant volume to (p_2, V_2).
   (iii) the gas expands adiabatically back to (p_1, V_1).
   Assuming constant heat capacities, show that the thermal efficiency is

   $$1 - \gamma \frac{(V_1/V_2) - 1}{(p_2/p_1) - 1}$$

5. A mug of tea has been left to cool from $90°$ C to $18°$ C. If there is 0.2 kg of tea in the mug, and the tea has specific heat capacity 4200 J K^{-1} kg^{-1}, show that the entropy of the tea has decreased by 185.6 J K^{-1}. Comment on the sign of this result.

6. Consider the inequality

   $$dS \geq \frac{\text{đ}Q}{T} \;.$$

   Is it possible for dS and $\text{đ}Q$ to have opposite signs? If it is, then give an example.

7. (L) Calculate the changes in entropy of the universe as a result of the following processes:
   (a) A copper block of mass 400 g and heat capacity 150 J K^{-1} at $100°$ C is placed in a lake at $10°$ C
   (b) The same block, now at $10°$ C, is dropped from a height 100 m into the lake.
   (c) Two similar blocks at $100°$ C and $10°$ C are joined together. [Hint: first find the final temperature, then reuse previous calculations]
   (d) A capacitor of capacitance 1 μF is connected to a battery of e.m.f. 100 V at $0°$ C. [To answer this you must think carefully about what happens when a capacitor is charged from a battery.]
   (e) The same capacitor after being charged to 100 V is discharged through a resistor at $0°$ C.
   (f) One mole of gas at $0°$ C is expanded reversibly and isothermally to twice its initial volume.
   (g) One mole of gas at $0°$ C is expanded reversibly and adiabatically to twice its initial volume.

8. A system consists of two different volumes of ideal gas, either side of a fixed thermally insulating partition. On one side there are 2 moles of gas at temperature $T_{1i} = 500\,$K. On the other side there are 4 moles of gas at temperature $T_{2i} = 200\,$K. The molar capacity at constant volume is $C_{V,\mathrm{m}} = (3/2)R$. (i) If the partition is made thermally conducting, find the final temperature throughout the system when equilibrium is attained, and find the net change in entropy of the complete system. (ii) Now return to the initial conditions, and suppose the partition is made thermally conducting again, but only for a short time, so that some heat transfer takes place, but not enough to reach equilibrium, after which the thermal insulation is reinstated. Show that the final temperatures on the two sides are related by

   $$T_{1f} + 2T_{2f} = 900\,\text{kelvin}$$

   and find an expression for the net change in entropy ΔS as a function of T_{1f}. Plot ΔS on a graph as a function of T_{1f}, and find where it reaches a maximum.

2 Problem set 2. Thermodynamic potentials and methods

thermodynamic potentials, natural variables, Maxwell equations, chemical potential, fundamental relation, magnetism, surface tension (chapter 11, 12, 13, 14)

2.1 Section A. More practice

1. 1 kg of water is warmed from 20°C to 100°C (a) by placing it in contact with a reservoir at 100°C, (b) by placing it first in contact with a reservoir at 50°C until it reaches that temperature, and then in contact with the reservoir at 100°C, and (c) by operating a reversible heat engine between it and the reservoir at 100°C. In each case, what are the entropy changes of (i) the water, (ii) the reservoirs, and (iii) the universe? (Assume the heat capacity of water is independent of temperature).

2. Two identical bodies of constant heat capacity C_p at temperatures T_1 and T_2 respectively are used as reservoirs for a heat engine. If the bodies remain at constant pressure, show that the amount of work obtainable is

$$W = C_p \left(T_1 + T_2 - 2T_f \right)$$

where T_f is the final temperature attained by both bodies. Show that if the most efficient engine is used, then $T_f^2 = T_1 T_2$.

3. The temperature inside the engine of a crane is $2000°$ C, the temperature of the exhaust gases is $900°$ C. The heat of combustion of petrol is 47 MJ/kg, and the density of petrol is 0.8 g/cm^3. What is the maximum height through which the crane can raise a 10000 kg load by burning 0.1 litre of petrol? [*Ans.* 18.6 metres.]

4. The operation of a diesel engine can be modelled approximately by the following cycle: (i) adiabatic compression from (p_1, V_1) to (p_2, V_2), (ii) heating at constant pressure to (p_2, V_3), (iii) adiabatic expansion to (p_4, V_1), (iv) cooling at constant volume back to (p_1, V_1). Sketch the cycle on a pV diagram. Find the efficiency in terms of the two compression ratios V_1/V_2 and V_3/V_2.

2.2 Section B. Potentials and Maxwell relations

(12.1, 13.2–13.5, 13.15)

1. In the absence of external fields, the chemical potential per particle in an ideal gas can be written

$$\mu = \mu_0(T) + k_B T \ln \frac{p}{p_0}$$

where p_0 is a constant and $\mu_0(T)$ is the value of μ at pressure p_0 and temperature T. In an 'atom trap' such a gas can be contained in a harmonic potential well $V(r) = \alpha r^2$, where α is a constant and r is the distance from the centre of the well. Using the chemical potential, or otherwise, show that under isothermal conditions the number density profile is $n = n_0 \exp(-\alpha r^2/k_B T)$.

2. A closed simple compressible system has work W done on it in a reversible process without heat exchange. (i) By how much does the internal energy change? (ii) Is it possible to tell, from the given information, the change in the Helmholtz function, enthalpy, and Gibbs function? (iii) Suppose the work were done in conditions of constant temperature. Now what can you say about U, F, H, G?

3. Derive all the Maxwell relations.

4. Sketch an isotherm and an adiabat passing through a given point p, V on the indicator diagram for a gas. Hence show that more work energy can be extracted from a gas in an isothermal expansion (between given volumes) than in an adiabatic one. Where has the energy for this extra work come from?

5. Give an example of a physical process which can take place in a closed system at constant pressure and temperature. What thermodynamic potential is unchanged in such a process?

6. A piece of rubber of length L is subject to work by hydrostatic pressure and a tensional force f.
   (i) Construct an expression for dU.
   (ii) Generate the potentials which have as proper variables (S,V,f) and (S,p,f)
   (iii) Derive the Maxwell relation (first developing any potential you may need)

$$\left.\frac{\partial S}{\partial L}\right|_{T,p} = -\left.\frac{\partial f}{\partial T}\right|_{p,L}$$

2.3 Section C. Applications (rod, surface, magnetization, solid)

(14.1, 14.3, 14.6)

1. Show that, for an elastic rod under tension f,

$$\left.\frac{\partial C_L}{\partial L}\right|_T = -T\left.\frac{\partial^2 f}{\partial T^2}\right|_L \tag{2}$$

   where C_L is the heat capacity at constant length.

2. The surface tension of liquid argon is given by $\sigma = \sigma_0(1-T/T_c)^{1.28}$ where $\sigma_0 = 0.038$ N/m and the critical temperature $T_c = 151$ K. Find the surface entropy per unit area at the triple point, $T = 83$ K.
   [$Ans.$ 2.58×10^{-4} J/K]

3. (L) The susceptibility χ of a paramagnetic substance is defined by $M = \chi H_{in}$ where M is the magnetization and H_{in} is the magnetic field inside the sample. For this question assume weak magnetization, such that $H_{in} \simeq H = B/\mu_0$, where B is the applied field. Many paramagnetic substances are described to good approximation by the Curie-Weiss law:

$$\chi = \frac{a}{T - T_c}$$

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where a and T_c are constants. When a sample is cooled by adiabatic demagnetization from a high field B to a low field B_0, the temperature falls from T_i to T_f. We would like to show that these temperatures are related by

$$\frac{T_f - T_c}{T_i - T_c} \simeq \frac{B_0}{B}. \tag{3}$$

To this end, consider the magnetic Helmholtz function $F = U - ST$. We have $\mathrm{d}F = -S\mathrm{d}T - m\mathrm{d}B$ and it is useful to consider $F(T, B)$. This can be written

$$F(T, B) = F(T, 0) + \int_0^B \left.\frac{\partial F}{\partial B}\right|_T \mathrm{d}B.$$

Use this to obtain $F(T, B) - F(T, 0)$ and hence derive

$$S(T, B) = S(T, 0) - \frac{aV}{2\mu_0}\frac{B^2}{(T - T_c)^2}.$$

The first term is the entropy at $B = 0$ for any given temperature. The second term is the magnetic contribution. If we assume that the *change* in entropy is dominated by the latter contribution, then for an adiabatic process obtain equation (3).

4. (L) A lump of sodium metal of volume $2 \times 10^{-4}\,\mathrm{m}^3$ is located in a cylinder containing a mole of argon gas at temperature $295\,\mathrm{K}$ and pressure $10^4\,\mathrm{Pa}$. Find the work done on the gas, and on the sodium metal, (i) when the pressure is increased isothermally to $10^7\,\mathrm{Pa}$, and (ii) when, starting from the same initial conditions, the temperature is increased isobarically to $360\,\mathrm{K}$. All processes may be considered reversible. [At STP, the isothermal bulk modulus of sodium is $B_T = 6.18 \times 10^9\,\mathrm{Pa}$ and the cubic expansivity is $\alpha = 2 \times 10^{-4}\,\mathrm{K}^{-1}$.]

Statistical and Thermal Physics

Φxford

hysics

Second year physics course A1

Dr A. A. Schekochihin and Prof. A. T. Boothroyd

Problem Set 1

(A. T. Boothroyd)

PROBLEM SET 1: Basic Thermodynamics

Problem set 1 can be covered in one tutorial or class held during Week 5 of Michaelmas Term

Functions of two variables

1.1 In polar coordinates, $x = r\cos\theta$ and $y = r\sin\theta$.

(a) The definition of x implies that

$$\frac{\partial x}{\partial r} = \cos\theta = \frac{x}{r}. \tag{1}$$

But we also have $x^2 + y^2 = r^2$, so differentiating with respect to r gives

$$2x\frac{\partial x}{\partial r} = 2r \qquad \Longrightarrow \qquad \frac{\partial x}{\partial r} = \frac{r}{x}. \tag{2}$$

But equations (1) and (2) imply that $\dfrac{\partial x}{\partial r} = \dfrac{\partial r}{\partial x}$. What's gone wrong?

(b) Show that

$$\left(\frac{\partial x}{\partial r}\right)_y \left(\frac{\partial r}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_r = -1$$

Expansions, cycles and heat engines

1.2 Two thermally insulated cylinders, A and B, of equal volume, both equipped with pistons, are connected by a valve. When open, the valve allows unrestricted flow. Initially A has its piston fully withdrawn and contains a perfect monatomic gas at temperature T_i, and B has its piston fully inserted, and the valve is closed. The thermal capacity of the cylinders is to be ignored. The valve is fully opened and the gas slowly drawn into B by pulling out the piston B; piston A remains stationary. Show that the final temperature of the gas is $T_f = T_i/2^{2/3}$.

[For a monatomic ideal gas, $\gamma = 5/3$.]

1.3 A possible ideal-gas cycle operates as follows:
(i) From an initial state (p_1, V_1) the gas is cooled at constant pressure to (p_1, V_2);
(ii) The gas is heated at constant volume to (p_2, V_2);
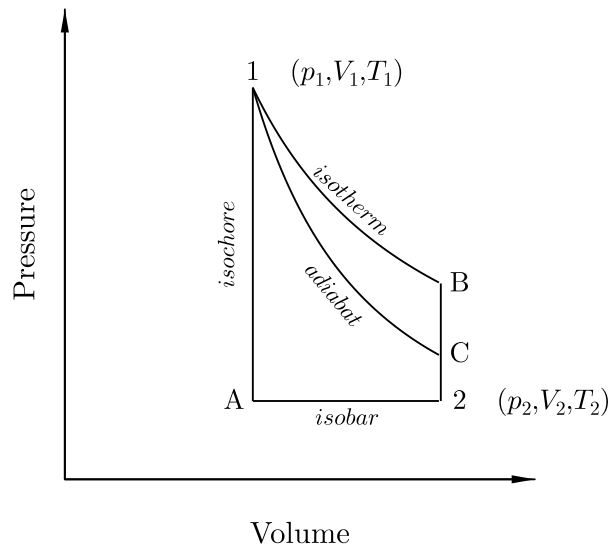(iii) The gas expands adiabatically back to (p_1, V_1).
Assuming constant heat capacities, show that the thermal efficiency is

$$1 - \gamma\frac{(V_1/V_2) - 1}{(p_2/p_1) - 1}.$$

(You may quote the fact that in an adiabatic change of an ideal gas, pV^γ stays constant, where $\gamma = C_p/C_V$.)
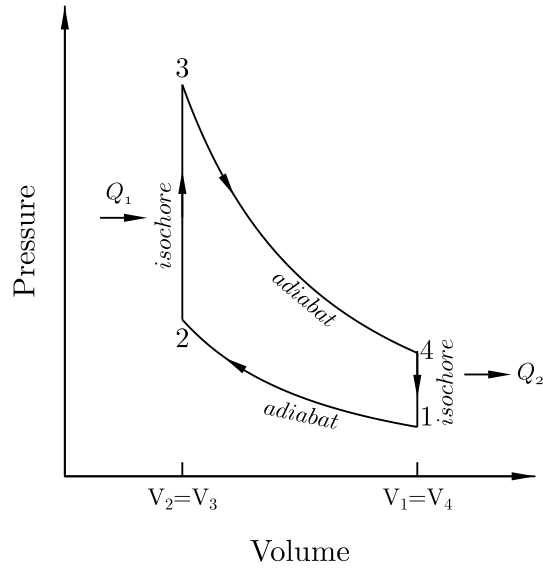
1.4 Show that the efficiency of the standard Otto cycle (shown above) is $1 - r^{1-\gamma}$, where $r = V_1/V_2$ is the compression ratio.

1.5 An ideal gas is changed from an initial state (p_1, V_1, T_1) to a final state (p_2, V_2, T_2) by the following quasi-static processes shown in the figure: (i) 1A2 (ii) 1B2 and (iii) 1C2. For each process, obtain the work that must be done on the system and the heat that must be added in terms of the initial and final state variables, and hence show that $\Delta U = C_V(T_2 - T_1)$ independent of path. (Assume that the heat capacity C_V is constant.)

1.6 A building is maintained at a temperature T by means of an ideal heat pump which uses a river at temperature T_0 as a source of heat. The heat pump consumes power W, and the building loses heat to its surroundings at a rate $\alpha(T - T_0)$. Show that T is given by

$$T = T_0 + \frac{W}{2\alpha}\left(1 + \sqrt{1 + 4\alpha T_0/W}\right).$$

Statistical and Thermal Physics

Φxford
Physics

Second year physics course: A1
Dr A. A. Schekochihin and Prof. A. T. Boothroyd

Problem Set 2

(A. T. Boothroyd)

Some useful constants

Boltzmann's constant	k_B	$1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Avogadro's number	N_A	$6.022 \times 10^{23}\,\mathrm{mol^{-1}}$
Standard molar volume		$22.414 \times 10^{-3}\,\mathrm{m^3\,mol^{-1}}$
Molar gas constant	R	$8.315\ \mathrm{J\,mol^{-1}\,K^{-1}}$
1 pascal (Pa)		$1\,\mathrm{N\,m^{-2}}$
1 standard atmosphere		$1.0132 \times 10^5\,\mathrm{Pa\,(N\,m^{-2})}$
1 bar (= 1000 mbar)		$10^5\,\mathrm{N\,m^{-2}}$

PROBLEM SET 2: Basic Thermodynamics

Problem set 2 can be attempted in Week 6 or 7 of Michaelmas Term. There is about one-and-a-half tutorials or classes worth of material. The starred problem is more difficult.

Entropy Changes

2.1 In a free expansion of a perfect gas (also called a Joule expansion), we know U does not change, and no work is done. However, the entropy must increase because the process is irreversible. How are these statements compatible with $dU = TdS - pdV$?

2.2 A mug of tea has been left to cool from 90°C to 18°C. If there is 0.2 kg of tea in the mug, and the tea has specific heat capacity $4200 \, \mathrm{J \, K^{-1} \, kg^{-1}}$, show that the entropy of the tea has decreased by $185.7 \, \mathrm{J \, K^{-1}}$. How is this result compatible with an increase in entropy of the Universe?

2.3 Calculate the changes in entropy of the Universe as a result of the following processes:

(a) A copper block of mass 400 g and heat capacity $150 \, \mathrm{J \, K^{-1}}$ at 100°C is placed in a lake at 10°C;

(b) The same block, now at 10°C, is dropped from a height of 100 m into the lake;

(c) Two similar blocks at 100°C and 10°C are joined together (hint: save time by first realising what the final temperature must be, given that all the heat lost by one block is received by the other, and then re-use previous calculations);

(d) A capacitor of capacitance $1 \, \mu\mathrm{F}$ is connected to a battery of e.m.f. 100 V at 0°C. (NB think carefully about what happens when a capacitor is charged from a battery.);

(e) The capacitor, after being charged to 100 V, is discharged through a resistor at 0°C;

(f) One mole of gas at 0°C is expanded reversibly and isothermally to twice its initial volume;

(g) One mole of gas at 0°C is expanded adiabatically to twice its initial volume;

(h) The same expansion as in (f) is carried out by opening a valve to an evacuated container of equal volume.

2.4 A block of lead of heat capacity $1 \, \mathrm{kJ \, K^{-1}}$ is cooled from 200 K to 100 K in two ways:

(a) It is plunged into a large liquid bath at 100 K;

(b) The block is first cooled to 150 K in one bath and then to 100 K in another bath.

Calculate the entropy changes in the system consisting of block plus baths in cooling from 200 K to 100 K in these two cases. Prove that in the limit of an infinite number of intermediate baths the total entropy change is zero.

2.5 Two identical bodies of constant heat capacity C_p at temperatures T_1 and T_2 respectively are used as reservoirs for a heat engine. If the bodies remain at constant pressure, show that the amount of work obtainable is

$$W = C_p \left(T_1 + T_2 - 2T_\mathrm{f} \right),$$

where T_f is the final temperature attained by both bodies. Show that if the most efficient engine is used, then $T_f^2 = T_1 T_2$. Calculate W for reservoirs containing 1 kg of water initially at 100°C and 0°C, respectively. (Ans: 32.7 kJ.)
(Specific heat capacity of water $= 4{,}200\,\mathrm{J\,K^{-1}\,kg^{-1}}$).

2.6* Three identical bodies are at temperatures 300 K, 300 K and 100 K. If no work or heat is supplied from outside, what is the highest temperature to which any one of these bodies can be raised by the operation of heat engines?[1]
(Ans: 400 K)

Thermodynamic potentials and calculus

2.7 [*This question is just some bookwork practice and should only take a couple of minutes.*]

(a) Using the first law $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ to provide a reminder, write down the definitions of the four thermodynamic potentials U, H, F, G for a simple p-V system (in terms of U, S, T, p, V), and give $\mathrm{d}U$, $\mathrm{d}H$, $\mathrm{d}F$, $\mathrm{d}G$ in terms of T, S, p, V and their derivatives.
(b) Derive all the Maxwell relations.

2.8 (a) Derive the following general relations

$$\text{(i)} \quad \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]$$

$$\text{(ii)} \quad \left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{C_V}T\left(\frac{\partial p}{\partial T}\right)_V$$

$$\text{(iii)} \quad \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$$

In each case the quantity on the left hand side is the appropriate thing to consider for a particular type of expansion. State what type of expansion each refers to.

(b) Using these relations, verify that for an ideal gas $\left(\frac{\partial T}{\partial V}\right)_U = 0$ and $\left(\frac{\partial T}{\partial p}\right)_H = 0$, and that $\left(\frac{\partial T}{\partial V}\right)_S$ leads to the familiar relation $pV^\gamma = \text{constant}$ along an isentrope.

2.9 Use the First Law of Thermodynamics to show that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\beta_p} - p$$

where β_p is the coefficient of volume expansivity and the other symbols have their usual meanings.

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[1]If you set this problem up correctly you may have to solve a cubic equation. This looks hard to solve but in fact you can deduce one of the roots [hint: what is the highest temperature of the bodies if you do nothing to connect them?]

Thermodynamics of non p–V systems

2.10 For a stretched rubber band, it is observed experimentally that the tension f is proportional to the temperature T if the length L is held constant. Prove that:

(a) the internal energy U is a function of temperature only;

(b) adiabatic stretching of the band results in an increase in temperature;

(c) the band will contract if warmed while kept under constant tension.

[You may assume that $\left(\frac{\partial L}{\partial f}\right)_T > 0$.]

2.11 For a fixed surface area, the surface tension of water varies linearly with temperature from $75 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ at 5°C to $70 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ at 35°C. Calculate the surface contributions to the entropy per unit area and the internal energy per unit area at 5°C.

[Ans: $\left(\frac{\partial S}{\partial A}\right)_T = 0.167 \times 10^{-3}\,\mathrm{J\,K^{-1}\,m^{-2}}$, $\left(\frac{\partial U}{\partial A}\right)_T = 121.3 \times 10^{-3}\,\mathrm{J\,m^{-2}}$]

An atomizer produces water droplets of diameter $0.1\,\mu\mathrm{m}$. A cloud of droplets at $35°\,\mathrm{C}$ coalesces to form a single drop of water of mass $1\,\mathrm{g}$. Estimate the temperature of the drop assuming no heat exchange with the surroundings. What is the increase in entropy in this process? (Specific heat capacity of water $c_p = 4{,}200\,\mathrm{J\,K^{-1}\,kg^{-1}}$.)

[Ans: $\Delta T = 1.73\,\mathrm{K}$, $\Delta S = 13.6 \times 10^{-3}\,\mathrm{J\,K^{-1}}$]

2.12 The magnetization M of a paramagnetic material is given by $M = \chi B/\mu_0$, where B is the magnetic flux density and the susceptibility χ follows Curie's law $\chi = C/T$ with C a constant.

If the heat capacity per unit volume at constant M is $c_M = a/T^2$, show that the heat capacity per unit volume at constant B is

$$c_B = \frac{a}{T^2}\left(1 + \frac{B^2 C}{\mu_0 a}\right).$$

If a sample is initially at temperature T_1 in an applied field of flux density B_1, show that the temperature after adiabatic reduction of the field to zero is

$$T_2 = \frac{T_1}{\left(1 + \frac{B_1^2 C}{\mu_0 a}\right)^{1/2}}.$$