

# Thermodynamics Problem sets

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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 questions 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)

- 0.1. The relaxation time of an ideal gas 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  $2 \times 10^{10}$  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  $10^{-5}$ .)

- 0.2. 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, mitosis (cell division), osmosis. Briefly discuss which aspects, if any, of these processes are quasistatic to reasonable approximation.
- 0.3. 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.
- 0.4. (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  $(p - N^2a/V^2)^{-1}$ .
- 0.5. **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.
- 0.6. 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?
- 0.7. One mole of a certain gas at low pressure obeys the equation of state

$$\left(p + \frac{a}{V_1^2} + \frac{d}{V_1^3}\right) \left(V_1 - b + \frac{f}{V_1}\right) = RT$$

where  $a, b, d, f$  are constants and the other symbols represent pressure, volume, temperature and the molar gas constant. Consider now  $n$  moles of this gas, having properties  $p, V, T$ . Find the equation of state. [Hint: it is easy enough if you reason precisely; do not guess!]

## 0.2 Section B. Partial math

(Exercises 5.1–5.4)

- 0.8. (a) 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.
- (b) 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, with the constant of integration set equal to zero.

- 0.9. 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  $dQ = C_V dT + \frac{RT}{V} dV$ . Show that  $dQ/T$  is a proper differential.

- 0.10. Derive the reciprocity theorem.

- 0.11. If  $x, y$  are functions of state, give an argument to prove that

$$\frac{dQ_{(p)}}{dx} = \frac{dQ_{(p)}}{dy} \frac{\partial y}{\partial x} \Big|_{(p)} \quad (1)$$

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

- 0.12. 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  $f/x$ ?

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

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

[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)

- 0.14. A constant volume gas thermometer contains a gas whose equation of state is the van der Waals equation. Another contains an ideal gas. The thermometers are employed without extrapolation to zero pressure. 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. Find the difference between the temperature measurements provided by these two thermometers at  $20^\circ\text{C}$ , and then at  $120^\circ\text{C}$ .

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

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

where  $V_0$ ,  $\alpha$  and  $\kappa$  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.

- 0.16. 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)

- 1.1. (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  $\Delta U$  and the heat  $Q$  entering the system. Apply your results to find

- (i)  $W$ ,
- (ii)  $\Delta U$ ,
- (iii)  $Q$

when the initial state is at volume  $21 \times 10^{-3} \text{ m}^3$  and temperature 290 K, and the final state is at  $22 \times 10^{-3} \text{ m}^3$ , 330 K, for a gas with  $\gamma = 1.4$ .

- 1.2. (i) Prove that in an adiabatic expansion of an ideal gas with constant heat capacities,  $pV^\gamma$  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.
- 1.3. An ideal gas at initial pressure  $p_1$  undergoes an adiabatic expansion from volume  $V_1$  to volume  $V_2$ . Assuming  $\gamma$  is constant, find the final pressure and show that the work done is

$$W = \frac{p_1 V_1}{\gamma - 1} \left( \left( \frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right).$$

- 1.4. An ideal gas is taken between the same initial and final states as in question 1.1, by an adiabatic expansion followed by heating at constant volume. Calculate (i) the work done on the gas and (ii) the heat absorbed.
- 1.5. 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  $L = 2L_0$ .

- 1.6. (L) A thermally insulated chamber contains some hot gas and a lump of metal. Initially the gas and the lump are 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.
  - (i) Will the final volume be the same in these two processes? (Give a clear answer and the reasoning).
  - (ii) Which process, (a) or (b), 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.]
- 1.7. (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.
- (i) Show that when the pressures are equalised, the temperature of the air in the chamber is  $\gamma T_0$ , 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.]
  - (ii) Consider the case of argon gas ( $\gamma = 5/3$ ) at  $50^\circ\text{C}$  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)

- 1.8. 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  $W > 0$  (e.g. to raise a load or charge a battery) while the system returns to its starting state. During any given heat transfer, the temperature stays constant. The energy associated with friction and the like is given by  $\epsilon \ll W$ ; in the following please answer for the case where  $\epsilon$  is entirely negligible, such that an equals sign means ‘equal up to small amounts of order  $\epsilon$ ’.
- (i) Kelvin’s statement of the Second Law of thermodynamics concerns the work that can be done by using heat energy. Does it assert the constraint  $W < Q$  in this scenario?
  - (ii) Is it possible to have  $W = Q$  (neglecting friction as explained above)?
  - (iii) Is it possible to realise the case  $Q_2 = 0$ , and thus  $W = Q_1$  (for  $Q_1 > 0$ )?
  - (iv) If  $W > 0$  then what can be deduced about the heat exchange processes?

- 1.9. 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.
- 1.10. 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

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

- 1.11. 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, find the thermal efficiency  $W/Q_{\text{in}}$ . [Hint: the algebra is easier here if you focus on heat in the first instance.]
- 1.12. A mug of tea has been left to cool from  $90^\circ\text{C}$  to  $18^\circ\text{C}$ . If there is  $0.2\text{ kg}$  of tea in the mug, and the tea has specific heat capacity  $4200\text{ J K}^{-1}\text{ kg}^{-1}$ , find the entropy change of the tea. Comment on the sign of the result.

- 1.13. Consider the inequality

$$dS \geq \frac{\delta Q}{T}.$$

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

- 1.14. Calculate the changes in entropy of the universe as a result of the following processes:
- (a) A copper block of mass  $400\text{ g}$  and heat capacity  $150\text{ J K}^{-1}$  at  $100^\circ\text{C}$  is placed in a lake at  $10^\circ\text{C}$
  - (b) The same block, now at  $10^\circ\text{C}$ , is dropped from a height  $100\text{ m}$  into the lake.
  - (c) Two similar blocks at  $100^\circ\text{C}$  and  $10^\circ\text{C}$  are joined together. [Hint: first find the final temperature, then reuse previous calculations]
- 1.15. Calculate the changes in entropy of the universe as a result of the following processes:
- (a) A capacitor of capacitance  $1\text{ }\mu\text{F}$  is connected to a battery of e.m.f.  $100\text{ V}$  at  $0^\circ\text{C}$ . [To answer this you must think carefully about what happens when a capacitor is charged from a battery.]
  - (b) The same capacitor after being charged to  $100\text{ V}$  is discharged through a resistor at  $0^\circ\text{C}$ .
  - (c) One mole of gas at  $0^\circ\text{C}$  is expanded reversibly and isothermally to twice its initial volume.
  - (d) One mole of gas at  $0^\circ\text{C}$  is expanded reversibly and adiabatically to twice its initial volume.
- 1.16. 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  $T_1$ . On the other side there are  $4$  moles of gas at temperature  $T_2$ . The initial conditions are  $T_1 = 500\text{ K}$  and  $T_2 = 200\text{ K}$ . The molar heat capacity at constant volume is  $C_{V,m} = (3/2)R$ .
- (i) If the partition is made thermally conducting, find the final temperature throughout the system when equilibrium is attained.

- (ii) Find the net change in entropy of the complete system in this case.
- (iii) 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

$$T_1 + 2T_2 = 900 \text{ kelvin}$$

and find an expression for the net change in entropy  $\Delta S$  as a function of  $T_1$ .

- (iv) Plot  $\Delta S$  on a graph as a function of  $T_1$ , 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

- 2.1. The specific heat capacity of water is 4200 J/K per kg, and may be taken as constant for the purposes of this question.

1 kg of water is warmed from 20°C to 100°C by each of the following processes:

- (i) by placing it in contact with a reservoir at 100°C,
- (ii) 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,
- (iii) by operating a reversible heat engine between it and the reservoir at 100°C.

For each case (i), (ii), (iii), find the entropy changes of the water, the reservoirs, and the universe. [Your answer will consist of a table of 9 values; please supply them in the order

- (i) water, reservoir, universe
- (ii) water, reservoir, universe
- (iii) water, reservoir, universe.]

- 2.2. 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

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

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

- 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<sup>3</sup>. What is the maximum height through which the crane can raise a 10000 kg load by burning 0.1 litre of petrol?
- 2.4. 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  $(p_1, V_1)$ .
- (a) Sketch the cycle on a  $pV$  diagram.
  - (b) Find the efficiency  $\eta$  in terms of the adiabatic index  $\gamma$  and the two ratios  $r \equiv V_1/V_2$  and  $x \equiv V_3/V_2$ , if the working fluid is modelled as an ideal gas of constant  $\gamma$ .
  - (c) Evaluate  $\eta$  for the values  $r = 15$ ,  $x = 3$ ,  $\gamma = 1.4$ .

### 2.2 Section B. Potentials and Maxwell relations

(12.1, 13.2–13.5, 13.15)

- 2.5. 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  $\mu$  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  $\alpha$  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  $n = n_0 \exp(-\alpha r^2/k_B T)$ .

- 2.6. A closed simple compressible system has work  $W$  done on it in a reversible process without heat exchange. (a) what is the change  $\Delta U$  in the internal energy? (b) Is it possible to tell, from the given information, the change in the Helmholtz function, enthalpy, and Gibbs function? (c) Suppose the work were done in conditions of constant temperature. Now what can you say about  $U, F, H, G$ ?
- 2.7. Derive all the Maxwell relations.
- 2.8. Sketch an isotherm and an adiabat passing through a given point  $p, V$  on the indicator diagram for a gas. Which is steeper? 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?
- 2.9. 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?
- 2.10. A piece of rubber of length  $L$  is subject to work by hydrostatic pressure and a tensional force  $f$ .  
 (a) Construct an expression for  $dU$ .  
 (b) Generate the potentials which have as proper variables  $(S, V, f)$  and  $(S, p, f)$   
 (c) 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)

- 2.11. Show that, for an elastic rod under tension  $f$ ,

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

where  $C_L$  is the heat capacity at constant length.

- 2.12. 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.  $2.58 \times 10^{-4}$  J/K]

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

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

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

$$\frac{T_f - T_c}{T_i - T_c} \simeq \frac{B_0}{B}. \quad (3)$$

To this end, consider the magnetic Helmholtz function  $F = U - ST$ . We have  $dF = -SdT - m dB$  and it is useful to consider  $F(T, B)$ . This can be written

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

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).

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

The next set is numbered 5; the sets numbered 3 and 4 are concerned with kinetic theory and are not included here.

## 5 Problem set 5. Fluids, flow process; radiation; stability; phase change

*non-ideal gas, flow process; stability and free energy; thermal radiation; first order phase change* (chapter 15, 16, 17, 18, 19, 20, 22)

$$\text{van der Waals' equation} \quad \left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT. \quad (4)$$

$$\text{Dieterici's equation} \quad p(V_m - b)e^{a/(RTV_m)} = RT. \quad (5)$$

$$\text{Virial expansion} \quad pV_m = RT\left(1 + \frac{B_2}{V_m} + \frac{B_3}{V_m^2} + \frac{B_4}{V_m^3} + \dots\right) \quad (6)$$

### 5.1 Section A. Real gas; Joule-Kelvin process

(15.1–15.3, 16.2, 16.3, 16.10)

5.1. Show that for a mole of van der Waals gas,

$$\left.\frac{\partial C_V}{\partial V}\right|_T = 0, \quad C_p - C_V = \frac{R}{1 - 2a(V - b)^2/(RTV^3)}.$$

[You may take as a starting point any formula which applies generally to any simple compressible system.]

5.2. The van der Waals equation is a cubic equation in  $V$ , having either three real roots or just one real root at any given  $p, T$ . For  $T < T_c$  and  $p < p_c$  there are three real roots. As  $T$  increases, these roots approach one another and merge at  $T = T_c$ . Therefore at the critical point the equation of state must take the form  $(V - V_c)^3 = 0$ . Use this to find the critical parameters in terms of  $a$  and  $b$ , by expanding the bracket and comparing with the van der Waals equation. (This method offers a convenient alternative to examining derivatives of the equation of state.)

5.3. (i) Starting from fundamental principles, obtain

$$\left.\frac{\partial T}{\partial V}\right|_U = -\frac{1}{C_V} \left(T \left.\frac{\partial p}{\partial T}\right|_V - p\right) \quad (7)$$

$$\left.\frac{\partial T}{\partial p}\right|_H = \frac{1}{C_p} \left(T \left.\frac{\partial V}{\partial T}\right|_p - V\right) \quad (8)$$

In each case also identify the type of process for which the quantity is relevant.

(ii) Verify that for an ideal gas  $\left.\frac{\partial T}{\partial V}\right|_U = 0$  and  $\left.\frac{\partial T}{\partial p}\right|_H = 0$ .

- 5.4. (L) A gas obeys the equation  $p(V-b) = RT$  and has  $C_V$  independent of temperature. Show that (a) the internal energy is a function of temperature only, (b) the ratio  $\gamma = C_p/C_V$  is independent of temperature and pressure, (c) the equation of an adiabatic change has the form  $p(V-b)^\gamma = \text{constant}$ .
- 5.5. (L) At modest pressures the equation of state of a gas can be written as  $pV = RT + Bp$  where  $B$  is a function of  $T$  only.
- (a) Find an expression for the Joule-Kelvin inversion temperature in terms of  $B$  and  $dB/dT$ .
- (b) For Helium gas between 5 K and 60 K,  $B$  can be represented as  $B = m - (n/T)$  where  $m = 15.3 \times 10^{-6} \text{ m}^3 \text{ mole}^{-1}$  and  $n = 352 \times 10^{-6} \text{ m}^3 \text{ K mole}^{-1}$ . From this information, estimate the inversion temperature for helium. For an expansion starting below the inversion temperature, comment on the efficiency of the process (i.e. cooling per unit pressure change) as the temperature falls.
- (c) In a helium liquifier, compressed helium gas at 14 K is fed to the expansion valve, where a fraction  $x$  liquifies and the remaining fraction  $(1-x)$  is rejected as gas at 14 K and atmospheric pressure. If the specific enthalpy of helium gas at 14 K is given by

$$h = a + b(p - p_0)^2$$

where  $a = 71.5 \text{ kJ kg}^{-1}$ ,  $b = 1.3 \times 10^{-12} \text{ kJ kg}^{-1} \text{ Pa}^{-2}$  and  $p_0 = 3.34 \text{ MPa}$  ( $= 33.4 \text{ atm}$ ), and the specific enthalpy of liquid helium at atmospheric pressure is  $10 \text{ kJ kg}^{-1}$ , determine what input pressure will allow  $x$  to achieve a maximum value, and show that this maximum value is approximately 0.18.

## 5.2 Section B. Thermal radiation

(19.2, 19.4, 20.5, 20.6)

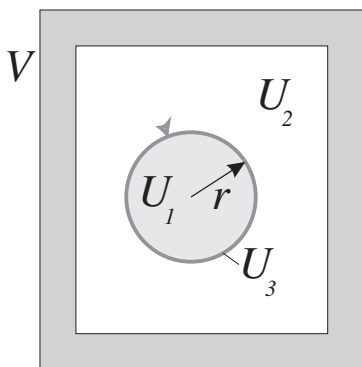
- 5.6. Bearing in mind that glass is a good absorber of infrared radiation, sketch on the same, labelled graph:
- (a) the spectral emissive power of a bathroom mirror at room temperature, as a function of wavelength, in the wavelength range 400 nm to 100  $\mu\text{m}$ .
- (b) the spectral energy density of radiation incident on a detector placed close to the mirror, when the mirror (still at room temperature) is used to reflect sunlight onto the detector.
- 5.7. State and prove Kirchoff's law.
- 5.8. Cavity radiation has an energy density  $u$  which depends on temperature alone:  $u = u(T)$ . Using this and  $p = u/3$ , derive the equation of state  $p = aT^4$  where  $a$  is a constant.
- 5.9. You are given that the flux of thermal radiation from a black body is  $\sigma T^4$  where  $\sigma \simeq 5.670373 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$  (the Stefan-Boltzmann constant), and the pressure of cavity radiation is given by  $p \simeq 0.9nk_B T$ , where  $n = \int_0^\infty \rho(\omega)/(\hbar\omega) d\omega$ . ( $n$  has dimensions of number density and may be called the number density of photons).

How does  $n$  depend on  $T$ ? Find the temperature at which the number of photons in a chamber of volume 25 litres is equal to one mole. [*Ans.*  $1.06 \times 10^6$  K]

- 5.10. A small spherical meteor is at a distance from the Sun of 100 Sun radii. It rotates rapidly about its centre of mass. It is black in the infra-red region and has reflectivity 0.75 for visible light. Estimate its temperature, given that the surface temperature of the Sun is 6000 K. [*Ans.* 300 K.]

### 5.3 Section C. Stability; phase change

(17.6; 22.1, 22.3, 22.4)



A composite system in a chamber of fixed volume  $V$ . The system comprises a rubber balloon and two fluids: one inside and one outside the balloon.

- 5.11. (L) Consider the example system shown in the figure. The radius  $r$  of the balloon is unconstrained. Model the two fluids as ideal gases, and suppose the rubber has a constant surface tension  $\sigma$  and heat capacity  $C$  (this model of rubber is rather simplistic; the question serves to establish a concept: the aim is to link maximum entropy to mechanical equilibrium).

(i) Show that changes in the total entropy and energy are governed by

$$\begin{aligned} dS &= (CdT + C_1dT + p_1dV_1 + C_2dT + p_2dV_2) / T, \\ dU &= dU_1 + dU_2 + CdT + \sigma dA \end{aligned}$$

where  $C_1, C_2$  are the constant-volume heat capacities of the two gases,  $T$  is the temperature,  $A = 4\pi r^2$ ,  $V_1 = (4/3)\pi r^3$  and  $V_2 = V - V_1$ . Hence show that the maximum entropy occurs when

$$(p_1 - p_2)dV_1 = \sigma dA$$

where  $p_1, p_2$  are the pressures in the fluids.

(ii) Comment on the physical interpretation of what has been shown in part (i).

(iii) Now suppose the chamber is in thermal contact with a reservoir at fixed temperature. Show that, in an isothermal change, the free energy is governed by

$$dF = \sigma dA - p_1dV_1 - p_2dV_2$$

and hence obtain the equilibrium condition again.

- 5.12. Starting from the fundamental relation for a closed simple mechanical system (i.e.  $dU = TdS - pdV$ ), prove that for a two-component system,

$$dG = -SdT + Vdp + \mu_1 dN_1 + \mu_2 dN_2, \quad (9)$$

where  $N_1, N_2$  and  $\mu_1, \mu_2$  are the particle numbers and chemical potentials in the two components. [You may quote the Euler relation and the Gibbs-Duhem relation without proof.]

- 5.13. (i) Prove that two substances in phase equilibrium must have the same chemical potential. (ii) Hence, or otherwise, derive the Clausius-Clapeyron equation.
- 5.14. The gradient of the melting line of water on a  $p$ - $T$  diagram close to  $0^\circ \text{C}$  is  $-1.4 \times 10^7 \text{ Pa/K}$ . At  $0^\circ \text{C}$ , the specific volume of water is  $1.00 \times 10^{-3} \text{ m}^3\text{kg}^{-1}$  and of ice is  $1.09 \times 10^{-3} \text{ m}^3\text{kg}^{-1}$ . Using this information, deduce the latent heat of fusion of ice.
- 5.15. (L) Using the Clausius-Clapeyron equation and simple physical models, estimate the temperature at which water boils at the top of mount Everest (altitude 29000 feet). (The air pressure is about 0.5 atmosphere at a height of 18000 feet.)
- 5.16. A pool of liquid in equilibrium with its vapour is converted totally into vapour in conditions of fixed temperature and pressure. What happens to the internal energy, the enthalpy, the Helmholtz function and the Gibbs free energy?

## 6 Problem set 6.

(optional) *the third law, the greenhouse effect, osmosis, nucleation in phase change*

Section A.

- 6.1. A proposal delivered to the Patent Office describes a heat engine which will achieve high efficiency by operating with the low temperature reservoir at a temperature close to absolute zero. Is such a heat engine physically possible? Could it make a useful contribution to the generation of electrical power? If not then why not?
- 6.2. Modelling the atmosphere as a layer with absorptivity  $\alpha$  in the infra-red, and transmissivity  $1 - \alpha$ , with the surface of the Earth modelled as black, show that the surface temperature of Earth is given by

$$T(\epsilon) = T(0)(1 - \epsilon/2)^{-1/4}$$

where  $\epsilon = \alpha$  is the emissivity of the atmosphere in the infra-red, and  $T(0)$  is the value in the absence of an atmosphere. If  $T(0) = 255\text{ K}$  and  $\epsilon = 0.78$ , what change in  $\epsilon$  will change  $T$  by one degree celcius?

- 6.3. If one places a mixture of salt and fresh-water ice in a bag with surroundings at STP, the temperature in the bag will slowly fall, reaching  $-10$  or  $-20$  degrees Celcius. Why is this? In particular, why does it not contravene the Second Law of thermodynamics? (treat the Clausius statement or the entropy statement or both).
- 6.4. Is it possible to cause a sample of liquid to evaporate by an isentropic process? If so, then is it an expansion or a contraction? Or could it be either, depending on circumstances?
- 6.5. During a hurricane, each hour 90 million tons of water are evaporated at the ocean surface at a temperature around  $27^\circ\text{ C}$ , and subsequently condensed at high altitude at temperature  $-53^\circ\text{ C}$ .
- (i) How much energy is thus absorbed and released per hour?
  - (ii) At the condensation stage, some of the energy goes to heat, and some to the wind energy. What is the smallest proportion that can go to heat?
  - (iii) Hence obtain a rough estimate of the power of the hurricane winds.
- 6.6. Describe how osmotic pressure arises.
- 6.7. (L) (i) Consider a spherical drop of liquid surrounded by a vapour, both at temperature  $T$ . Show that the Gibbs function of the entire system is given by

$$G = G_v(T, p) + G_l(T, p_l) + (p - p_l)V_l + 4\pi r^2\sigma$$

where subscripts  $v$  and  $l$  refer to vapour and liquid respectively,  $r$  is the radius of the drop,  $\sigma$  is its surface tension, and  $p = p_v$ .

(ii) Treating the liquid as incompressible, obtain

$$G = G_v(T, p) + G_l(T, p) + 4\pi r^2\sigma.$$



(iii) Hence obtain

$$G = N\mu_v - \frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \sigma$$

where  $\Delta g = n_l(\mu_v - \mu_l)$  and  $\mu_v, \mu_l$  are the values of the chemical potentials at  $(T, p)$ .

(iv) In the above we have not assumed equilibrium between the phases, only that the liquid and the vapour separately have well-defined temperature and pressure. If we now assume phase equilibrium, the condition is not  $\Delta g = 0$ . Why not? What is the correct condition on these chemical potentials at phase equilibrium?

(v) Sketch a graph of  $G(r)$  and briefly describe the role of *condensation nuclei* in the condensation of a vapour.

(v) Obtain Kelvin's formula for the pressure in a vapour in phase equilibrium with liquid droplets of the critical radius.

- 6.8. The Maxwell construction is a method to locate the isotherms in a mixed-phase region of an indicator diagram ( $pV$  diagram), starting from a formula for the equation of state, such as the van der Waal's formula. (i) State this construction, in the form of a statement about areas on the diagram. (ii) By considering the Helmholtz function, or otherwise, derive the Maxwell construction.