Thermodynamics

2nd year physics

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We will base our tutorials around **Adkins**, *Equilibrium Thermodynamics*, 2nd ed (McGraw-Hill). Zemansky, *Heat and Thermodynamics* is good for experimental methods. Read also the relevant chapter in Feynman Lectures vol 1 for more physical insight.

1st tutorial: The First Law

Read Adkins chapters 1 to 3.

Terminology

Function of state. It is important to be clear in your mind about what we mean by a *function of state*. Most physical quantities we tend to use in physics are functions of state, for example mass, volume, charge, pressure, electric field, temperature, entropy. A formal definition is

> A function of state is a physical quantity whose change, when a system passes between any given pair of states, is independent of the path taken.

(the 'path' is the set of intermediate states that the system passes through during the change). The idea is that if a physical quantity has this property, then its value *depends only on the state of the system, not on how the system got into that state*, so that is why we call it a 'function of state'. Heat and work are **not** functions of state, because they don't obey the formal definition above, and this is because they each describe an energy exchange *process*, not a physical *property*.

Some terminology concerning differentials. You will meet the terminology 'exact' and 'inexact' differential. The distinction is important, but I think this choice of terminology is not very good. It has become established however and now we are stuck with it. I prefer another terminology: 'proper' and 'improper'. The word 'inexact' is a bit misleading because it appears to suggest a lack of precision, but this is not what it is meant to mean. All it means is the following:

1. Any small quantity can be called a differential.
2. If the small quantity is a change in a *function of state*, then it is an exact differential. If is not a change in any function of state, then it is an inexact differential. An inexact (or improper) differential refers to a small *amount* of something, but it is not a small *change* in any function of state.

Problems

The problems consist of some which are brief, intended to illustrate a concept, and others which are longer and require careful argument. To guide you on the type of answer required, the quick ones are marked '$\triangleright$'. It you don't see the '$\triangleright$' mark, you need to make sure you answer carefully, or you will get muddled later on.

1▷ **exact/inexact differential**. (a) Consider the following small quantity: $y^2dx + xydy$. 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 $y^2dx + 2xydy$. Find (by trial and error or any other method) a function f of which this is the total differential.

2▷ **Function of state**. Our physical system will be a lake of water. Some of the properties of the lake are the depth of the water, the temperature, the salinity, etc. Suppose that water can enter the lake by two routes: either by flowing down a river into the lake, or by falling as rain. Suppose it can leave the lake by two routes: evaporation, or flowing out into the outlet stream. Suppose further that there is no difference between rain water and river water: once the water is in the lake, it is not possible to tell where it came from.

Which of the following quantities are functions of state?:

1. The depth of the water
2. The total volume of water in the lake
3. The amount of rain water in the lake
4. The temperature of the water
5. The amount of river water in the lake

3. **Quasistatic** *et al.* Draw a Venn diagram to show the relationships between the following concepts: reversible, irreversible, quasistatic, isentropic.
Your diagram should have four regions on it. Give an example process for each region.
Where does the process of slowly squeezing toothpaste out of a tube lie on the diagram?

N.B. the word 'adiabatic' has two meanings in physics: in one convention it means merely no heat transfer (same as 'adiathermal') in the other it means a process which is both reversible and involves no heat transfer (same as 'isentropic'); I will adopt the second convention.

4. Define carefully what we mean by a **reversible** process in thermodynamics. (It is better to do this without using the word 'hysteresis'. However, if you want to invoke that concept, you may, but then you must also explain what it means.)

Thermometry

5▷ A constant volume gas thermometer contains a gas whose equation of state is

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

and another, of identical construction, contains a different gas which obeys the ideal gas law $pV = RT$. The thermometers are calibrated at the ice and steam points. Show that they will give identical readings for a temperature. (Assume that the thermometers are constructed so that all the gas is at the temperature being measured).

6. 1 mole of a certain gas at low pressure obeys the equation given in the previous question, with $a = 0.08$ Jm^3, $b = 3 \times 10^{-5}$ m^3, and the other symbols have their usual meanings.

(a) Find the equation of state for n moles of this gas. [Hint: don't guess—in the past, all students who thought the answer could be written down without thought have got it wrong. Rather, consider a system of n moles of the gas, having pressure p_n, V_n, T_n. Then you are looking for the equation relating T_n to p_n and V_n. You can get it by picturing the n moles as if they consisted of n 'lumps' of 1 mole each sitting next to each other, in conditions where each lump obeys the equation above.]
(b) A constant volume gas thermometer of volume 10^{-3} m^3 contains 0.05 mole of this gas. What is the pressure in the thermometer at 95°C? Compare this with the pressure of the same amount of ideal gas at the same temperature and volume.

Partial maths

7. w is a function of three variables x, y and z. Prove that

$$\text{(a)} \qquad \left(\frac{\partial w}{\partial x}\right)_{y,z} = \frac{1}{\left(\frac{\partial x}{\partial w}\right)_{y,z}},$$

$$\text{(b)} \qquad \left(\frac{\partial w}{\partial x}\right)_{y,z}\left(\frac{\partial x}{\partial z}\right)_{w,y}\left(\frac{\partial z}{\partial w}\right)_{x,y} = -1.$$

These are the reciprocal and reciprocity relations for functions of three variables.

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

$$\left(\frac{\partial x}{\partial y}\right)_C = \frac{\left(\frac{\partial \ln B}{\partial y}\right)_x - \left(\frac{\partial \ln A}{\partial y}\right)_x}{\left(\frac{\partial \ln A}{\partial x}\right)_y - \left(\frac{\partial \ln B}{\partial x}\right)_y}$$

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

Work

9▷ Derive the formula $đW = -pdV$, for work done by reversible compression of a gas, by starting from classical mechanics. How is the formula modified if there is friction?

10. [Comment for Physics and Philosophy students: you don't need anything beyond school electromagnetism to answer this problem. Everything is defined in the question.] In some circumstances the work required to magnetise a piece of material is given by

$$đW = \mathbf{B} \cdot d\mathbf{m}$$

where $\mathbf{B}$ is the magnetic field which would have been present in the absence of the material, and $\mathbf{m}$ is the total magnetic moment of the lump of material[1]. Assume the material and the field are uniform, then the dipole moment per unit volume (called magnetisation) is $\mathbf{M} = \mathbf{m}/V$. At high temperatures the behaviour is well approximated by Curie's Law, $\chi_H = a/T$, where $a = 0.19$ K, in which the susceptibility χ_H is defined by $\mathbf{M} = \chi_H \mathbf{H}$ and $\mathbf{H}$ is defined through the formula $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$.

(a) Use the above information to find the relationship between $\mathbf{B}$, $\mathbf{M}$ and χ.
(b) Hence obtain the equation of state (formula relating T to $\mathbf{B}$ and $\mathbf{m}$) for a lump of material

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[1] N.B. a careful argument is needed to derive this formula, because another formula $đW = -\mathbf{m} \cdot d\mathbf{B}$ is valid in another case, depending on how the system is defined.

of given volume V.
(d) Calculate the work done on a specimen of volume 10^{-5} m^3 by placing it in a solenoid and increasing the magnetic field from zero to 1 Tesla at 4.2 K.

Thermodynamic reasoning

11. Use the first law 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. Hint: consider a path, consisting of two straight line portions, between two points on an isothermal.

12. Gas is contained at high pressure in a cylinder insulated on the outside. The volume of the cylinder can be varied by moving an insulated frictionless piston. The heat capacities of cylinder and gas are comparable. Sketch on one diagram the pressure-volume relations for the gas,

(a) if the pressure is reduced to atmospheric slowly enough for the temperature of the cylinder to be equal to that of the gas at all stages;
(b) if the pressure is reduced to atmospheric fast enough (but still quasistatically) for the cylinder not to cool at first; the pressure is then maintained at atmospheric until the cylinder and gas attain the same temperature.

Use the first law to explain (convincingly!) why the temperature reached in process (a) **must** be lower than the final temperature reached in process (b).

13. Write down the first law and hence express c_V and c_p in terms of a derivative of U and other quantities. For an ideal gas, U depends only on temperature, and this means that $\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V = dU/dT$ (we will prove this later. N.B. it is not true in general, only for an ideal gas). Using this and the equation of state, find $c_p - c_V$ for an ideal gas.

14. The first law of thermodynamics is often quoted in the form "Heat is a form of energy (as is work) and energy is conserved." This is a perfectly respectable statement, and is the one given by Feynman. However, Adkins in section 3.2 gives a somewhat different statement. Discuss carefully the relationship between these two ways of quoting the first law.

2nd tutorial: The Second Law and entropy

Read Adkins chapters 4,5 and Feynman vol. 1 chapter 44

Problems

In the following, when you need to use the specific heat capacity of water, use the value 4200 J K^{-1} kg^{-1} and assume it does not depend on temperature.
(Think about whether this is at constant pressure or constant volume, or whether the distinction makes much difference for water).
For the molar gas constant, use $R = 8.3$ J K^{-1} $mole^{-1}$.
For Celcius to Kelvin conversions use 0 °C = 273 K.

Basic ideas

1▷ Does the *Carnot cycle* refer only to an ideal gas, or is there a Carnot cycle for any system?

2▷ Let us refer to the standard diagram showing heat flow and work for a heat engine operating between two thermal reservoirs as an *energy flow* diagram. Draw the simplest energy flow diagram you can think of which shows a heat engine which is impossible by the Kelvin statement of the 2nd law, and another which is impossible by the Clausius statement.

3▷ [standard proofs but make sure you understand and can state them clearly] Prove that the Clausius statement of the 2nd law is true *if and only if* the Kelvin statement is true.

The following comments on logic may help. For the 'if' part you must prove that $K \Rightarrow C$, for the 'only if' part you must prove that not-K $\Rightarrow$ not-C. These are two separate jobs because while the statement 'there are blue cows' logically implies 'there are cows', the second does not imply the former. To prove that $K \Rightarrow C$ it is sufficient to prove that not-C $\Rightarrow$ not-K (think about it!).

4▷ In each cycle, a heat engine absorbs heat Q_1 from a thermal reservoir at temperature T_1 and delivers heat Q_2 to a reservoir at a lower temperature T_2, and produces work W.
(a) How is the efficiency of the heat engine defined?
(b) Write down the relationship between the heats and the temperatures for the case of a reversible engine. How would your expression change for a non-reversible engine?
(c) What is the maximum possible efficiency of a heat engine operating between these two reservoirs?

5. Consider the following discussion of Newton's 2nd law, and then answer the question on temperature at the end.

The usual statement of Newton's 2nd law has a weakness in that it talks about "force" without defining what is meant. We can avoid this weakness as follows. Define "force" to mean that which causes the momentum of a body to change (but we say nothing yet about the size of the force). Consider various physical systems which can supply a force, e.g. an elastic band (note, I don't assume Hooke's law) or a rocket motor. We argue that when a given force-providing system is in the same conditions then it must provide the same force, no matter what object it may be pushing or pulling. For example, a given elastic band of given length and temperature pulls by a given amount. (If this were not so, we could find physical situations where it would lead to impossible behaviour such as a self-accelerating closed system). Now imagine we have two bodies whose 'quantity of matter' is different, and we would like to have a sensible definition of 'quantity of matter'. We proceed as follows. We attach the force-providing system (elastic band) to body

1, and maintain the force-providing system in fixed conditions (by pulling on the other end of the band to keep its length constant). The body will accelerate. We measure its acceleration, a_1 (this can be measured without ambiguity because it only involves distance and time). Now attach the force-providing system to the other body, 2, and repeat the experiment, making sure the force-providing system is in the same conditions in the two experiments. Thus obtain acceleration a_2. Now repeat the experiments with a number of quite different force-providing systems (e.g. rocket motor, attracting capacitor plates, surface tension, etc.). It is found that in such experiments, the ratio a_1/a_2 is independent of the force-providing system and of the speeds involved (as long as no friction or viscosity is present). We therefore can take it to be a property of the bodies 1 and 2 alone. We then arrive at a definition of inertial mass: we define inertial mass M to be such that the inertial masses of two bodies 1 and 2 are in the ratio of their accelerations when the same force is applied to each:

$$\frac{M_1}{M_2} = \frac{a_2}{a_1}.$$

This allows all masses to be related to some given mass which can be taken as the unit of mass. The choice of unit mass is arbitrary.

How is absolute thermodynamic temperature defined?

6. Prove Clausius's theorem, and hence that entropy is a function of state.

1st Law, heat and work

7. One mole of an ideal gas with $\gamma = c_p/c_V = 1.4$ is taken from its initial state of 290 K and 21×10^{-3} m^3 to a final state of 330 K and 22×10^{-3} m^3. This transformation is carried out quasistatically along a straight line on a $p - V$ diagram. Calculate the change in internal energy, the work done and the heat absorbed by the system.

8. Write down the formula relating p and V during an adiabatic expansion of an ideal gas whose heat capacities are independent of temperature. A ideal gas is taken between the same initial and final states as in the previous question, by an adiabatic expansion followed by heating at constant volume. Calculate the work done and heat absorbed.

9. A machine compresses 10 mole/minute of helium, assumed to behave as an ideal gas, from 1 to 10^6 Pa pressure. What rate of flow of cooling water, initially at 290 K, is needed if the compression is to be made isothermal at 300 K?

Heat engines

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

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

11. A heat engine operates between a tank containing 10^3 m^3 of water and a river at a constant temperature of 10°C. If the temperature of the tank is initially 100°C, what is the maximum amount of work which the heat engine can perform? Answer the problem algebraically before you substitute in the numbers [You need to treat a small amount of heat dQ and then perform an integration]. Show that your result can be expressed in the form $W = \Delta U - T_0\Delta S$, and interpret the symbols physically.

12. 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 $T_f^2 = T_1 T_2$.

13. 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 $\gamma = c_p/c_V$.)

14. (optional—only attempt it when you have completed the rest). The air-standard Otto cycle gives a simplified account of the events occuring in a petrol engine. The cycle is described in the text books. Show that the efficiency is given by $1 - r^{1-\gamma}$ where r is the compression ratio.

Entropy

15. Give a careful statement of the relationship between entropy and heat. Is entropy extensive or intensive? What dimensions does it have? Under what circumstances can it make sense to think of entropy 'flowing' from one place to another?

16. 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 185.7 J K^{-1}. Comment on the sign of this result.

17. 1 kg of water is warmed from 20°C to 100°C (a) by placing it in contact with a large 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).

18. Calculate the change in entropy of 1 kg of water when it is heated from 15 to 100°C and completely vaporized, all at 1 atm pressure.
Does the change in entropy imply any irreversibility in the process?
(The latent heat of vaporization of water at a pressure of 1 atm is 2.3×10^6 J kg^{-1}.)

19. Calculate the changes in entropy of the universe as a result of the following processes:
(a) A copper block of mass 400 g and thermal 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: 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 reuse previous calculations)

(d) A capacitor of capacitance 1 μF 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 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.

3rd tutorial: thermodynamic potentials and Joule-Kelvin process

Read Adkins chapter 7,8,9 and recall the final sections of chapter 3. (we will skip chapter 6 but you should have a skim read of it for your general knowledge). The parts of chapter 8 which will be considered in the next tutorial (i.e. adiabatic demagnetisation and radiation) can be omitted at this stage, and we will not be considering thermoelectric effects (end of chapter 9). For further information on liquification of gases, you may like to consult Zemansky.

Problems

Basic concepts

1▷ (a) Using the first law $dU = TdS - pdV$ 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 dU, dH, dF, dG in terms of T, S, p, V and their derivatives.
(b) Derive all the Maxwell relations.

2▷ (a) 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 than in an adiabatic one. Where has the energy for this extra work come from?
(b) Why is the Helmholtz function F sometimes called 'free energy'?
(c) Give an example of a physical process which can take place at constant pressure and temperature. What thermodynamic potential is unchanged in such a process?
(d) By modifying part (c) or otherwise, give an example of an adiathermal reversible physical process in which a volume change can take place at constant pressure. What thermodynamic potential is unchanged in such a process?
(e) In a free expansion (also called Joule expansion), we know U does not change, and no work is done. However, the entropy must increase because the process is irreversible. Are these statements compatible with the 1st law $dU = TdS - pdV$? How is the work done related to pdV in general?

3. 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)

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

Energy, heat capacity and equation of state

4. (a) Show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

N.B. This is a remarkable result which we could not know from the 1st law alone. It is completely general.
(b) Show that, if only the equation of state of a system is known, then it is possible to calculate the work done in an isothermal process, but not in an adiabatic one.
(c) By considering U as a function of T and V, or otherwise, show that knowledge of the equation of state and C_V (the heat capacity at constant volume) is sufficient to enable the internal energy

change ΔU to be calculated for any process. Write down the integral expressing ΔU in terms of the other information.
(d) Hence show how the work done in an adiabatic process could be obtained.

Expansions: basic methods

6. Derive the following general relations

$$
\begin{aligned}
&\text{(a)} \quad \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right)\\
&\text{(b)} \quad \left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{C_V}T\left(\frac{\partial p}{\partial T}\right)_V\\
&\text{(c)} \quad \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left(T\left(\frac{\partial V}{\partial T}\right)_p - V\right)
\end{aligned}
$$

In each case the quantity of the left hand side is the appropriate thing to consider for a named type of expansion. Identify the type of expansion, by giving the names of the people it is named after, if any, and briefly describing what takes place.

7. Using the relations derived in question 6, 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 $pV^\gamma =$ constant along an isentrope.

8. 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 $p(V-b)^\gamma =$ constant.

Joule-Kelvin effect

9▷. (a) Locate the Joule-Kelvin effect on your Venn diagram from 1st problem sheet, question 3. (b) Prove that enthalpy is constant in a Joule-Kelvin expansion.

10. Describe a practical apparatus for the liquification of ^{4}He using the Joule-Kelvin effect. (For ^{4}He the normal boiling point is near 4 K and the inversion temperature for the Joule-Kelvin effect is about 50 K).

11. At modest pressures the equation of state of a real gas can be written as $pV = RT + Bp$ where B is a function of T only. Find an expression for the Joule-Kelvin inversion temperature in terms of B and dB/dT.

For Helium gas between 5 K and 60 K, B can be represented as $B = m - (n/T)$ where $m = 15.3 \times 10^{-6}$ m^3 mole^{-1} and $n = 352 \times 10^{6}$ m^3 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.

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 $a = 71.5$ kJ kg^{-1}, $b = 1.3 \times 10^{-12}$ kJ kg^{-1}Pa^{-2} and $p_0 = 3.34$ MPa (= 33.4 atm), and the specific enthalpy of liquid helium at atmospheric pressure is 10 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.

12. Write down the equation of state of a general Van der Waals gas. Determine whether a Joule-Kelvin expansion produces heating or cooling:
(a) when the attractive force between the molecules is neglected, but the molecular volume is taken into account
(b) when the molecular volume is neglected, but the attractive force is taken into account
Give a brief physical explanation of these observations, bearing in mind that for an ideal gas there is no temperature change.

4th tutorial: thermal radiation, phase change, heat conduction

Read Adkins parts of chapter 8 you may have skipped before, and chapter 10 sections 10.1 to 10.5. Glance at the rest of chapter 10, so that you are aware of at least one example of a 2nd order phase transition.

Thermal radiation: basic ideas

The basic proofs here are easy to write down, but it is a lot harder to be clear in one's mind about what the proofs and the symbols really mean.

1▷ (a) Give the SI units for the following quantities: energy density u (that is, energy per unit volume), and spectral energy density ρ (that is, energy per unit volume per unit frequency range).
(b) Write down the expression relating u and ρ.
(c) If ρ is the energy density per unit frequency range, and η is the energy density per unit wavelength range, write down the expression relating ρ and η for electromagnetic radiation.
(d) Derive the relationship between energy density u and energy flux ϕ for a collimated beam of light. [Hint: consider the volume of light which passes across a given area in a given time]. (Energy flux is also called intensity, it is power per unit area.)
(e) Which of these properties, u, ρ or ϕ is a typical photo-detector, such as our eyes, directly sensitive to?

[N.B. some authors use $u(\nu)$ and $u(\lambda)$ for ρ and η, which is poor notation. Others use u_ν, and u_λ, which is acceptable.]

2▷ An otherwise empty enclosure has electromagnetic radiation inside it which is in thermal equilibrium with the walls of the enclosure. Give an argument to show that the energy per unit volume (u) of the radiation must depend only on the temperature, not on the shape or composition of the cavity walls.

3▷ Give an argument to show that the spectral energy density ρ of such cavity radiation must depend only on frequency and temperature.

4▷ A potter's kiln is loaded with various pots, of various colours and textures. The kiln has a well-sealed door so that the interior can reach a close approximation to thermal equilibrium, and is heated until the interior glows orange. A window in the wall is made small enough to allow an observer to look in without noticeably disturbing the conditions inside the cavity. Describe what will be seen through the window.

Radiation having the form of the radiation found inside a thermal cavity is called *thermal* radiation.

5▷ Prove that, in conditions of thermal equilibrium, any body which absorbs all the radiation incident on it must emit precisely thermal radiation, not some other kind. (This is why thermal radiation is also called *black body* radiation). It seems intuitively clear that the temperature of the radiation emitted should be the same as that of the body emitting it, but have you proved this as well? (If not, then do so).

6▷ Let the emissivity ϵ be defined as the ratio between the spectral emissive power e of a surface at given temperature, and the spectral emissive power of a black body at the same temperature. Prove that $\epsilon(\nu) = \alpha(\nu)$ where α is the absorptivity of the surface.

7. In the previous question you derived Kirchoff's law. However, to understand it properly we need to agree on what is meant by the concept of 'emissive power' of a surface. Bearing in mind that glass is a good absorber of infrared radiation, sketch on the same (clearly 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 μm.
(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.

8. A confused student puts forward the following argument. "Red paint appears red (under white light illumination), and this is to do with the fact that it absorbs other colours such as green and blue. Therefore, according to Kirchoff's law, it should be a good emitter of green and blue, and a relatively poor emitter of red. Therefore it should appear blue-green, and not red after all." This is a contradiction. Where did the student go wrong?

9. Describe one kind of electromagnetic radiation which you can think of which is *not* black body radiation, even approximately, and identify some features which distinguish it from black body radiation.

Phase change

10. Outline the conditions required for equilibrium between phases of a substance with respect to first-order phase transitions, and derive the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{L}{T(V^v - V^l)}$$

stating the physical meaning of the symbols. [N.B. Be careful: whereas Adkins gives a derivation, Blundell and Blundell do not: two of the steps they make are merely stated without justification. You need to justify whatever steps you write down.]

11. The gradient of the melting line of water on a p–T diagram close to 0° C is -1.4×10^7 Pa/K. At 0° C, the specific volume of water is 1.00×10^{-3} m^{3}kg^{-1} and of ice is 1.09×10^{-3} m^{3}kg^{-1}. Using this information, deduce the latent heat of fusion of ice.

12 (optional). Using the Clausius-Clapeyron equation show that, provided equilibrium between liquid and vapour is maintained, and assuming the specific heats of the two phases are constant, the latent heat of vapourisation L varies with temperature as follows:

$$\frac{dL}{dT} = \frac{L}{T} + c_p^v - c_p^l - \frac{L}{V^v - V^l}\left[\left(\frac{\partial V^v}{\partial T}\right)_p - \left(\frac{\partial V^l}{\partial T}\right)_p\right]$$

where V^v and V^l are volumes per mole of vapour and liquid respectively, and c_p^v, c_p^l are heat capacities per mole at constant pressure.
Hint (if you need it): use the idea introduced in problem 17.

13. (a) State the functional form for the variation with height of pressure in the atmosphere, at fixed temperature. [Look it up if you don't know it already].
(b) From the Clausius Clapeyron equation, roughly estimate the temperature at which water boils at the top of mount Everest (altitude 8854 m). [The air pressure is about 0.5 atmosphere at a height of 18 km, $L = 4.5 \times 10^4$ J mol^{-1}for water.]

14. 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 free energy and the Gibbs free energy?

Heat conduction and the diffusion equation

15. By considering conservation of energy in a situation of heat flow, derive the heat diffusion equation

$$\frac{\partial^2 T}{\partial z^2} = \frac{C}{K}\frac{\partial T}{\partial t}$$

for a 1-dimensional problem (or $\nabla^2 T = (C/K)\partial T/\partial t$ in 3 dimensions).

16. The temperature at the surface of a thick wall of specific heat capacity C and thermal conductivity K is given by $T_0 \sin \omega t$. Find an expression for the temperature at a distance z into the wall. Use this analysis to explain the value of a cellar for storing wine.

17. Blundell problem 7.1.