Thermodynamics

2nd year physics

some additional questions

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Attempt ALL the questions (Part A and Part B). (Some are quick.)

Some 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 a *proper* differential. If is not a change in any function of state, then it is an *improper* differential. An improper ($\equiv$ 'inexact') differential refers to a small *amount* of something, but it is not a small *change* in any function of state.

Part A: Basic ideas and the First Law

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$\triangleright$ **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.)

5. 1 mole of a certain gas at low pressure obeys the equation of state

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

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.]

6. This question requires careful reasoning, but it is only about conservation of energy.

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).

7. 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. Show how *heat* can be defined in a rigorous manner. [Hint: start by using the 1st law as given in Adkins.]

Part B: The Second Law and entropy

For Clausious' theorem, I recommend you consult **Adkins**, *Equilibrium Thermodynamics*, 2nd ed (McGraw-Hill).

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

The chapter in Feynman Lectures is useful for gaining more physical insight.

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. 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. IMPORTANT! Present and prove Clausius's theorem, and hence that entropy is a function of state.

7. 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, $(d/dx)(\ln f) = (1/f)df/dx$).