CHAPTER 1
INTRODUCTORY REMARKS

1.1 *Introduction*

Thermodynamics is a subject that has a wide variety of applications, including many in practical and engineering contexts. However, by choice, I shall be treating this subject from a very "academic" point of view, in which disembodied forces will compress ideal gases with frictionless pistons, seemingly far removed from the real engines of steel and gasoline which engineers must design. This approach may appeal to those with an academic bent – but is it likely to be useful to the aspiring engineer who lives and works in the real world? Need the practical engineer know and understand all this airy-fairy mumbo-jumbo? I would just argue this – that the "academic" approach deals with the *fundamental physical principles* upon which all practical applications must be built, and that an engineer above all others must thoroughly understand these principles. The fundamental principles do not cease to apply in the practical world!

I don't expect to get down to serious thermodynamics in the opening chapter. Instead I shall just discuss a few isolated, unrelated miscellaneous bits and pieces that I thought worth doing. Furthermore, anyone who opens a book on thermodynamics will see the symbol ∂ liberally sprinkled over almost every page, so I thought I'd write a short chapter – Chapter 2 - on partial derivatives. That will not be intended as a formal course in mathematics, but just a brief summary of the main properties of partial derivatives that you are likely to need. Thus I shan't get down to serious thermodynamics until Chapter 3.

1.2 *Caloric, Calories, Heat and Energy*

It has long been understood that heat is a form of energy. But this has not always been so, and indeed it was not generally accepted until the middle of the nineteenth century. Before then, heat was treated as though it were some sort of "imponderable (weightless) fluid" known as *caloric*, which could flow out of one body into another. It is true that as long ago as 1799 Humphrey Davy showed that ice could be melted merely by rubbing two pieces together without the need of any "caloric", and indeed this could not be explained by the "caloric" theory. Davy argued – quite correctly – that friction between two bodies must generate "a motion or vibration of the corpuscles of bodies", and that the observation of the melting of ice by rubbing alone showed that "we may reasonably conclude that this motion or vibration is heat". Likewise at about the same time Benjamin Thompson, Count Rumford, showed that the boring of cannon continuously produced heat in proportion to the amount of work done in the boring process, and the amount of heat that could be so produced was apparently inexhaustible. This again should have sounded the death knell of the caloric theory, and, like Davy, Rumford correctly suggested that heat is a form of motion.

In spite of this evidence and the arguments of Davy and Rumford, it wasn't until the middle of the nineteenth century that caloric theory finally died, and this was a result of the famous experiments of James Prescott Joule to determine the *mechanical equivalent of heat*.

There is some question as to whether the name should be pronounced "jool" (to rhyme with fool) or "jowl" (to rhyme with fowl). Joule was from a beer-brewing family in Manchester, in the North of England. In a north of England accent, "jowl" would be a preferred pronunciation, while "jool" would come more naturally in the south of England, although most modern Mancunians, like the rest of us, nowadays say "jool". The uncertainty in the pronunciation is an old one, and was used by the brewery (which no longer exists) in Joule's day as an advertising slogan for the beer. I am indebted to Dr Graham McDonald of the Joule Laboratory, Salford University, who found the actual advertising slogan for Joule's Ales:

> Do you pronounce it Joule's to rhyme with Schools,
> Joule's to rhyme with Bowls, or Joule's to rhyme with Scowls?
> Whatever you call it, by Joule's, or Joule's, or Joule's.
> It's GOOD!

In the nineteenth century (and continuing to today) the metric unit of heat was the *calorie* (the quantity of heat required to raise the temperature of a gram of water through one Celsius degree), and the imperial unit was the *British Thermal Unit* (the quantity of heat required to raise the temperature of a pound of water through one Fahrenheit degree). What Joule did was to show that the expenditure of a carefully measured amount of work always produced the same carefully measured amount of heat. He did this by using falling weights to drive a set of rotating paddles to stir up a quantity of water in a calorimeter, the motion (kinetic energy) of the water being damped by a system of fixed vanes inside the calorimeter. The amount of energy expended was determined by the loss of potential energy of the falling weights, and the amount of heat generated was determined by the rise in temperature of the water.

He deduced that the "mechanical equivalent of heat" is 772 foot-pounds per British thermal unit. That is, 772 foot-pounds of work will raise the temperature of a pound of water through one Fahrenheit degree. In more familiar metric units, the mechanical equivalent of heat is 4.2 joules per calorie. He wrote: "If my views be correct,... the temperature of the river Niagara will be raised about one fifth of a degree by its fall of 160 feet."

(*Exercise*: Verify this by calculation or by measurement, whichever you find more convenient.)

Once we have accepted that heat is but a form of energy, there should be no further need for separate units, and the joule will serve for both. That being so, we can interpret Joule's experiment not so much as determining the "mechanical equivalent of heat", but rather as a measurement of the specific heat capacity of water.

In spite of this, the calorie is still (regrettably) used extensively today. Part of the reason for this is that, in measuring heat capacities, we often drop a hot sample into water and

measure the rise in temperature of the water. This tells us rather directly what the heat capacity of the sample is in calories – i.e. the heat capacity *relative to* that of water. I suspect, however, that the calorie remains with us not for scientific reasons, but because old habits die hard.

There are several problems associated with the continued use of the calorie. Roughly, the calorie is the heat required to raise the temperature of a gram of water through 1 C$^{\circ}$. For precise work, however, it becomes necessary to state not only the isotopic constitution (and the purity) of the water, but also through *which* Celsius degree its temperature is raised. Thus in the past we have defined the calorie as "one hundredth of the heat required to raise the temperature of a gram of water from 0 $^{\circ}$C to 100 $^{\circ}$C"; or again as "the heat required to raise the temperature of a gram of water from 14.5 $^{\circ}$C to 15.5 $^{\circ}$C". This latter is about 4.184 joules, but there is really no need to know this conversion factor, unless you are specially interested in the specific heat capacity of water (which, by the way is rather larger than many common substances).

(You may have noticed that I have sometimes written $^{\circ}$C and sometimes C$^{\circ}$, and you may have wondered which is correct, or whether the degree symbol should be used at all. This will be discussed in Chapter 3.)

The "calories" that nutritionists quote when talking about the calorific value of foods, is actually the kilocalorie and it is sometimes (but by no means always) written Calorie, with a capital C. How much simpler it would all be if all of us just used joules!

There is yet another problem associated with the continued use of "calories". That is that we often come across formulas and equations in thermodynamics in which a mysterious factor "J" appears. For example, there is a well-known equation $C_P - C_V = R/J$. This relates the specific heat capacities of an ideal gas at constant pressure and volume to the universal gas constant R. It is supposed to be understood in the equation that C_P and C_V are to be expressed in calories and R is to be expressed in joules. The conversion factor between the two units, J, is the mechanical equivalent of heat, or the number of joules in a calorie. This conversion factor between units will not be used in these notes, and all quantities expressing heat of energy will be measured in the same units, which will normally be joules. The equation quoted above will be rendered simply as $C_P - C_V = R$. (The letter J, not in italics, will, of course, continue to be used to denote the unit the joule, but not J, in italics, for a conversion factor.)

1.3 *Extensive and Intensive Quantities*

There is a useful and important distinction in thermodynamics between *extensive* (or "capacitive") and *intensive* quantities.

Extensive quantities are those that depend upon the amount of material. Examples would include the volume, or the heat capacity of a body. The *heat capacity* of a *body* is the amount of heat required to raise its temperature by one degree, and might be expressed in J C$^{\circ -1}$.

Intensive quantities do not depend on the amount of material. Temperature and pressure are examples. Another would be the *specific heat capacity* of a *substance*, which is the amount of heat required to raise *unit mass* of it through one degree, and it might be expressed in J kg^{-1} C$^{\circ\,-1}$. This is what is commonly (though loosely) called "the specific heat", but we shall use the correct term: *specific heat capacity*.

Incidentally, we would all find it much easier to understand each other if we all used the word "specific" in contexts such as these to mean "per unit mass".

"Molar" quantities are also intensive quantities. Thus the "molar heat capacity" of a substance is the amount of heat required to raise the temperature of one *mole* of the substance through one degree. I shall have to define "mole" in the next section.

Some authors adopt the convention that extensive quantities are written with capital letters, and the corresponding intensive quantities are written in small letters. Thus *C* would be the heat capacity of a body in J C$^{\circ\,-1}$ and *c* would be the specific heat capacity of a substance in J kg^{-1} C$^{\circ\,-1}$. This is undeniably a useful distinction and one that many will find helpful. I have a few difficulties with it. Among these are the following: Some authors (not many) use the opposite convention – small letters for extensive quantities, capitals for intensive. Some authors make exceptions, using *P* and *T* for the intensive quantities pressure and temperature. Also, how are we to distinguish between extensive, specific and molar quantities? Three different fonts? This may indeed be a solution – but there is still a problem. For example, we shall become familiar with the equation $dU = T\,dS - P\,dV$. Here *U*, *S* and *V* are internal energy, entropy and volume. Yet the equation (and many others that we could write) is equally valid whether we mean extensive, specific or molar internal energy, entropy and volume. How do we deal with that? Write the equation three times in different fonts?

Because of these difficulties, I am choosing *not* to use the capital letter, small letter, convention, and I am hoping that the context will make it clear in any particular situation. This is, I admit, rather a leap of faith, but let's see how it works out.

1.4 *Mole*

According to our present state of knowledge, a mass of 12 grams of the ^{12}C isotope of carbon contains 6.022 141 99 × 10^{23} atoms. This number is called *Avogadro's number*. A *mole* of an element is the amount of that element that has the same number of atoms as there are atoms in 12 grams of ^{12}C, and a mole of a compound is the amount of that compound that has the same number of molecules as there are atoms in 12 grams of ^{12}C. Likewise a mole of geese is 6.022 141 99 × 10^{23} geese and a mole of baseball caps is 6.022 141 99 × 10^{23} baseball caps.

Why do we define Avogadro's number in terms of 12 grams of carbon-12? This is a long story involving the history of physics and chemistry. None of us was born with a

complete knowledge of physics and chemistry and it took a long time to reach our state of knowledge today. We did not always proceed along our path with complete logic, and doubtless, if we did, we might have defined Avogadro's number differently. I am not going to go into the history of how we arrived at this particular definition. Suffice it to say that, if you know that the molecular weight of nitrogen gas (a diatomic molecule) is 28, then 28 grams of nitrogen has Avogadro's number of molecules in it. Indeed the phrase "molecular weight" is not a happy one; it would be better to call it the "molar mass", which is 28 grams.

We might note, however, that when we are doing "SI" calculations, based on MKS units, we shall usually use the *kilomole*, which is $6.022\ 141\ 99 \times 10^{26}$ molecules.

1.5 *Prepositions*

Prepositions play an important part in thermodynamics! Heat may be supplied **to** a system or lost **from** it. Work may be done **on** a gas or **by** it.

An answer to a question in thermodynamics of "5 joules" is meaningless unless you make it clear and unambiguous whether the system lost 5 joules of heat or gained 5 joules, or whether the gas did 5 joules of work, or you did 5 joules of work on the gas. And it is of no avail to say that the answer is "−5 joules" in the vague hope that I might know what you mean by the minus sign. You must explicitly state in words whether 5 joules was lost or gained − or your reader, or your examiner, will not understand you (and will give you no marks) or will misunderstand you (and will deduct some marks).

I used to tell students that if they wrote "5 joules" without the necessary preposition, they would get *no marks* for their answer. If they used a preposition, but chose the *wrong one* (the gas lost 5 joules instead of gaining it) I would take a mark off. Be warned!

1.6 *Applicability of Equations*

There seem to be lots and lots of equations in thermodynamics. Some of them are of very general applicability. For example the equation $dU = dQ + dW$, which is known as the First Law of Thermodynamics, tells us that the increase in the internal energy of a system is equal to the heat supplied **to** it plus the work done **on** it, and it is obviously of very general applicability and is true whatever the nature of the system. An equally well known equation is $PV = RT$. But this equation, which relates pressure, molar volume and temperature, applies *only to an ideal gas*. It doesn't apply to a vapour (which is a gas that is close to the temperature at which it will condense), and still less does it apply to a liquid or a solid. Although we often deal in thermodynamics with a gas held inside a cylinder, thermodynamics is by no means confined to gases, let alone ideal gases.

This section is just an advance warning to be conscious, whenever you see or use an equation, whether the equation is of great generality or whether it applies only to a

particular substance or to some special thermodynamic process or to a narrow set of circumstances.