CHAPTER 7
THE FIRST AND SECOND LAWS OF THERMODYNAMICS

7.1 *The First Law of Thermodynamics, and Internal Energy*

The First Law of thermodynamics is:

The **increase** of the *internal energy* of a system is equal to the sum of the *heat* added **to** the system plus the *work* done **on** the system.

In symbols:

$$dU = dQ + dW. \qquad\qquad 7.1.1$$

You may regard this, according to taste, as any of the following

A fundamental law of nature of the most profound significance;

or   A restatement of the law of conservation of energy, which you knew already;

or   A recognition that heat is a form of energy.

or   A definition of *internal energy.*

Note that some authors use the symbol E for internal energy. The majority seem to use U, so we shall use U here.

Note also that some authors write the first law as $dU = dQ - dW$, so you have to be clear what the author means by dW. A scientist is likely to be interested in what happens **to** a system when you do work **on** it, and is likely to define dW as the work done **on** the system, in which case $dU = dQ + dW$.   An engineer, in the other hand, is more likely to be asking how much work can be done **by** the system, and so will prefer dW to mean the work done **by** the system, in which case $dU = dQ - dW$.

The internal energy of a system is made up of many components, any or all of which may be increased when you add heat **to** the system or do work **on** it. If the system is a gas, for example, the internal energy includes the translational, vibrational and rotational kinetic energies of the molecules. It also includes potential energy terms arising from the forces between the molecules, and it may also include excitational energy if the atoms are excited to energy levels above the ground state. It may be difficult to calculate the total internal energy, depending on which forms of energy you take into account. And of course the *potential* energy terms are always dependent on what state you define to have zero potential energy. Thus it is really impossible to define the total internal energy of a system uniquely. What the first law tells us is the *increase* in internal energy of a system when heat is added **to** it and work is done **on** it.

Note that internal energy is a *function of state*. This means, for example in the case of a gas, whose *state* is determined by its pressure, volume and temperature, that the internal energy is uniquely determined (apart from an arbitrary constant) by *P, V* and *T* – i.e. by the state of the gas. It also means that in going from one state to another (i.e. from one point in *PVT* space to another), the change in the internal energy is *route-independent*. The internal energy may be changed by performance of work or by addition of heat, or some combination of each, but, whatever combination of work and energy is added, the change in internal energy depends only upon the initial and final states. This means, mathematically, that *dU* is an *exact differential* (see Chapter 2, Section 2.1). The differentials *dQ* and *dW*, however, are *not* exact differentials.

Note that if work is done on a Body by forces in the Rest of the Universe, and heat is transferred to the Body from the Rest of the Universe (also known as the Surroundings of the Body), the internal energy of the Body increases by $dQ + dW$, while the internal energy of the Rest of the Universe (the Surroundings) decreases by the same amount. Thus the internal energy of the Universe is constant. This is an equivalent statement of the First Law. It is also sometimes stated as "Energy can neither be created nor destroyed".

7.2 *Work*

There are many ways in which you can do work **on** a system. You may compress a gas; you may magnetize some iron; you may charge a battery; you may stretch a wire, or twist it; you may stir a beaker of water.

Some of these processes are *reversible*; others are irreversible or dissipative. The work done in compressing a gas is reversible if it is quasistatic, and the internal and external pressures differ from each other always by only an infinitesimal amount. Charging a lead-acid car battery may be almost reversible; charging or discharging a flashlight battery is not, because it has a high internal resistance, and the chemical reactions are irreversible. Stretching or twisting a wire is reversible as long as you do not exceed the elastic limit. If you do exceed the elastic limit, it will not return to its original length; that is, it exhibits elastic *hysteresis*. When you magnetize a metal sample, you are doing work on it by rotating the little magnetic moments inside the metal. Is this reversible? To answer this, read about the phenomenon of magnetic hysteresis in Chapter 12, Section 12.6, of Electricity and Magnetism.

Work that is reversible is sometimes called *configuration work*. It is also sometimes called *PdV work*, because that is a common example. Work that is not reversible is sometimes called *dissipative work*. Forcing an electric current through a wire is clearly dissipative.

For much of the time, we shall be considering the work that is done **on** a system by *compressing* it. Solids and liquids require huge pressures to change their volumes significantly, so we shall often be considering a *gas*. We imagine, for example, that we have a quantity of gas held in a cylinder by a piston. The work done in compressing it in a reversible process is *–PdV*. If you are asking yourself "Is *P* the pressure that the gas is exerting on the piston, or the pressure that the piston is exerting on the gas?", remember that we are considering a reversible and quasistatic process, so that the difference between the two is at all stages infinitesimal. Remember also that in calculus, if *x* is some scalar quantity, the expression *dx* doesn't mean vaguely the "change" in *x* (an ill-defined

word), but it means the *increment* or *increase* in *x*. Thus the symbol *dV* means the *increase* in volume, which is negative if we are doing work **on** the gas by *compressing* it. In any case whether you adopt the scientist convention or the engineer convention (try both) the first law, when applied to the compression or expansion of a gas, becomes

$$dU = dQ - PdV. \qquad\qquad 7.2.1$$

7.3 *Entropy*

Definition: If an infinitesimal quantity of heat *dQ* is added to a system at temperature *T*, and if no irreversible work is done on the system, the increase in entropy *dS* of the system is defined by

$$dS = \frac{dQ}{T}. \qquad\qquad 7.3.1$$

Question: What are the SI units of entropy?

Note that, since *dQ* is supposed to be an infinitesimal quantity of heat, any increase in temperature is also infinitesimal. Note also that, as with internal energy, we have defined only what is meant by an *increase* in entropy, so we are not in any position to state what *the* entropy of a system is. (Much later, we shall give evidence that the molar entropy of all substances is the same at the absolute zero of temperature. It may then be convenient to define the zero of the entropy scale as the molar entropy at the absolute zero of temperature. At present, we have not yet shown that there is an absolute zero of temperature, let alone of entropy.)

To the question "What is meant by entropy?" a student will often respond with "Entropy is the state of disorder of a system." What a vague, unquantitative and close to meaningless response that is! What is meant by "disorder"? What could possibly be meant by a statement such as "The state of disorder of this system is 5 joules per kelvin"? Gosh! I would give nought marks out of ten for such a response! Now it *is* true, when we come to the subjects of statistical mechanics, and statistical thermodynamics and mixing theory, that there is a sense in which the entropy of a system is some sort of measure of the state of disorder, in the sense that the more disordered or randomly mixed a system is, the higher its entropy, and random processes do lead to more disorder and to higher entropy. Indeed, this is all connected to the second law of thermodynamics, which we haven't touched upon yet. But please, at the present stage, entropy is defined as I have stated above, and, for the time being, it means nothing less and nothing more.

It will have been noted that, in our definition of entropy so far, we specified that no irreversible work be done on the system. (The addition of heat to a system – e.g. by allowing heat to flow naturally into it from a hotter body – is irreversible.) What if some irreversible work *is* done? Let us suppose that we do work on a gas in two ways. (I choose a gas in this discussion, because it is easier to imagine compressing a gas with *PdV* work than it is with a solid or a liquid, because the compressibility of a solid or a liquid is relatively low. But the same argument applies to any substance.) We compress it with the piston, but, at the same time, we also stir it with a paddle. In that case, the work done **on** the gas is *more* than –*PdV*. (Remember that –*PdV* is positive.) If we didn't compress it at all, but only stirred it, *dV* would be zero, but we would still have done work on

the gas by stirring. Let's suppose the work done **on** the gas is $\delta W = -PdV + \delta W_{irr}$. The part δW_{irr} is the irreversible or dissipative part of the work done **on** the gas; it is unrecoverable as work, and is *irretrievably* converted to heat. You cannot use it to turn the paddle back. Nor can you cool the gas by turning the paddle backwards.

We can now define the increase of entropy in the irreversible process by $TdS = dQ + dW_{irr}$; that is, $dS = \dfrac{dQ + dW_{irr}}{T}$. In other words, since dW_{irr} is irreversibly converted to heat, it is just as though it were part of the addition of heat.

In summary, $$dU = dQ + dW$$
and $$dU = TdS - PdV$$

apply whether there is reversible or irreversible work. But only if there is no irreversible (unrecoverable) work does $dQ = TdS$ and $dW = -PdV$. If there is any irreversible work, $dW = -PdV + dW_{irr}$ and $dQ = TdS - dW_{irr}$.

Of course there are other forms of reversible work than PdV work; we just use the expansion of gases as a convenient example.

Note that P, V and T are state variables (together, they define the state of the system) and U is a function of state. Thus the *entropy*, too, is a *function of state*. That is to say that the change in entropy as you go from one point in PVT-space to another point is route-independent. If you return to the same point that you started at (the same state, the same values of P, V and T), there is no change in entropy, just as there is no change in internal energy.

Definition: The *specific heat capacity C* of a substance is the quantity of heat required to raise the temperature of unit mass of it by one degree. We shall return to the subject of heat capacity in Chapter 8. For the present, we just need to know what it means, in order to do the following exercise concerning entropy.

Exercise. A litre (mass = 1 kg) of water is heated from 0 °C to 100 °C. What is the increase of entropy? Assume that the specific heat capacity of water is $C = 4184$ J kg^{-1} K^{-1}, that it does not vary significantly through the temperature range of the question, and that the water does not expand significantly, so that no significant amount of work (reversible or irreversible) is done.

Solution. The heat required to heat a mass m of a substance through a temperature range dT is $mCdT$. The entropy gained then is $\dfrac{mCdT}{T}$. The entropy gained over a finite temperature range is therefore $mC\displaystyle\int_{T_1}^{T_2}\dfrac{dT}{T} = mC\ln(T_2/T_1) = 1 \times 4184 \times \ln(373.15/273.15) = 1305\,\mathrm{J\,K^{-1}}$.

7.4 *The Second Law of Thermodynamics*

In a famous lecture entitled *The Two Cultures* given in 1959, the novelist C. P. Snow commented on a common intellectual attitude of the day - that true education consisted of familiarity with the humanities, literature, arts, music and classics, and that scientists were mere uncultured technicians and ignorant specialists who never read any of the great works of literature. He described how he had often been provoked by such an attitude into asking some of the self-proclaimed intellectuals if they could describe the Second Law of Thermodynamics – a question to which he invariably received a cold and negative response. Yet, he said, he was merely asking something of about the scientific equivalent of "Have you read a work of Shakespeare?"

So I suggest that, if you have never read a work of Shakespeare, take a break for a moment from thermodynamics, go and read *A Midsummer Night's Dream*, and come back refreshed and ready to complete your well-rounded education by learning the Second Law of Thermodynamics.

We have defined entropy in such a manner that if a quantity of heat dQ is added reversibly to a system at temperature T, the increase in the entropy of the system is $dS = dQ/T$. We also pointed out that if the heat is transferred *irreversibly*, $dS > dQ/T$.

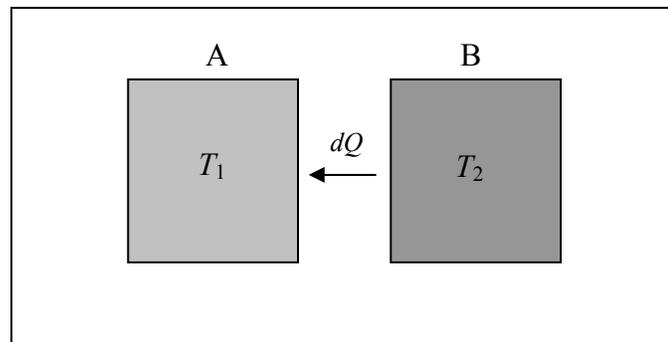Now consider the following situation (figure VII.1).

FIGURE VII.1

An isolated system consists of two bodies, A at temperature T_1 and B at temperature T_2, such that $T_2 > T_1$. Heat will eventually be exchanged between the two bodies, and on the whole more heat will be transferred from B to A than from A to B. That is, there will be a *net* transference of heat, dQ, from B to A. Perhaps this heat is transferred by radiation. Each body is sending forth numerous photons of energy, but there is, on the whole, a net flow of photons from B to A. Or perhaps the two bodies are in contact, and heat is being transferred by conduction. The vibrations in the hot body are more vigorous than those in the cool body, so there will be a net transfer of heat from B to A. However, since the emission of photons in the first case, and the vibrations in the second place, are random, it will be admitted that it is not impossible that at some time more photons may move from A to B than from B to A. Or, in the case of conduction, most of the atoms

in A happen to be moving to the right while only a few atoms in B are moving to the left in the course of their oscillations. But, while admitting that this is in principle possible and not outside the laws of physics, it is exceedingly unlikely to happen in practice; indeed so unlikely as hardly to be taken seriously. Thus, in any natural, spontaneous process, without the intervention of an External Intelligence, it is almost certain that there will be a net transfer of heat from B to A. And this process, barring the most unlikely set of circumstances, is irreversible.

The hot body will *lose* an amount of entropy dQ/T_2, while the cool body will *gain* an amount of entropy dQ/T_1, which is greater than dQ/T_2. Thus the entropy of the *isolated system as a whole increases* by $dQ/T_1 - dQ/T_2$.

From this argument, we readily conclude that *any natural, spontaneous and irreversible thermodynamical processes taking place within an isolated system are likely to lead to an increase in entropy of the system.* This is perhaps the simplest statement of the *Second Law of Thermodynamics.*

I have used the phrase "is likely to", although it will be realised that in practice the possibility that the entropy might decrease in a natural process is so unlikely as to be virtually unthinkable, even though it could in principle happen without violating any fundamental laws of physics.

You could regard the Universe as an isolated system. Think of a solid Body sitting somewhere in the Universe. If the Body is hot, it may spontaneously lose heat to the Rest of the Universe. If it is cold, it may spontaneously absorb heat from the Rest of the Universe. Either way, during the course of a spontaneous process, the entropy of the Universe increases.

The transference of heat from a hot body to a cooler body, so that both end at the same intermediate temperature, involves, in effect, the mixing of a set of fast-moving molecules and a set of slow-moving molecules. A similar situation arises if we start with a box having a partition down the middle, and on one side of the partition there is a gas of blue molecules and on the other there is a gas of red molecules. If we remove the partition, eventually the gases will mix into one homogeneous gas. By only a slight extension of the idea of entropy discussed in courses in statistical mechanics, this situation can be described as an increase of entropy – called, in fact, the entropy of mixing. If you saw two photographs, in one of which the blue and red molecules were separated, and in the other the two colours were thoroughly mixed, you would conclude that the latter photograph was probably taken later than the former. But only "probably"; it is conceivable, within the laws of physics, that the velocities of the blue and red molecules separated themselves out without external intervention. This would be allowed perfectly well within the laws of physics. Indeed, if the velocities of all the molecules in the mixed gases were to be reversed, the gases would eventually separate into their two components. But this would seem to be so unlikely as never in practice to happen. The second law says that the entropy of an isolated system is *likely* (*very* likely!) to increase with time. Indeed it could be argued that the increase of entropy is the criterion that defines the direction of the *arrow of time*. (For more on the arrow of time, see Section 15.12 of the notes on Electricity and Magnetism of this series. Also read the article on the arrow of time by Paul Davis, *Astronomy & Geophysics* (Royal Astronomical Society) **46**, 26 (2005). You'll probably also enjoy H. G. Wells's *The Time Machine*.)

Note that, in the example of our two bodies exchanging heat, one *loses* entropy while the other *gains* entropy; but the gain by the one is greater than the loss from the other, with the result that there is an *increase* in the entropy *of the system as a whole*. The principle of the increase of entropy applies to an *isolated* system.

In case you have ever wondered (who hasn't?) how life arose on Earth, you now have a puzzle. Surely the genesis and subsequent evolution of life on Earth represents an increase in order and complexity, and hence a *decrease in the entropy of mixing*. You may conclude from this that the genesis and subsequent evolution of life on Earth requires Divine Intervention, or Intelligent Design, and that the Second Law of Thermodynamics provides Proof of the Existence of God. Or you may conclude that Earth is not an isolated thermodynamical system. Your choice.