CHAPTER 5
THERMODYNAMIC PROCESSES

We shall be considering what happens when we perform certain *processes* on various *systems*. The processes will usually entail either doing work on a system or adding heat to it, or perhaps we shall allow the system to do work on its surroundings, or the system may lose heat to its surroundings.

Often the system we have in mind will be a gas enclosed by a movable piston inside a cylinder, but it need not be that. The system may be a solid or a liquid, in which there is little change in volume. Or the system may have several phases, such as gas, liquid and solid. There may be several components to the system – for example, a mixture of chemicals. Or the system may be a magnetic material, and we do work on it by putting it in a magnetic field and magnetizing it. Some fundamental thermodynamical laws apply to *any* thermodynamical system and are of great generality. Other laws may apply only to certain specific types of system, and we must always be on our guard to recognize which are general laws applicable to any system, and which are special equations applicable only to particular systems.

We shall, in our imagination, carry out processes under various ideal conditions. Thus, we may imagine a process to be *isothermal* (carried out at constant temperature) or *isobaric* (constant pressure) or *isochoric* (constant volume).

We may imagine a process in which no heat is added to or is lost from the system. Such a process is *adiabatic.*

A process may be *quasistatic* or *nonquasistatic*. Let us imagine that we have a box of gas, and we suddenly heat one wall of the box by pushing that wall up against a source of heat. Not all of the gas will immediately become hotter. At first, the gas near to the heated wall will start to warm up, while the gas at the far end of the box will scarcely be aware of what has happened. Eventually, heat will permeate throughout the box, but this may take some time, and the system is not at all in static equilbrium while these changes are taking place. Likewise, if we have a gas held inside a cylinder by means of a movable piston, and we suddenly move the piston inwards. This will not result in an immediate change to a higher pressure throughout the gas. At the very most the information about the new position of the piston can travel through the gas only at the speed of sound. Considerable local turbulence is likely to be caused, and it will be some time before the gas settles down to its new uniform pressure throughout. Both of these processes are *nonquasistatic*.

For a process to be *quasistatic*, the pressure and temperature of the system must differ from those of its surroundings by only an infinitesimal amount at all times during the process; the process must take place slowly, so that the system passes through an infinite succession of quasi-equilibrium states. The prefix "quasi" is often translated as "almost"; a more precise meaning is "as it were" or "as if it were". The reader will conclude that there cannot ever literally be any process that is truly static. This is also true of other processes, such as isothermal and adiabatic processes. Such processes are limiting theoretical processes. A real process may be intermediate between the ideal extremes, although it may also be quite close to one of the ideal extremes.

Suppose we do work on a system – for example, by compressing it. Now let us allow the system to do work on us by expanding again to its original state (i.e. its original volume, temperature and pressure). If the work done **by** the system in returning to its original state is equal to the work we originally did **on** the system, that process is called *reversible*. If there is friction between the piston and the cylinder walls, the process is not reversible; all the forces involved during the process must be conservative forces. Further, for a process to be truly reversible, it must also be quasistatic, so that the pressure and temperature of the system must at all times differ from those of its surroundings by only an infinitesimal amount. However, it is possible in the case of the gas enclosed in a cylinder by a moveable piston with friction between piston and cylinder for the process to be quasistatic, but it is not reversible. In other words, for a process to be reversible, it is a necessary condition that it also be quasistatic, but this is not a sufficient condition. A reversible process must be quasistatic, but a quasistatic process need not be reversible.

Heating a system by stirring it with a paddle is an irreversible process. Heating by *stirring* or by *friction* are the most obvious examples of irreversible system. While they are not the only examples (see if you can think of more) they are the most obvious examples, and might serve as quick rule of thumb in an exam.

As we encounter various equations in thermodynamics, we must be on our guard to distinguish between very general relations applicable to all *systems* and all *processes* from equations that apply only to certain types of system, or only to certain types of processes.

A few more words will be of interest. A *closed* system is one in which no matter can enter or leave. An *isolated* system is one in which no matter or energy (heat) can enter or leave. A *diathermal* wall is one through which heat can freely flow. A closed cylinder with thin copper diathermal walls, sitting in a water bath, is not isolated. If the cylinder is closed and wrapped in a thick coat of asbestos or glass wool, is highly polished, and is surrounded by a vacuum, it can probably be regarded as isolated.