

# 1 Heat and Work

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## 1.1 Introduction

Thermodynamics is the study of the interconversion of heat, work and other forms of energy. It is called a phenomenological subject in that it treats of the phenomena that occur in real macroscopic systems and not of their microscopic or molecular causes. Thus, if we heat a liquid at atmospheric pressure we find that it expands, if we heat it at a fixed volume we find that the pressure rises. Thermodynamics is that part of science which gives us relations between such quantities as the amount of heat supplied in each case, the increase of volume and the rise of pressure. Some of these quantities may be difficult to measure, and one of the principal uses of thermodynamics is their calculation from the more accessible quantities. Such calculations tell us nothing, however, of the molecular mechanisms in the liquid that cause the increase in volume or the rise of pressure.

If we wish to calculate, not one macroscopic property in terms of another, but to estimate both from our knowledge of the behaviour of molecules, then we must go beyond the relations of classical thermodynamics. This extension is called statistical thermodynamics, and we touch on some of its engineering uses in the last chapter. The bulk of the book is, however, confined to the principles and chemical engineering applications of classical thermodynamics.

Heat and work are particularly important forms of energy as far as thermodynamics is concerned. Historically, all of the early work on the subject involved these two forms of energy and their interconversion. Thus, in the early years of the nineteenth century, the steam engine was in regular use and attempts to improve its efficiency, for the conversion of thermal energy into mechanical energy, were of great economic importance. Conversion in the opposite direction had been observed many years earlier and perhaps the most famous reported observation is that of Rumford who, in 1798, noticed that

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during the boring of cannon, tremendous amounts of heat were generated. Interpretation of observations such as these were clouded at the time by the credence given to the old caloric theory of heat, and it was not until the 1840s and the work of Joule that thermodynamics, as we know it, began to see the light of day.<sup>1</sup>

In spite of apparent preoccupation with heat and work, particularly in the early parts of this book, much of what we say will ultimately have a much wider interpretation. We shall be applying our results to situations which, at first sight, do not appear to involve them in any important way. We shall examine not only physical processes, which may involve both heat and work, but also chemical processes, where their role is less obvious. We could, although we shall not do so, examine processes which take place in strong magnetic or electric fields (work being done against the field), but the study of such situations is more appropriate to physics textbooks. We could also examine biological processes, such as the exchange of chemical and mechanical energy in muscle, but we leave them to books on biochemistry. Thermodynamics has applications in all branches of science and engineering, but in this textbook we select material which is important to the chemical engineer.

### 1.2 Equilibrium

Before going further, we must introduce the concept of equilibrium. This is something which is difficult to define formally, and we do not attempt a rigorous definition. A system is said to be in equilibrium if (a) it does not change over the time scale of interest to us, and (b) a small change made to it may be reversed, so returning the system to its starting point. The time scale of interest varies with the situation and each case must be examined individually. For example, if a hot aqueous solution of a soluble salt is cooled, a point will be reached at which we would expect crystallisation to occur. However, if the cooling process is slow, it is possible to 'supercool' the solution, no crystallisation taking place. Let us maintain it at the temperature then reached and ask whether the situation is in equilibrium. If our time scale is measured in minutes, then we would usually find no further change in the supercooled solution and we can say the solution is in a state of equilibrium. If, however, our time scale is measured in days, in all probability crystallisation will occur due to nucleation and our supercooled state cannot be considered to be the equilibrium one; this description belongs to the crystallised state.

What we have just described is very similar to equilibrium in the mechanical situations represented in Figure 1.1. Ball A sitting at the bottom of the valley is in a position of *stable equilibrium* and this corresponds to the crystallised solution. Ball B in a local depression at the top of the hill is said to be in *metastable equilibrium*, and corresponds to the supercooled solution; formally we say that ball B is stable with respect to small displacements, but not to large ones. Ball C is in a *non-equilibrium* position, as it is spontaneously rolling downhill.

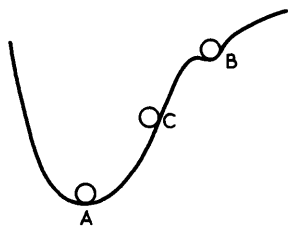


Figure 1.1. Equilibrium in a mechanical situation

We give two more examples to clarify our ideas on equilibrium.

(a) A mixture of hydrogen and oxygen at room temperature is at equilibrium. If we introduce a catalyst, chemical reaction occurs, and not until reaction stops is equilibrium restored. By analogy with Figure 1.1, we would say that the unreacted mixture was in metastable equilibrium and the final state in stable equilibrium. But we can make quite large changes in the pressure and temperature of the hydrogen-oxygen mixture, and we can then reverse these, thus restoring the system to its original state. In the absence of a catalyst these large changes do not cause reaction, and so the region of metastability is far from small, that is in this case, it is more like a deep hole in the side of the hill, rather than the shallow depression of Figure 1.1. The metastable system is therefore coming close to what can quite properly be called stable equilibrium and, conversely, what we usually think of as stable equilibrium is really nothing more than the limiting case of metastable equilibrium, for even the fully reacted system, water, might under appropriate circumstances, undergo nuclear reaction to a state of even lower energy.

(b) A vessel containing gas at a uniform temperature and pressure is at equilibrium. If there is a temperature gradient present we would not normally consider it to be at equilibrium. But, when the vessel is a very long capillary tube, our time of interest is small compared to the time thermal conduction takes to even out the temperature gradient, and when we consider only changes which, when reversed, allow the original temperature gradient to be restored, then the system may be taken as being at equilibrium. Thus, for example, a long capillary tube made of rubber and containing gas can be squeezed uniformly by application of an external pressure. This changes the state of the gas within the tube, but there will not necessarily be a significant flow of gas molecules along the tube. Thus, if the external pressure is relaxed, we can return the gas to its original state and with the original temperature gradient intact. It therefore conforms to our requirements for an equilibrium state. The situation is analogous to example (a) where the unreacted hydrogen-oxygen mixture is at equilibrium with respect to changes in pressure and temperature only if the chemical reaction is 'frozen' in the unreacted state.

Thermodynamics deals only with equilibrium situations and, in particular, changes from one equilibrium situation to another, such as from A to B in Figure 1.1, or vice versa. The change may pass through non-equilibrium

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positions en route, as clearly happens if the ball rolls down the hill, but this does not affect the applicability of thermodynamics. It is required only that the initial and final positions are in equilibrium with respect to the change we are considering.

The inability of thermodynamics to deal with other than equilibrium situations has one very important consequence. We are unable to say anything about the rate at which a process happens, for any natural or spontaneous process goes through a series of non-equilibrium positions. If a process is undergoing change, we can describe the position (thermodynamically) when it comes to a stop, but we can say nothing about the rate at which it gets there. In the hydrogen-oxygen reaction we can investigate the products of reaction and even, as we shall see, predict what they are, but thermodynamics gives us no clue as to whether the reaction takes one second or one year to come to completion. There have, in recent years, been developments in a subject called 'non-equilibrium thermodynamics', which attempts to deal with rate processes, but apart from the title its connection with 'equilibrium thermodynamics', which is what we are concerned with here, is small and will not be discussed in this book.

### 1.3 Temperature

An understanding of the concepts of work and pressure is essential to the study of mechanical systems, and we presume the reader to be familiar with them. They are also important in thermodynamics, but here we have, in addition, the concepts of heat and temperature to contend with. We examine now some of the properties of the latter.

Consider two bodies well separated from one another. Each will be separately at equilibrium in the sense given in Section 1.2. If we bring the bodies into contact so that energy, in the form of heat, can flow from one to the other, we notice that the heat flow takes place in one direction only, and we say that the body which gives up heat is hotter than the other. After the bodies have been in contact for some time, we notice that heat flow falls off and then stops. We now have equilibrium between them, and we say that they are at the same 'temperature', this being the quantity we use to measure 'hotness'. If we bring the two bodies together and find no heat flow, we conclude that both are at the same temperature. The same is true of any third body which we may bring up and which, when in contact with the other two, does not transfer any heat in either direction.

It is pertinent to ask, at this point, how in fact we know that there has been a flow of heat. It is our experience that we can only infer that heat has flowed if the two bodies we have brought into contact have changed in some observable way. Thus, if they are two pieces of metal, measurements of their volume (or length) tells us whether any change is taking place; if we have gas contained in a vessel of fixed volume, measurement of pressure does the same. We use these

observations, not only to determine equality of temperature, but to provide a monotonic scale of temperature. We do this by associating a numerical value of temperature with each measurement of volume in the case of our pieces of metal, or with each measurement of pressure for the gas at constant volume. The way we do this is quite arbitrary. We could, for example, choose a scale in which the temperature was proportional to the pressure in the case of the gas at constant volume; or we could choose to make it inversely proportional. The most frequently used thermometer is one which uses the expansion of a liquid, typically alcohol or mercury, in a glass vessel, but there is no reason to suppose that, even if we define our temperature scale as being linear in changes of the liquid volume, both alcohol and mercury will give the same value for the measurement of any arbitrary temperature. It is clear, therefore, that we have available an almost infinite number of thermometric devices and a similarly large number of temperature scales.

The observations which we have made in this section are often embodied in the so-called *zeroth law of thermodynamics* ('zeroth' since it is more primitive than the first, second and third laws which, nevertheless, preceded it historically). In science, a law is a statement of an important generalisation from experience and, in general, the title is reserved for basic ideas which are fundamental to the subject. Clearly, the existence of the quantity 'temperature' and its measurable properties fit this requirement. The zeroth law is:

if, of three bodies, A, B and C, A and B are separately in thermal equilibrium with C, then A and B are in thermal equilibrium with one another.

It is, in many respects, a trivial statement, almost, one might say, a statement of the obvious. Nevertheless, it is a statement which has to be made before it is possible to quantify the concept of temperature.

We leave temperature, for the moment, in this somewhat unsatisfactory state, with its multiplicity of scales, to return to it later in Chapter 3 after we have introduced the second law of thermodynamics. We shall see there that it is possible to choose one particular scale having thermodynamically desirable properties. However, it will help, in the meantime, if the reader thinks of temperature as expressed on the scale of the constant volume gas thermometer, that is, the temperature as indicated by measurements of the pressure of a gas contained in a vessel of constant volume. This leads to temperatures which are never negative and in which large numbers are associated with hot bodies, small numbers with cold.

## 1.4 Definitions

In thermodynamics, the part of the physical world which we are investigating is called the *system*. It may be a very simple part, such as a beaker in which a chemical reaction is carried out on the laboratory bench, or it may be very much more complex, such as a complete air liquefaction plant.

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That part of the remainder of the physical world which can in any significant way affect or be affected by the system we call the *surroundings*. Thus, the burner which supplies heat to the beaker is part of the surroundings. The Earth's atmosphere, which supplies air to the liquefaction plant, forms part of the surroundings in the second example. It is true that the atmosphere is in contact with the beaker in the first example also, but we do not need to consider it as part of the surroundings unless it has a significant effect on the reaction taking place.

In general, we expect the interaction between the system and its surroundings to result in the transfer of (a) thermal energy, i.e. heat, (b) mechanical energy, i.e. work and (c) material from one to the other. If the nature of the system is such that only heat and/or work is transferred to or from the surroundings, we call the system *closed*. If, in addition, there is transfer of material, that is molecules, then the system is said to be *open*. Thus, the chemical reaction taking place in the beaker is a closed system, provided that there is no loss or gain of gaseous material to or from the atmosphere. The air liquefaction plant is an open system since it takes in material from the atmosphere, that is from the surroundings.

A system which is thermally isolated from the surroundings is said to be *adiabatic*. It is as though the system were surrounded by walls which are impenetrable by heat. This is not a completely hypothetical concept, for a double-walled vacuum flask with silvered walls (Dewar vessel) is an excellent approximation to an adiabatic enclosure. In fact, without such a vessel, the experimental aspects of thermodynamics, particularly calorimetry, would be impracticable. In an adiabatic closed system, the only way that any changes can be made to the system is by transferring energy in the form of work.

In the design of large chemical plant, the chemical engineer might therefore ask how is he to decide what constitutes his system. Consider the case of a methane liquefier, Figure 1.2. Methane is stored under pressure in a series of cylinders. The methane gas is fed, via the compressor, to the liquefaction unit. Since the latter requires an input stream at a constant pressure of e.g. 100 bar, the compressor must be operated in such a way as to boost the dwindling gas

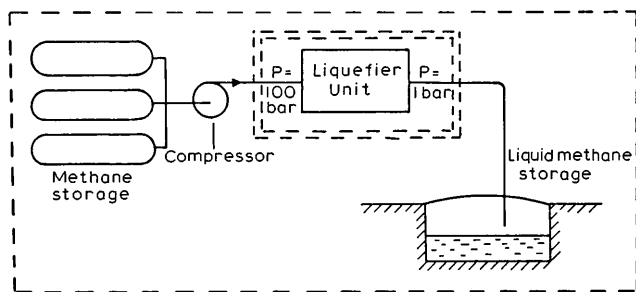


Figure 1.2. Methane liquefaction plant

pressure in the storage cylinders to this figure. The liquid methane leaves the liquefier at 1 bar pressure and is led to a storage tank. If the engineer takes as his system the whole plant, that is the whole area within the singly broken lines on the diagram, then he clearly has a closed system since, although heat and work (the latter is needed to drive the compressor) pass through this boundary, no methane does so. However, the engineer could, quite justifiably, focus his attention on the liquefier unit since this is the most difficult part of the plant to design, so that he defines his system as that which is enclosed by the double broken lines. Now the system is open since we have a gaseous methane input stream and a liquid methane output stream; the remainder of the plant forms part of the surroundings. During start up, we have gaseous methane going in and no liquid methane coming out. However, once the plant has been operating for some time, we reach a steady state in which the amount of gaseous methane entering, equals the amount of liquid methane flowing out. There is now no net change in the amount of material within the system. Such a state of affairs is of sufficient importance to warrant its being classified as a *steady state flow system*. In general, the chemical engineer attempts to design the various components of a plant to operate under steady state flow conditions. The reasons for this are largely economic, and they become more and more compelling, the larger the plant under consideration. In this book we are only rarely concerned with open systems in which the amount of material is changing with time. Most of the discussion is on closed systems and on steady state flow systems.

In order to be quantitative about what happens inside a system, we shall find it necessary to talk about its *properties*. If the system is a simple one, such as a piece of metal, then mass, volume and temperature are obvious candidates for the name property. Pressure might be added as another property, and is obviously appropriate if the system is a gas. However, what constitutes a property in the case of the methane liquefier discussed above? Mass and volume are both reasonable for we can evaluate the mass and volume of the whole plant by summing over its various components. But pressure and temperature are more difficult since these vary throughout the plant. There is not just one value of pressure, for example, which can be ascribed to the plant. We must, therefore, define a property more formally, and consider which properties are relevant to thermodynamics.

We define a property by describing methods of measuring it. The value of that property, at any one time, is the result of the measuring operation performed at that time. The value must be unique, so that different methods of measurement of the same property give the same result, and it must be independent of the past history of the object or system, that is, a property is a characterisation of the system as we find it now. Clearly, mass, volume, pressure and temperature conform to this definition, even in the case of the methane liquefier. We may take a measurement of pressure by inserting a probe into the plant *at some point*, and measuring the pressure at that point. The result will be a meaningful value and, therefore, may be classed as

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a property. Clearly, we can make many pressure measurements at points throughout the plant. The values obtained will, in general, be different, and so we find that many properties of the plant or system are measurements of pressure. This is obviously inconvenient in any thermodynamic computation and so we nearly always break down our plant into simpler components, choosing these so that, as far as possible, the pressure and temperature, for example, are uniform throughout that component. Thus, in the methane liquefier, one component would be the gaseous methane storage. A second one would be the liquid methane storage. This leaves a residual number of components, in this case the compressor and the liquefier unit, in which there are pressure and temperature gradients. We shall see later how it is possible to avoid the need for a detailed knowledge of these, and how to base our calculations on the characteristics of the input and output streams only.

We can divide the properties considered so far, mass, volume, pressure and temperature, into two classes. The first, mass and volume, can be evaluated for a whole system by summation over the component parts. Such properties are called *extensive*. The second, temperature and pressure, may be looked upon more as point values, or, more precisely, as properties whose values approach a finite and non-zero limit as the size of a system which includes the selected point approaches zero. These properties are called *intensive*. The two classes do not embrace all possible properties. Thus,  $V^2$  is a property. If a volume  $V$  is considered as made up of two parts  $V_1$  and  $V_2$  then, since

$$V^2 \neq V_1^2 + V_2^2 \quad (1.1)$$

$V^2$  cannot be classed as extensive. It is clearly not intensive either. Properties of this type are hardly ever useful in thermodynamics, and in this book we are concerned only with intensive and extensive properties.

When we know the values of a sufficient number of properties of a system so as to specify it completely, we say that we know the *state* of the system. Thus, if two systems are to be in the same state, then they must both have the same value for every property. Since a system has, in general, a large number of properties, our aim is to find a set of the *minimum number* of properties which specify its state. We should like also to find the rules which enable us to calculate as many other properties as is possible from this minimum set.

The minimum number of properties necessary to specify the state of a system can be determined only from our experience of the physical world; it cannot be found in any theoretical way. Consider the case of a sample of gas, which we assume to be homogeneous. Our experience tells us that if we know the values of pressure, temperature and amount of material, we have specified completely the state of the gas. It has just one value for the volume, given by an expression of the type

$$V = f(P, T, n) \quad (1.2)$$

We see that  $P$ ,  $T$  and  $n$  do not form a unique set of properties which may be



used to specify the state of the system;  $P$ ,  $T$  and  $V$ , or  $V$ ,  $T$  and  $n$ , etc. also form adequate sets.

The minimum number of properties needed to specify the state of a system varies with the latter's complexity. Thus, to take a simple extension to the example above, if the gas is a two-component mixture, in addition to  $P$ ,  $T$  and  $n$ , we need to determine the composition.

Although any type of property may be used to specify the state of a system, we find that when we come to determine the rules relating one property to another, we can do this only if we restrict our considerations to the intensive and extensive properties which describe systems at equilibrium. The properties in this subject are termed *functions of state* or *state functions*.

Functions of state have a number of important mathematical properties. Consider the case of the volume,  $V$ , of a system. Any infinitesimal change in the volume can be denoted by  $dV$ , that is as a differential of the function of state. Thus, if in any process the volume of the system changes, and if the process can be represented by a series of infinitesimal steps, the total volume change is given by

$$\text{Volume change} = \int_1^2 dV = V_2 - V_1 \quad (1.3)$$

where the limits on the integral sign imply that the system starts in state 1 with volume  $V_1$ , and the process continues until the system reaches state 2 with volume  $V_2$ . The value of the integral ( $V_2 - V_1$ ) is independent of the particular path or route by which the volume was changed. The process may have been such that the volume increased uniformly from  $V_1$  to  $V_2$ , or there may have been an initial contraction followed by an expansion, or any other more complex process. The value for the change in volume, however, is independent of all of this, and depends only on the properties of the system in state 1 and on the properties in state 2. Mathematically, a differential quantity such as  $dV$ , which may be integrated in this way, is called a *perfect differential*, or a *total differential*, or an *exact differential*.

Differences in the values of state functions, of which  $V_2 - V_1$  is just one example, are frequently encountered in thermodynamics, and for convenience we use the shorthand notation

$$V_2 - V_1 \equiv \Delta V \quad (1.4)$$

This 'capital delta' notation is used only for changes in state functions and not for any other purpose.

Finally, it is clear from the argument above that if the material in a closed system starts in state 1, and the process is such that the system is ultimately returned to state 1, there will have been no net change in any of the functions of state. Thus, in the case of the volume we can write

$$\Delta V = \oint dV = 0 \quad (1.5)$$

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where the symbol  $\oint$  is used to show that the integral is over a closed path. The same is true for steady flow of unit amount of material through a series of processes if they ultimately return the material to state 1. A process which brings the material back to its original state in this way is called a *cycle*.

### 1.5 Heat and work

Heat and work are quantities quite different in character from the properties—functions of state—which we have considered so far. Thus, if our system consists of a gas contained within a vessel, although it is perfectly proper to talk of the pressure of the gas or of its volume, it is meaningless to talk of its heat or work. If, however, our gas, which we assume to be at sufficiently high pressure, is allowed to push a piston along a cylinder, and if we connect the piston to a crank by means of a connecting rod, as in an internal combustion engine, we can perform useful mechanical work. That is, we can transfer energy, in the form of work, from the system to some other object or system in the surroundings. Similarly, if we have a vessel which contains substances which react together exothermically,\* we can transfer energy, this time in the form of heat, to another body in the surroundings merely by bringing them into thermal contact. We can thus look upon both work and heat as ‘energy in transit’ to the surroundings from the system, or vice versa.

That heat and work are not functions of state can be seen clearly by considering a simple example. Let us assume that we wish to increase the temperature of a piece of metal from, say 20 °C to 30 °C. One way to do this would be to supply the necessary heat from a suitable burner. Clearly no work is involved in this process. A second way would be to rub the piece of metal on a rough surface and thereby increase the temperature by friction. This time, work will have been performed in overcoming friction, but no heat will have been supplied. Thus, although the state of the metal is the same at the end of each process—same temperature, pressure and mass—and the changes in these properties are the same in each process—as is required for a function of state—the work done in the first case differs from that done in the second, as also does the heat supplied. Therefore, neither heat nor work can be functions of state.

This example shows that work can be converted into heat by friction. A paddle wheel rotating in a vessel of liquid has the same effect. Strictly speaking, both processes result in an increase in the temperature of the system rather than in the direct conversion of work into heat. But material at a temperature above ambient can act as a source of thermal energy, and we may therefore talk loosely of the conversion of work into heat. Such conversion, by means of a paddle wheel, was the one carried out by Joule in the mid-nineteenth century. He took great pains to measure accurately the amount of energy in the form of work which he had to supply to raise the temperature of a certain mass of water.

\* An exothermic reaction is one which, when carried out at constant temperature, gives out heat.

Knowing the amount of heat which he would have had to supply to obtain the same temperature rise, he calculated the constant of proportionality, known as the 'mechanical equivalent of heat', relating the work supplied to the heat to which it was equivalent. Subsequent investigations on other situations in which work is converted into heat have shown that, provided the effect of the work is purely one of raising the temperature of the system, the constant of proportionality has always the same value. We might say that conversion of work into heat can be carried out with 100% efficiency. In the SI system of units advantage has been taken of this fact, and the mechanical equivalent of heat set equal to unity, so that both heat and work can be measured in the same units, namely joules. Its constancy, in all circumstances, is also the essential content of the first law of thermodynamics which we consider in Chapter 2.

In contrast, our experience with the conversion of heat into work always leads to a conversion efficiency of less than 100%. For example, the mechanical energy provided by a steam turbine is often only 40–50% of the thermal energy supplied to raise the steam. Some of the inefficiency arises from mechanical difficulties such as friction, but this represents only a small part of the loss. There is, therefore, something more fundamental involved, and we shall see what this is when we come to consider the second law of thermodynamics.

It is often said that work represents a higher form of energy than heat. That is, we can always convert a given quantity of work into heat whenever we wish, but once we have got the energy as heat, we cannot go back to work without some losses in the process. The maximum efficiency of the latter process we consider in Chapter 3 under the heading 'availability'.

Thermodynamics is a quantitative subject and in the earlier part of this book we are concerned with calculating the heat or work which is transferred to or from a system. To take a concrete example, let us assume that we wish to know how much work we need to supply a compressor in order to compress a given amount of air. We have the choice of either measuring this at the motor, using a dynamometer, or of calculating it from the known dimensions, etc., of the compressor. The first method involves an investigation of what is happening in the surroundings, the second of what is happening in the system. Since both measure the same quantity we can choose whichever is the more convenient. However, only in a few cases can we do the necessary calculations on the system, and we are often forced to examine what is happening in the surroundings.

When a particular system is undergoing a certain process, we can transfer heat and/or work to or from it. Since it is more convenient to treat heat and work as algebraic quantities in calculations, we require a convention as to their sign. Whenever heat, symbol  $Q$ , or work, symbol  $W$ , is transferred to the system from the surroundings, we shall treat it as positive. Thus, for example, a system which is losing heat to its surroundings will be characterised by  $Q$  having a negative value. This convention is the one recommended by the

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International Union of Pure and Applied Chemistry (IUPAC) and is used by many authors. Unfortunately, however, many other authors, particularly of the older textbooks, adhere to this convention for  $Q$  but use the opposite one for  $W$ .

There is a second convention for  $Q$  and  $W$ . In solving a problem it is frequently convenient to set up a differential equation to represent an infinitesimal change in the process, and then to evaluate the total process by integration. This equation may involve the differentials of state functions such as  $dV$  and  $dP$ , together with differentials of the non-state functions heat and work. The latter we represent by  $dQ$  and  $dW$  as a reminder that they are not state functions.  $dQ$  and  $dW$  may be integrated just as  $dV$  and  $dP$  but, whereas the value obtained by integration of a state function (such as  $dV$  or  $dP$ ) depends only on the initial and final states of the system, the one obtained by integration of  $dQ$  or  $dW$  depends also on the route taken during the process.

### 1.6 Work

The transfer of mechanical energy, as work, can take place in many ways. For example, in the generation of electricity, mechanical energy is first produced by a steam turbine. This is transferred, as work, to an electrical generator. This, in turn, produces electricity which can perform electrical work. If we use this electrical work to drive a motor, then once more we have mechanical energy. This interconversion of one form of work into another can, in principle, be carried out with 100% efficiency provided we can eliminate losses from friction, etc. This interconvertibility is characteristic of all forms of work.

Perhaps the simplest situation in which we can calculate the work required to bring about a process, is the lifting of a mass against the force of gravity. If the mass  $m$  is raised a distance  $h$ , then the increase in the potential energy of the mass, and therefore the work required to raise it is

$$W = mgh \quad (1.6)$$

where  $g$  is the acceleration due to gravity. If, however, the mass were not constant, as would be the case if we used for the mass a leaky bucket which, though initially full of water, steadily lost its contents, we should have to break down the process into a large number of small steps, each of height  $dh$  and for which the small amount of work required would be

$$dW = mg \, dh \quad (1.7)$$

where  $m$  would now be a variable quantity. The total work required is obtained by integration

$$W = \int dW = g \int m \, dh \quad (1.8)$$

The expression for  $dW$  is of the form

$$\begin{aligned} dW &= \text{force} \times \text{distance through which the force moves} \\ &= mg \times dh \end{aligned} \quad (1.9)$$

and this is what we generally find for all of the various types of work which we consider.

Since, in principle, one form of work can be converted into another with 100% efficiency, we frequently have recourse to the work done in raising a mass against gravity as a device for calculating the work involved in other, more complex, situations. All we require is that we can postulate some machinery which will convert the actual work into 'raising against gravity' work.

## 1.7 Work in a closed system

The commonest situation involving work in a closed system is the one in which a three-dimensional system expands or contracts against an external pressure. For simplicity, let the system be a rectangular object of sides  $a \times b \times c$ , and let the external pressure which is supplied by the surroundings be  $P_{\text{ext}}$ . Since pressure is, by definition, the force per unit area acting on the surface and normal to it, the total force acting on one side of the box  $a \times b$  is  $P_{\text{ext}}ab$ , Figure 1.3. If now dimension  $c$  increases to  $c + dc$  the surroundings are 'pushed back' a

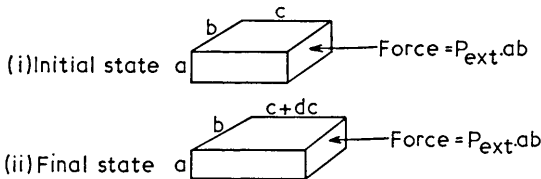


Figure 1.3. The expansion of a rectangular object

distance  $dc$  and the system (the box) does work on the surroundings numerically equal to  $P_{\text{ext}}ab \, dc$ .

On our convention of the work done on the system being counted as positive, the work done on the system by the surroundings during the infinitesimal expansion process is

$$dW = -P_{\text{ext}}ab \, dc \quad (1.10)$$

Since the increase in the volume of the box

$$dV = ab \, dc \quad (1.11)$$

we can simplify (1.10) to

$$dW = -P_{\text{ext}} \, dV \quad (1.12)$$

where  $dV$  is the change in volume of the system, and not of the surroundings.

It is readily seen that if the other two dimensions of the box increase in a similar manner, the work done on the system is given by similar equations, and provided that  $P_{\text{ext}}$  is the same on all faces of the box, summing the various work terms gives (1.12) again, where  $dV$  now refers to the total change in the volume of the box, no matter on which face or faces it takes place. A simple extension to the argument shows that (1.12) holds for systems of arbitrary shape.

## 14 HEAT AND WORK

### Exercise

Show that (1.12) applies for the work done when a sphere expands uniformly against an external pressure.

If the system expanding against an external pressure is a rigid cylinder containing gas sealed by a frictionless piston, Figure 1.4, then the only external pressure we need concern ourselves with is the one acting on the piston.

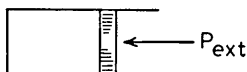


Figure 1.4. The expansion of gas against an external pressure

Comparison with the three-dimensional object expanding in one dimension which we considered above leads again to

$$dW = -P_{\text{ext}} dV \quad (1.12)$$

The pressure of the gas in the cylinder is irrelevant in evaluating the work done by the surroundings on the system (the gas). Any displacement of the piston means that work is done as given by (1.12). In practice, if the gas pressure inside differs from that outside, then some mechanical restraints or catches are required to hold the piston in any chosen position, but the operation of such a catch need not involve the performance of a significant amount of work.

An alternative calculation of the work performed by a gas expanding against an external pressure can be made by placing the cylinder so that its axis is vertical and, instead of supplying a restraining force on the piston from an external pressure, supplying an equal force by placing a mass  $m$  on the piston, Figure 1.5. If we assume that the pressure of the surrounding atmosphere is

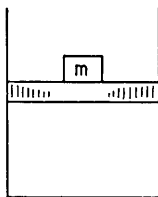


Figure 1.5. The expansion of gas against a gravitational force

zero, and that the piston is weightless and of area  $\mathcal{A}$ , then, with the value of  $m$  given by

$$mg = P_{\text{ext}} \mathcal{A} \quad (1.13)$$

the force on the piston will be the same as before. A displacement of the piston upwards by a distance  $dh$  raises the mass  $m$  by this same amount and thereby does work on the mass, of  $mg dh$ . Since we consider the mass as part of the surroundings, we have once more the work done by the surroundings on the

system

$$\begin{aligned}
 dW &= -mg \, dh \\
 &= -P_{\text{ext}} \mathcal{A} \, dh \\
 &= -P_{\text{ext}} \, dV
 \end{aligned}
 \tag{1.14}$$

If there are no pressure gradients within the cylinder and the (uniform) pressure  $P$  of the gas within it is equal to the external pressure  $P_{\text{ext}}$  we can write

$$dW = -P \, dV \tag{1.15}$$

and now *both* properties on the right hand side of this equation are properties of the system.

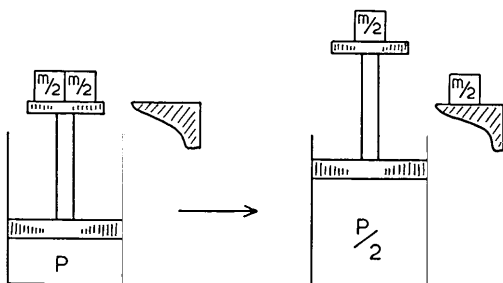


Figure 1.6. Raising a mass by means of expansion of a gas

Consider gas at pressure  $P$  in a cylinder, Figure 1.6, and sealed by a weightless piston which can slide freely without friction. Again we take the surrounding pressure as zero. If the gas pressure is to be equal to the external pressure, here supplied by a mass  $m$  on the piston of area  $\mathcal{A}$ , then

$$P = mg/\mathcal{A} \tag{1.16}$$

Let us slide off sideways on to a suitably placed platform one half of the mass  $m$ . This operation clearly does not involve the performance of work. The forces on the piston are now unbalanced and it rises until the pressure of the gas is  $\frac{1}{2}P$ , when the internal pressure is once more balanced by the external force supplied by the mass  $\frac{1}{2}m$ , which is equivalent to an external pressure

$$P_{\text{ext}} = \frac{1}{2}mg/\mathcal{A} = \frac{1}{2}P \tag{1.17}$$

The calculation of the work done by the surroundings on the system we have already done in differential form (1.14), and integration of this gives

$$\begin{aligned}
 W &= - \int_{V_1}^{V_2} P_{\text{ext}} \, dV \\
 &= -P_{\text{ext}}(V_2 - V_1) \\
 &= -\frac{1}{2}P(V_2 - V_1)
 \end{aligned}
 \tag{1.18}$$

where  $V_1$  is the initial volume of the gas and  $V_2$  the final volume.

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Although the external pressure is equal to the internal (gas) pressure (i) at the beginning when  $P_{\text{ext}} = P$ , and (ii) at the end when  $P_{\text{ext}} = \frac{1}{2}P$ , it is clearly not so during the expansion, and we cannot replace  $P_{\text{ext}}$  in (1.18) by the internal pressure as an alternative method of integration. However, we can imagine that the mass  $m$  is divided into a large number of parts, as it would be if it were formed from a pile of fine sand, Figure 1.7. Consider first the case in which the process takes place adiabatically, that is the system neither gains nor loses

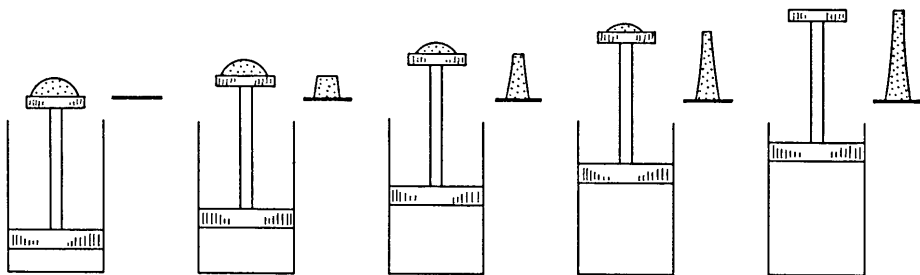


Figure 1.7. Raising a pile of sand by expansion of a gas

thermal energy from the surroundings. If we remove the grains of sand from the piston one by one, piling them so that they remain at the level at which they are removed from the piston, we have the sequence depicted. Since the removal of any one grain unbalances the forces exerted on the piston only by a very small amount, and only a small displacement of the piston is needed to restore equilibrium, we can consider the device as being essentially in equilibrium all of the time. Let the mass of sand on the piston be  $m$  when the height of the piston is  $h$ , and the mass of each grain of sand removed from the piston be the differential quantity  $dm$ , and let  $dh$  be the corresponding distance which the piston rises. Then the work done by the surroundings (sand) on the system (gas) by the removal of one grain is

$$\begin{aligned} dW &= -mg \, dh \\ &= -P_{\text{ext}} \, dV \\ &= -P_{\text{gas}} \, dV \end{aligned} \quad (1.19)$$

where we have used the fact that  $P_{\text{ext}}$  and  $P_{\text{gas}}$  differ only infinitesimally during the removal of one grain. Thus, for the whole process in which a substantial amount of sand is removed from the piston, the work done on the system is

$$\begin{aligned} W &= \int dW \\ &= - \int P_{\text{gas}} \, dV \end{aligned} \quad (1.20)$$

This process is essentially equivalent to a *single* expansion stroke of the engine shown in Figure 1.8, in which the piston drives a flywheel via a crank



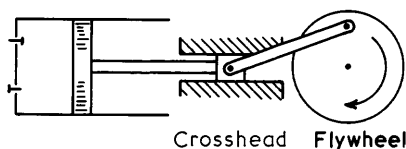


Figure 1.8. Reciprocating expansion engine

and crosshead. If a source of high pressure gas is momentarily connected to the cylinder when the piston is near the cylinder head (in an internal combustion engine this is done by igniting a hydrocarbon/air mixture), the forces on the piston will be approximately balanced during the expansion stroke, the compressive forces within the connecting rod varying in such a manner as to keep them so. In view of the interconvertibility of mechanical work, the work done during one stroke of this rather complicated machine can be calculated from the changing properties of the gas by solving the much simpler problem of a mass of sand being raised against gravity.

A process of this type, in which the system goes through a series of infinitesimally small steps, keeping essentially at equilibrium all the time, we call a *reversible* process. It is reversible in the sense that if we replace the grains of sand, one by one, on top of the piston, taking them from the pile by the side in the reverse order to that in which they were placed there, the process can be made to reverse itself. It retraces exactly the path which it took during expansion. No additional work is needed to lift on the grains of sand as all their movements are sideways. At the end of the reverse process the device is indistinguishable from its state at the beginning. Contrast this situation with that needed to reverse Figure 1.6. Any reversal requires that we first lift the mass  $\frac{1}{2}m$  from the platform on to the piston, and this requires us to supply work. At the end of the process, therefore, the surroundings have lost energy and so the conditions for reversibility are not fulfilled. We say that such a process is *irreversible*.

For the reversible process described above, we can plot the instantaneous values of pressure and volume of the gas on a  $P$ - $V$  diagram represented in Figure 1.9a by the line 1-2. We call this the path of the process, and it follows from (1.20) that the work done on the gas is the negative of the area under line  $1 \rightarrow 2$ .

If the reversible process is not adiabatic, and heat is supplied to the gas as it is expanding, the instantaneous values of pressure will be greater than in the adiabatic case, and we must expect the value of the integral in (1.20) to be numerically larger. Again we analyse the situation by using the pile of sand device, taking off the grains adiabatically one by one, but in between the removal of each grain we supply a small amount of heat, keeping the volume constant as we do it. The path of this process is shown in Figure 1.9b and by making the steps smaller and smaller, we have in the limit the situation shown

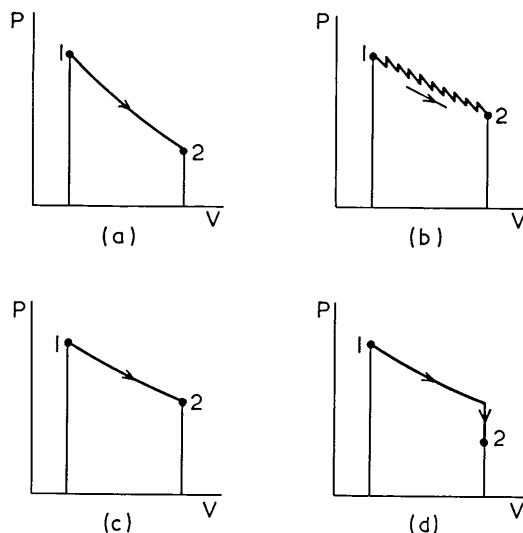


Figure 1.9. Reversible expansion processes

in Figure 1.9c, which represents a process in which heat is supplied continuously to the gas as it expands. In Figure 1.9b the number of steps is arbitrary, but the shape of each step, and in particular the length of each vertical constant volume element of it, is determined by the amount of heat supplied to the system as it expands. If heat is removed they will, of course, occur in the opposite direction.

The process depicted in Figure 1.9b is reversible in the same way that the corresponding adiabatic process was. The only difference between the two return paths is that in this latter example we must remove exactly the same amount of heat from the gas as we supplied in the forward path at each particular step in the process. We defer consideration of how heat can be transferred reversibly until Chapter 3. It is sufficient, at this point, to know that, as far as the system is concerned, there is no problem in the reversible absorption of heat provided that we do not allow temperature gradients to develop within the gas.

Since no work is done during the heating stages in Figure 1.9b (there is no change in volume and so  $P dV$  is zero) all the work comes from the adiabatic stages, and once more we find that the total work done on the gas is equal to the negative of the area under the line  $1 \rightarrow 2$ . This applies also to the limiting case in Figure 1.9c. Now if we extend the process shown in c to d, that is if we cool the gas at constant volume until the final values of  $P$  and  $V$  are the same as in a, no additional work is done, and the total work done remains equal to the negative of the area under the curve. This area, in Figure 1.9d, is not equal to that in Figure 1.9a, in spite of the fact that the initial and final conditions, 1 and 2, are the same in each case.

Thus we see that the work accompanying a change in volume in a closed system is  $-\int P dV$  whatever the path and whatever the process. It is a result which is applicable without exception to all closed system reversible processes and, for example, applies even to the expansion part of the work (usually termed  $P$ - $V$  work) in a process which involves, in addition, electrical work. A battery would form one such system.

The argument given shows also, see Figure 1.9b, that it is always possible to devise a reversible route between any two states provided that both can be represented uniquely on a  $P$ - $V$  diagram. This latter requires that, for a fixed amount of material, only two additional independent variables, such as  $P$  and  $V$ , are necessary to determine the state of the system. If the system is, say, a binary mixture, the composition, if it changes, must be considered as an additional independent variable, and the points 1 and 2 in Figure 1.9 no longer represent unique states. The figure therefore tells us nothing about the existence, or otherwise, of a reversible route between them, but, if we have other evidence which shows that one or more reversible processes in a binary system do indeed follow the route as represented on the  $P$ - $V$  diagram of Figure 1.9, then the work done is  $-\int P dV$ , as indicated.

Although the work of the type we have been considering ( $P$ - $V$  work) is by far the most important encountered in chemical engineering, it is not the only one. We examine here one other example: electrical work. If the surroundings supply electrical energy to a system then we can write that the work done by them on the system in taking an infinitesimal charge  $dq$  through a potential difference  $\varphi$  is

$$dW = \varphi \cdot dq = \varphi i \cdot dt \quad (1.21)$$

where we have used that  $dq = i \cdot dt$  ( $i$  = current and  $t$  = time). That the energy supplied is work rather than heat is apparent from the fact that a motor can be used to convert the electrical energy into mechanical energy with 100% efficiency, assuming that there are no losses from friction, etc.

## 1.8 Work in a steady state flow system

A machine operating under steady flow conditions must produce, or be supplied with, work at a constant rate. Such machines are usually rotary, e.g. a compressor, a fan, a blower or a turbine. These are used to compress a fluid by the input of work, or, in the case of expanders, to produce work from a source of high pressure fluid. A thermodynamic analysis shows that these machines are all essentially equivalent, a fact which we illustrate by considering just two machines: (a) a turbine and (b) a reciprocating compressor.

### Turbine

A turbine is a steady state flow device for obtaining work from a source of high pressure fluid. It consists of a series of banks of blades fixed alternately to the

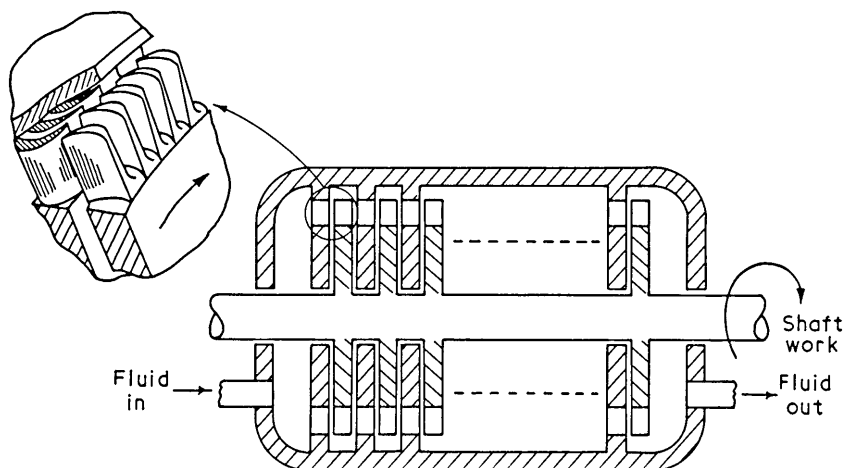


Figure 1.10. Turbine (schematic)

casing and the rotor, see Figure 1.10. The blades are shaped so that, when fluid flows through the turbine, the rotor turns and does work outside the turbine. This useful work is called *shaft work* or, more briefly just *work*. Shaft work is not the only form of mechanical energy which is involved in the operation of a turbine. The moving fluid has kinetic energy and as its speed may change as it passes through the turbine, so also will its kinetic energy.

In general, if we wish to determine the amount of shaft work performed by a given turbine, we can do this only by attaching a suitable machine to the turbine shaft and measuring how much work is done on this external machine per unit mass of fluid flowing through the turbine. A suitable external machine would be a dynamometer, and since this is equivalent to raising a weight against gravity, we can in effect convert the turbine output into 'raising against gravity' work. Clearly, this approach to the analysis of the operation of a turbine does not involve a knowledge of what happens inside the turbine casing, we are examining only the interaction between the 'system' and its 'surroundings'. However, just as in certain closed systems it is possible to calculate the work from a knowledge of the behaviour within the system itself, so also is it possible to determine shaft work in certain steady state flow systems by considering only the system. A full study of this belongs more properly to the field of fluid mechanics, but we consider here sufficient of it for our purposes.

We take as our example an idealised version of an impulse turbine, since this is the simplest from a mathematical point of view. Consider one flow channel through the first stage of the turbine, as shown in Figure 1.11 (a fixed plus moving pair of banks of blades forms a stage). The fixed blades form a converging channel, usually termed a nozzle, so that the fluid flowing through is accelerated, driven by the pressure drop across it. The emerging fluid has, therefore, a higher kinetic energy, but a lower pressure than the ingoing fluid.

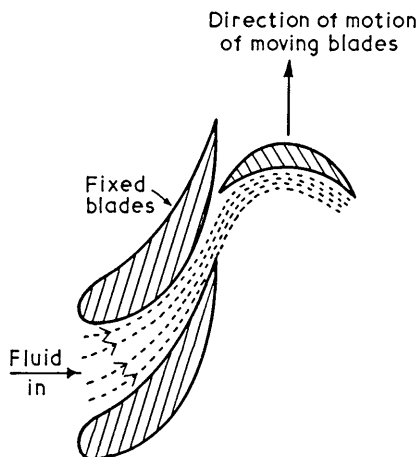


Figure 1.11. Turbine (detail) showing flow of fluid through the blades

This accelerated fluid impinges on the particular blade in its path—the blade being attached to the rotor—and drives it round, thus contributing to the shaft work from the turbine. The fluid loses kinetic energy in the process. In an impulse turbine, it is usually arranged that (i) all of the kinetic energy gained in the flow through the fixed blades is given up to the moving blades immediately following, and (ii) there is no pressure drop in the fluid flowing through the moving blades, that is, all pressure drops take place in the fixed bank of blades.

If there are no frictional losses, the flow is considered 'one-dimensional', even if the channel is curved, and we can calculate the kinetic energy which the fluid stream gains on passing through the fixed blades and, if all of it is transferred to the moving blades, this is equal to the shaft work which the turbine performs. Consider an element of fluid within a nozzle, Figure 1.12. The input velocity of the fluid entering the element is  $\mathcal{V}$ , and the exit velocity  $\mathcal{V} + d\mathcal{V}$ . If  $\mathcal{A}$  is the cross sectional area at that point then,

$$\text{the net force on this element of fluid} = -\mathcal{A} dP \quad (1.22)$$

and

$$\text{the mass flow rate, } \dot{m}, = \mathcal{A}\mathcal{V}/v \quad (1.23)$$

where  $v$  is the volume of the fluid per unit mass under the conditions of pressure and temperature prevailing within this element of the nozzle. From the laws of

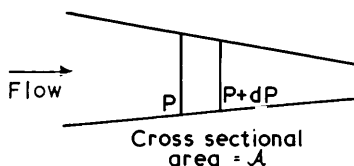


Figure 1.12. Fluid flow through an element of a nozzle

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mechanics the net force on the element of fluid must be equal to the rate of change of momentum. Thus

$$\begin{aligned} -\mathcal{A} dP &= \dot{m} d\mathcal{V} \\ &= \mathcal{A} \mathcal{V} / v d\mathcal{V} \end{aligned} \quad (1.24)$$

or

$$v dP + \mathcal{V} dv = 0 \quad (1.25)$$

We multiply this equation by  $\dot{m}$  and integrate over the whole length of the turbine ( $\dot{m}$  is constant during this integration), obtaining

$$-\int_{\text{input}}^{\text{output}} \dot{m} v dP = [\frac{1}{2} \dot{m} \mathcal{V}^2]_{\text{input}}^{\text{output}} \quad (1.26)$$

and we observe that the right hand side of this equation is the rate of increase in kinetic energy of the fluid as it passes through the nozzle. We can write the left hand side of (1.26) in terms of the volumetric flow rate  $\dot{V}$  by noting that  $\dot{V} = \dot{m}v$ , but an even more general formulation leaves unspecified the time taken for a given mass of fluid to flow through the nozzle, viz:

$$-\int_1^2 \dot{V} dP = KE_{\text{out}} - KE_{\text{in}} \quad (1.27)$$

where  $P_1$  and  $V_1$  refer to the pressure and volume of the given mass of gas at the input to the nozzle and  $P_2$  and  $V_2$  refer similarly to the output.

For a frictionless impulse turbine the gain in kinetic energy by the fluid as it passes through the nozzle is equal to shaft work produced by the complete stage of the turbine of which it is part. Thus, following the convention given in Section 1.5, that we consider work supplied to a system as positive,

$$\text{the work supplied to the turbine} = + \int_1^2 \dot{V} dP \quad (1.28)$$

In a multistage turbine, the output of one stage immediately forms the input to the next stage. Adding the various integrals gives

$$\text{Total work} = \int_1^a \dot{V} dP + \int_a^b \dot{V} dP + \cdots + \int_z^2 \dot{V} dP = \int_1^2 \dot{V} dP \quad (1.29)$$

where the limits 1 and 2 now refer to the overall  $P$  and  $V$  for the whole turbine and the limits  $a, b, c$ , etc. refer to the values at the intermediate stages.

We see that in a multistage turbine it is not necessary for all the kinetic energy gained by the fluid in moving through one nozzle to be entirely converted into shaft work by the blades immediately following, for any excess kinetic energy is not lost, but merely carried over to the next stage. The situation regarding the kinetic energy of the fluid entering the first stage and leaving the last stage is more complicated. If the kinetic energy of the input stream equals that of the output stream then there is no net effect on the magnitude of the shaft work which remains  $\int_1^2 \dot{V} dP$ . If, however, there is an

imbalance, the deficiency must be made up from the shaft work, that is

$$\text{shaft work} = \int_1^2 V dP + KE_{\text{out}} - KE_{\text{in}} \quad (1.30)$$

Similarly, if the input and output streams of the turbine are at different levels, work must be done against gravity in raising the fluid; this too must be done at the expense of the shaft work, giving

$$\text{shaft work} = \int_1^2 V dP + KE_{\text{out}} - KE_{\text{in}} + PE_{\text{out}} - PE_{\text{in}} \quad (1.31)$$

Fortunately, in the majority of steady state flow systems of interest to chemical engineers, the changes in kinetic energy and potential energy are small compared with the other energy changes. In such cases we may neglect these smaller terms and this is implied throughout this book unless a statement is made to the contrary.

The machine we have been considering as a turbine, that is a device for producing work from a source of high pressure fluid, can be operated in reverse, when it becomes a turbo-compressor. This requires a source of low pressure fluid to be connected to what was the output side of the turbine and an external source of work to be connected to the rotor shaft. Provided that the same assumption of frictionless flow through the machine remains true, the analysis of the turbo-compressor is the same as that of the turbine; the magnitude of the various forces remains the same, but they act in the opposite direction. The shaft work to be supplied to the compressor is, therefore, also

$$\int_1^2 V dP + KE_{\text{out}} - KE_{\text{in}} + PE_{\text{out}} - PE_{\text{in}} \quad (1.32)$$

It is not the negative of (1.31), since what was considered the input stream for a turbine is the output stream for a turbo-compressor, whereas subscript 1, by convention, always refers to the input stream of whatever device is under investigation. If kinetic and potential energy can be neglected

$$\text{Shaft work} = \int_1^2 V dP \quad (1.33)$$

These machines are called reversible since when operated in the reverse direction all aspects of the process are retraced in the opposite direction. Thus, for example, the magnitude of the heat and work, pressure and temperature changes, will remain the same, but are of opposite sign. In a practical turbo-compressor or turbine there will be frictional losses and if these assume significant proportions the machines are not reversible. A given turbo-compressor (say) may in principle be operated in reverse as a turbine; if there is friction, in neither case is the shaft work given by  $\int_1^2 V dP$ . We may compare this situation with that prevailing in the closed system where the work to be supplied is equal to  $\int_1^2 -P dV$  only if the process is reversible.

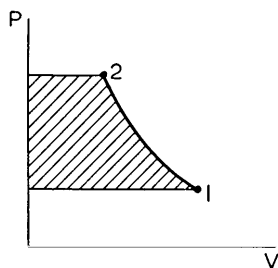


Figure 1.13. Work done in a steady state flow process

Evaluation of the shaft work  $\int_1^2 V dP$  requires a knowledge of how the volume per unit mass  $v$  ( $V = mv$ ) varies with pressure  $P$  along the length of the turbine or turbo-compressor. Once this path is known, work may be evaluated as the area shown shaded in Figure 1.13.

### Reciprocating compressor

Figure 1.14 shows in diagrammatic form a reciprocating compressor which has spring loaded inlet and outlet valves. The vessels on the inlet and outlet pipes are for damping out the pressure fluctuations which would otherwise occur.

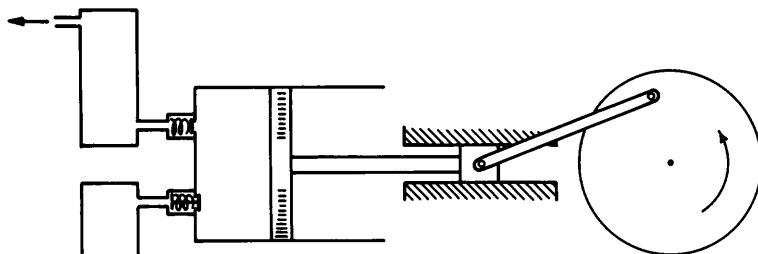


Figure 1.14. Reciprocating compressor

Thus, although compression of the fluid in the cylinder is carried out in 'batches', provided the frequency of compression strokes is high enough, the overall performance of the cylinder plus pulsation dampeners results in steady state flow compression. In a modern reciprocating compressor the approximation is a good one, even if the pulsation dampeners are only lengths of tubing.

As for the turbine, we can always determine the work required for compression by examining the work supplied by the motor driving the compressor. However, we can again in certain cases determine it from what happens within the compressor itself.

In an idealised reciprocating compressor, we assume that the piston displaces completely all material within the cylinder and thus, at the beginning of the intake stroke, the volume and pressure can be represented as point 4, Figure



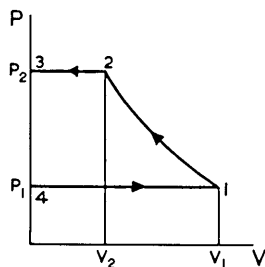


Figure 1.15.  $P$ - $V$  diagram for a reciprocating compressor ( $V$  = instantaneous volume of cylinder)

1.15. During the intake stroke the pressure is maintained essentially constant, represented by the horizontal line 4–1. Once the compression stroke begins, point 1, the input valve closes and the pressure rises until the output pressure  $P_2$  is reached, point 2. The output valve then opens and the compressed gas displaced at an essentially constant pressure  $P_2$ .

The work done per cycle may be evaluated as the sum of the various steps, but this is complicated by the fact that, although step 1–2 is closed and no work is done in step 3–4, steps 4–1 and 2–3 are open and the gas flows non-steady state. However, since the piston is solely responsible for the transfer of work to the gas, we can, where necessary, examine the forces on the piston as a means of determining these particular work terms.

We consider the case of a compressor in which all movements of the piston are carried out reversibly (see Section 1.7 on reversible processes in a closed system)—an adequate approximation if a flywheel is interposed between the piston and driving motor—and where the external pressure is zero. The only forces of the piston arise, therefore, on one side from the gas being compressed, and on the other from the compressive forces in the connecting rod. In a reversible process they are equal. Thus, during the intake stroke 4–1, if  $\mathcal{A}$  is the cross sectional area of the piston, the work done on the piston is equal to the product of the stroke ( $V_1/\mathcal{A}$ ), and the force on the piston ( $P_1\mathcal{A}$ ), that is

$$\text{Work done on the piston by the gas} = V_1/\mathcal{A} \cdot P_1\mathcal{A} = P_1 V_1 \quad (1.34)$$

and similarly, during the displacement stroke 2–3,

$$\text{Work done by the piston on the gas} = P_2 V_2 \quad (1.35)$$

Using the result already obtained for the work done during step 1–2 (a closed system), the total work done by the piston during one complete cycle, which is equal to the work input to the gas, is

$$\begin{aligned} W_{\text{cycle}} &= -P_1 V_1 + \int_1^2 -P \, dV + P_2 V_2 \\ &= \int_1^2 V \, dP \end{aligned} \quad (1.36)$$

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The final step, identifying  $W_{\text{cycle}}$  with  $\int_1^2 V dP$ , is made by examining the areas in Figure 1.15 which represent  $P_1 V_1$ ,  $\int_1^2 -P dV$  and  $P_2 V_2$ . The work done on the gas per cycle is, therefore, represented as the area enclosed by 1–2–3–4.

### Exercise

Show that (1.36) still holds when the pressure external to the compressor is  $P_{\text{atm}}$ , and constant.

## 1.9 Conclusions

We can generalise the results of Sections 1.7 and 1.8 as ‘in all reversible processes, the work done in closed and steady state flow systems is  $-\int_1^2 P dV$  and  $\int_1^2 V dP$  respectively, provided that changes of kinetic energy can be neglected’. Although formally we have proved this only for the systems discussed there, it is a result which has been found to hold for all reversible processes. Thus, for example, in a real reciprocating compressor, the piston cannot displace all of the gas as some is trapped in the ports leading to the inlet and outlet valves. Figure 1.15 no longer represents accurately the compression process, for the volumes of gas within the compressor at points 3 and 4 are not zero. Nevertheless, as we shall show in Chapter 5, if the compressor acts in a reversible manner, the work done is still expressible as  $\int_1^2 V dP$ . If the process is not reversible, we cannot calculate the work by these methods. In the case of a closed system we can use  $\int_1^2 -P_{\text{ext}} dV$  but this has no steady state flow counterpart. For these irreversible steady state flow systems we can determine the work only by examining what is happening in the surroundings, by the use of a dynamometer or similar device, or by conversion of the work into heat and the measurement of this.

Finally, we note that (1.36) explains why the work involved in a closed system process is not normally equal to the shaft work involved in the corresponding steady state flow process. The difference between these two work terms is the net work,  $(P_2 V_2 - P_1 V_1)$ , often called flow work, required to get the material into and out of the steady state flow device and whether this is positive or negative depends entirely on the relative magnitude of  $P_2 V_2$  and  $P_1 V_1$ .

## Problems

1. An ordinary electrically powered domestic refrigerator is operated in a closed, thermally insulated room. What happens to the ‘average temperature’ in the room (a) if the refrigerator door is kept shut, and (b) if it is left open?
2. One of the largest Newcomen ‘atmospheric’ steam engines built in the eighteenth century used a cylinder of 1.8 m diameter, fitted with a piston with a

stroke of 3 metres. In operation, the cylinder was first filled with steam at atmospheric pressure to extend the piston fully, and then a spray of cold water was injected to condense the steam very rapidly, leaving the cylinder essentially evacuated. Atmospheric pressure would then push the piston into the cylinder and, by means of suitable attachments to the piston rod, do work. Taking atmospheric pressure as 1 bar, how much work could an ideal Newcomen engine do per stroke? If the engine operates at 10 strokes per minute, what is the power?

3. The pressure on 1 kg of silver is increased at a constant temperature, from 1 to 1000 bar. The density at 1 bar is  $10\,500\text{ kg m}^{-3}$  and the compressibility constant at  $10^{-11}\text{ m}^2\text{ N}^{-1}$ . Calculate the work of compression.

4. A pump is used to deliver  $0.001\text{ m}^3\text{ s}^{-1}$  of hydraulic oil, assumed incompressible, at a pressure of 1 kbar ( $=1000\text{ bar}$ ) from a reservoir at 1 bar. What power is required to operate it?

5. A turbo-compressor is used to compress carbon dioxide from 1 to 20 bar. Assuming that the process can be carried out reversibly and isothermally at 300 K, calculate the work required per mole, given that at 300 K the  $P$ - $V$ - $T$  properties of carbon dioxide follow the equation  $P(v-b)=RT$  with  $b=-0.000\,11\text{ m}^3\text{ mol}^{-1}$ .

## Answers

1. If the compressor motor runs continuously, the average temperature rises by the same amount in both (a) and (b) since the rate of supply of electrical energy (the only energy input) is unchanged. If the motor runs intermittently under thermostatic control, the temperature rise will be greater in (b) than in (a) since the 'on' period is greater.

2.  $\text{Work} = -P_{\text{ext}} \Delta V = -760\text{ kJ}$ .  
 $\text{Power} = 127\text{ kW}$ .

3.  $\text{Work} = -\int P\,dV = 4.75\text{ J}$ .

4.  $\text{Work} = \int V\,dP$ , hence  $\text{power} = 99.9\text{ kW}$ .

5.  $\text{Work} = \int V\,dP = RT \ln(P_2/P_1) + b(P_2 - P_1) = 7.26\text{ kJ mol}^{-1}$

## Note

1. D. S. L. Cardwell, *From Watt to Clausius, the rise of thermodynamics in the early industrial age*, Heinemann, London, 1971.