# Topic 5: Thermodynamic Processes

## 5.1 Introduction

We have said that heat and work are path-dependent quantities: the amount of heat you need to supply to a system, or the amount of work you need to do, to take it from state A to state B depends on the path you take to get there. But what, in this context, do we mean by “path”?

Let’s consider an ideal gas, with equation of state . (The same ideas will apply to any system, but the variables we use to specify the system may be different.) For a fixed mass of gas, the state of the gas is defined by any two of the variables , because we can always use the equa­tion of state to find the third. So we can specify our initial and final states as points on a plot of *P* against *V*. As the gas moves from state A to state B, it will pass through intermediate states, each of which can also be specified as a point on the *PV* plot. Therefore, any path between A and B is repre­sented by a line joining A and B on the plot, and conversely any line joining A and B on the plot is a possible—if not necessarily practical—way in which the gas could be taken from state A to state B by supplying some combination of heat and work.

In general, these paths will not be analytically calculable—we’d have to model the system in a compu­ter to work out exactly how to move the gas from state A to state B along some random wiggly path. Therefore, we restrict our attention to those paths that lead to simple equations that we can solve. This is, of course, what the 19th century developers of thermodynamics also did, since they had no computers to do the calculations for them. Real applications of thermodynamics, e.g. real engines, do not follow these simple paths, but it is often possible to construct an idealised version of the engine that does, and this will give us some insight into how the engine performs. Later in the course we will look at idealised versions of some typical engines, including steam engines, petrol engines and diesel engines.

## 5.2 Thermodynamic functions of state

To define the state of a system, we have to specify its properties. The properties that are useful for this are the ones that do not depend on the prior history of the state: for example, we cannot use the work done on a system to define its state, because the amount of work that has been done to put the system into some state A depends on its history. Properties of a system that depend only on its current state and not on its history are called **functions of state**. Examples of functions of state include pres­sure, temperature, volume, mass, density, magnetisation, electric charge, etc. Examples of variables which are *not* functions of state include, as we have seen, history-dependent variables such as work done and heat supplied, and also things that can change without changing the state, such as the kinetic energy of one atom of a gas (the temperature depends on the *average* kinetic energy, not the kinetic energy of one individual particle). The properties of a particular system may create rela­tion­ships be­tween functions of state, and these are called **equations of state**. The only equation of state we are using in this course is the ideal gas law, but there are many others: for example, numerous modi­fi­cations of the ideal gas law designed to make it a better representation of real gases (the best known of these is the van der Waals equation of state, but there are many others), equations of state for nuclear matter, used to model the behaviour of neutron stars in astrophysics, equations of state for solid materials used to model their behaviour in the context of engineering or geology, and so on.

## 5.3 Reversible and irreversible processes

If a system is left undisturbed for a long time, it will settle into equilibrium with its surroundings. In a system in equilibrium, all the functions of state have fixed, stable, well-defined values. If we slowly make an incremental change to one of the properties, say volume, the system will move from the ori­ginal equilibrium to a new, very slightly different one. We can move it back to its original equi­li­brium by reversing the change, or we can continue to move it towards a new equilibrium in a different state. A slow process like this, where the system is never significantly out of thermal equilibrium, is called a **quasistatic process**.

In many cases, quasistatic processes are **reversible**: that is, if we reverse the direction of change, we can move the system back to its original state along the same path. This is not always true: for exam­ple, processes that involve friction are never reversible—there’s no way that the heat you generated as you dragged that large box over the carpet can ever be collected together and reassembled into the work that was expended in doing the dragging, however slowly you did it.

Changes of state that involve *rapid* changes to one or more functions of state are obviously not quasi­static, and in general are **irreversible**: for example, if you were to expand a volume of gas slowly by moving a piston, that would be reversible, but if you expand it rapidly by setting off an explosion, that would be irreversible. Most real thermodynamic processes are irreversible—you cannot refill your petrol tank by reversing the action of your engine. When we study the action of heat engines later in the course, we will use idealised paths on the *PV* plot which *are* quasistatic and irreversible.

Given that the laws of physics are reversible, it may seem surprising that so many real-world processes are not. Later in the course we will explore this using the concept of **entropy**, and next year you will study the microscopic-level interpretation of entropy as part of statistical mechanics.

## 5.4 The differential form of the First Law

In order to calculate the heat supplied and work done along a particular path on the *PV* plot, we will use the differential form of the First Law. For an infinitesimal change d*U*, we have

The symbol đ indicates an **inexact differential**. For an **exact differential** such as d*U*, we can write   
regardless of exactly how we do the integral. This is the same thing as saying that *U* is a function of state. On the other hand, *Q* and *W* are not functions of state, so the result of doing such an integral over đ*Q* or đ*W* would depend on the path we took from to .

In order to *do* an integral over đ*Q* or đ*W*, we need to express it in terms of variables that *are* functions of state. For example, if we can write , and we can use an equation of state to relate *P* to *V* along a particular path, then we can calculate *W* along that path, because both *P* and *V* are func­tions of state so the integral is well-defined.

## 5.5 Processes with a constant function of state

One way to simplify our calculations is to consider processes where one of the relevant functions of state is held constant throughout the process. When we are using an ideal gas as our working fluid, the relevant functions of state are *pressure, temperature* and *volume.*

### Isobaric processes

**Isobaric processes** take place at constant **pressure** (the word derives from the Greek for “equal weight”). On a *PV* plot, an isobaric process is a horizontal line. Because the pressure is constant, calculating the work done in an isobaric process is simple:   
where and are the initial and final volumes respectively. Also, by definition, , where is the heat capacity of the working fluid at constant pressure. The initial and final tempera­tures and can be calculated using the equation of state.

Isobaric processes are common in real life: if you heat something in an open container, the process is isobaric (but not, in general, either quasistatic or reversible—you can’t “un-cook” something by refri­gerating it!).

### Isothermal processes

**Isothermal processes** take place at constant **temperature**. For an ideal gas, since , an iso­thermal process on a *PV* plot is a curve with . Since the internal energy of an ideal gas is deter­mined by its temperature, *U* does not change during an isothermal process, so .

The work done during an isothermal process can be calculated by using . Assuming a fixed mass of gas, 𝑛, *R* and *T* are all constant, so

### Isochoric processes

**Isochoric processes** take place at constant **volume** (because the word “isochoric”, which comes from the Greek for “equal space”, is not common and is not obviously connected to volume, the word “iso­volumic” is often used instead). An isochoric process is a vertical line on a *PV* plot. Since the work done by a gas is and , no work is done by a gas during an isochoric process, so . By definition, , where is the heat capacity of the working fluid at constant volume.

### *Example 5.1*

Suppose we take one mole of a monatomic ideal gas at pressure *P*1, volume *V*1, and heat it at constant pressure until it reaches volume V2. We then heat it at constant volume until it reaches pressure P2. What are (i) the heat supplied, (ii) the work done, (iii) the change in internal energy?

If instead we first heat the gas at constant volume until it reaches pressure *P*2, and then heat it at constant pressure until it reaches volume *V*2, what are the heat supplied, work done and change in internal energy?

### *Answer*

Let’s label the four states A, B, C and D, where A is , B is , C is and D is .

From the ideal gas law, , we see that , , and . Since we have one mole of a monatomic ideal gas, the heat capacity at constant pressure is , and the heat capacity at constant volume is .

The heat supplied going from A to B is . From B to C the heat sup­plied is . Therefore, the total heat supplied is

There is no work done in the isochoric process from B to C, so the total work done *on* the gas is just

The change in internal energy is .

If we start with the isochoric step, . Then the isobaric step gives . The total heat supplied is

There is no work done from A to D, so the total work done on the gas is

The change in internal energy is .

Note that the change in internal energy is the same in both cases, as it should be, because internal energy is a function of state. However, the heat supplied and the work done both differ. If we were to combine this as a cycle ADCBA, running the first path in reverse, the net work done on the gas would be , i.e., since , the gas would *do* net work on its surroundings. This is the basis on which **heat engines** work: they convert heat to work by tracing out a closed cycle on the *PV* plot.

Also note that, since for one mole of gas, we can write as . This is what we should expect: we saw above that for an isochoric process , and as *U* and *T* are both functions of state it must therefore always be true that .

## 5.6 Adiabatic processes

Isobaric, isochoric and isothermal processes are three of the simple paths we will use to construct idealised heat engines. The fourth path is slightly different: instead of constraining one of the functions of state, we constrain one of the variables of the First Law, namely *Q*. An **adiabatic process** is a reversible process in which there is no heat flow, i.e. and Note that an adiaba­tic process is *not* isothermal: the internal energy of the working fluid does change, but it changes be­cause work is done, not because heat is supplied.

If the working fluid is 𝑛 moles of an ideal gas, we know that , where is the molar heat capacity, and . Since , we can write   
and separating variables gives   
We can now integrate this from to (corresponding to to ) to get   
Taking antilogs of this gives

Since we usually work in terms of *P* and *V*, it is useful to eliminate *T* using . This gives   
But we know that (see example 4.1), so we can write this as

If we define , we can take the root of this to obtain the final result

Using this and , we also have   
(not, of course, numerically the same constants!).

This allows us to determine the work done along an adiabatic path. If we know the initial pressure and volume, we can calculate , say. Then

But since is constant, we can write . Therefore we can simplify this to

Note that, because , this must be equal to the change in internal energy, . This is easily verified using the ideal gas law.

## *Example 5.2*

One mole of nitrogen, initially at a pressure of 101 kPa and a temperature of 25° C, is adiabatically compressed to half its original volume. What are its final pressure and temperature? How much work has been done? [Nitrogen gas is a diatomic molecule, and at room temperature it has .]

### *Answer*

Since the final volume is half the initial volume, kPa.

Likewise, using equation 5.5, K = 120° C.

The initial volume is m3, so the work done is   
 kJ to three significant figures.

In real life, adiabatic processes are often *fast* processes: no heat is transferred because the system does not have time to reach equilibrium. However, when we do calculations in this course, we shall assume that adiabatic processes take place slowly and reversibly within a container that is completely insulated from its surroundings, so that no heat flows in or out.

## *Example 5.3*

A typical bedroom contains about 2500 moles of air. Find the change in the internal energy of this much air when it is cooled from 35.0o C to 26.0o C at a constant pressure of 1.0 atm. Treat the air as an ideal diatomic gas with .

### *Answer*

=20.79 J/mol/K, so

To cool 2500 moles of air by 9 degrees, an air conditioner needs to extract this much energy and transfer it to the air outside.