# Topic 4: The First Law of Thermodynamics

## 4.1 Introduction

In general, a thermodynamic system is a collection of objects that is convenient to regard as a unit, and that may have the potential to exchange energy with its surroundings (e.g. popcorn kernels heated in a pot expand and does work as it exerts an upward force and moves the lid). Such a process, in which there are changes in the state of a thermodynamic system is a thermodynamic process.

The first law of thermodynamics relates heat supplied, work done and internal energy. In fact, it is simply a statement of energy conservation:

**The total energy of an isolated system is constant.**

Here, an “isolated system” is one which is not in any sort of contact with the outside world: it is not exerting or subjected to any forces, it is not supplying or being supplied with heat or any other form of energy. In this form, the law seems like a statement of the obvious. The first law is more useful if we permit some contact with the outside world:

**The change in the internal energy of a system is equal to the heat supplied to the system plus the work done on the system.**

This can be expressed mathematically as   
where is the change in internal energy, *Q* is the heat supplied ***to*** the system, and *W* is the work done ***on*** the system. Note the sign conventions here: if the system actually radiates heat, , and if the system does work on its surroundings, .

## 4.2 Heat and work

Both heat and work are forms of energy. Heat is the energy that flows between two systems in thermal contact with each other if they are not in thermal equilibrium, i.e. heat flow results from a difference in temperature. We have seen that the temperature of a body is related to the average kinetic energy of its constituent atoms, so we can conclude that *heat is energy transfer associated with random motion of atoms.*

Work, on the other hand, is energy transfer associated with *directed* motion, and in particular with the application of a force. In one dimension, we can write   
In the next section we will see that we need to treat this integral with great care, because it is **path dependent**. Suppose I need to move a box from my office (E43) to Clive Tadhunter’s office (E37), which is on the other side of the mid-corridor fire door. If I can simply move it the 10 m or so down the corridor, I will have done some amount of work , where in this case is 10 m. However, if the fire door is jammed shut because of some fault, and I have to walk down several flights of stairs to the Hicks SE exit, up Hounsfield Road, into the main entrance on D floor, up the stairs to E floor, and along the corridor to E37, I will have done considerably more work to achieve the same end result. The same is true of heat: the amount of heat I need to supply to raise the temperature of an object by a certain amount depends on the way that I do it, in other words the path that the temperature takes from *T* to . This path dependence of heat and work turns out to be critical to practical applications of thermo­dyna­mics, as we will see later in the course. The difference between the ordered motion of work and the disordered motion of heat is also very important, as we will see when we consider the Second Law and the concept of entropy.

### Some examples of work

In general, we have, for a force *F* applied over a small displacement , . (This is assuming that the force and the displacement are parallel; if they are not, we need to write where **F** and **Δx** are vectors.)

For gases, it is usually more useful to work in terms of pressure: since where *A* is the area over which the pressure acts, the work done by pressure *P* is , where is the change in the volume of the gas. Note that the work done ***on*** the gas, which is what we usually want for the First Law, is equal to .

Other forms of work include stretching a spring, where where *f* is the force applied to the spring and is the change in its length, expanding a liquid droplet ( where *γ* is the surface tension and is the change in area), applying an electric field to a charged particle, and so on. In the rest of the course we shall usually be using , but it is important to remember that the First Law does not *only* apply to expanding gases!

## 4.3 Internal energy

The internal energy of a system is the total energy of its constituent particles. This includes the transla­tional, rotational and vibrational energy that we considered in section 3.4, and also the potential ener­gy due to forces between atoms, which we neglected in the ideal gas but which are obviously impor­tant in liquids and solids.

Unlike heat and work, internal energy is a **function of state**: it is determined only by the current pro­perties of the system, not by its history. If I take a system that is in state A (say, a gas with a specified pressure, temperature and volume), and by supplying heat and/or doing work I take it to state B, the change in its internal energy *is not path dependent*: whatever combination of heat and work I applied, in whatever order, the change in the internal energy will be the same.

### *Example 4.1*

One mole of a monatomic ideal gas, say argon, is enclosed in a container which has one movable wall, so that the gas remains at the same pressure as the outside environment. (Neglect any frictional for­ces.) The gas is heated at con­stant pressure by an amount .

1. What is the work done on the gas?
2. What is the change in the internal energy of the gas?
3. What is the heat supplied to the gas?
4. What is the relation between the molar heat capacity at constant pressure, *cP*, and the molar heat at constant volume, *cV*?

### *Answer*

If the gas is heated at constant pressure, then since (for one mole), the volume must change. The amount of work done *by* the gas is , so the amount of work done *on* the gas is .

From equation 3.5, we know that the change in the internal energy of the gas is . (As this is a monatomic ideal gas, its internal energy is just the kinetic energy of its atoms: there are no rotational or vibrational degrees of freedom to worry about.)

Therefore from the First Law we have .

But by definition we know where *cP* is the molar heat capacity at constant pressure, and at constant volume we know that since no work is done. Therefore, as we have pre­viously deduced (see equation 3.7) , and so .

Note that although a more complicated gas, such as isobutane from example 3.2, would have a larger value of *cV*, it would still be true that , since the work done by the gas pressure would be the same (provided that the gas could be treated as an ideal gas).

## 4.4 Cyclic Process

A process that eventually returns a system to its initial state is called a cyclic process. For such a process, the final state is the same as the initial state, so the total internal energy change must be zero. If a net quantity of work *W* is done on the system, an equal amount of energy must have flowed into the system as heat *Q*.

Every day your body (a thermodynamic system) goes through a cyclic process. Heat is added by metabolizing food, and your body does work in breathing, walking, and other activities. If you return to the same state at the end of the day, the net change in your internal energy is zero i.e. so .

### *Example 4.2*

One gram of water (1 cm3) becomes 1671 cm3 of steam when boiled at a constant pressure of 1 atm (101 kPa). Compute (i) the work done vaporizing the water and (ii) its increase in internal energy.

Note: The heat of vaporization at this pressure is LV = 2.26 x 106 J/kg.

### *Answer*

The water does work

So the work done on the water is J. From Eqn 2.6,

The first law of thermodynamics holds for thermodynamic processes of all kinds,

Over 90% of the heat remains in the system as an increase in internal energy, with the remainder leaving the system at it expands from liquid to vapour.