

2. The Laws of Thermodynamics

1. Energy conservation and the first law of thermodynamics

The law of conservation of energy has developed over time to embrace an ever wider concept of energy. Following the discussion of the various forms of energy from the previous lecture we know that it should relate to all the known fundamental forces of physics. The term mass-energy is sometimes used in more recent formulations of the law because of the realisation that mass is just another form of energy and because it is not yet familiar enough to be regarded simply as energy.

A simple statement of the law of conservation of energy is:

1st Law of Thermodynamics

Energy is a fundamental quantity which can neither be created or destroyed, only changed from one form to another

Like most laws it raises unanswered questions, in this case about the nature of energy itself. We will not be concerned here with attempts at definition. As laws go it is very well established and no counter-examples have ever been identified. It is very all embracing. For example, if we assume it has always applied, we can state that the total energy associated with our Universe is the same as at the time of the Big Bang and this has consequences for the fate of the Universe.

So much for meta-Physics. The first law of thermodynamics is a limited reformulation of the general law. As such is it of more practical use and plays a key role in engines, pumps etc.

Before proceeding to state and examine the law we need a few basic concepts:

A thermodynamic system –

a) Closed system: is a fixed quantity of mass which is separated from the surroundings by system boundaries; can be either movable or fixed.

b) Open system (control volume): the system is defined by fixed boundaries through which heat, work, and mass can flow.

- an *adiabatic* process is one in which no heat crosses the boundary of the system, e.g. a perfectly insulated system
- an *isothermal* process is one that involves no change of temperature
- a *reversible* process is one in which the complete system can be restored to its initial state

The *internal energy function* (denoted by U) is an abstract concept which includes all the internal energy of a substance (kinetic, potential on a microscopic, associated with the thermodynamic state of the substance)

First let us consider the simple case of an adiabatic process. If work, W , is done on a system the internal energy will change. We say that the internal energy function has changed its value from say U_A to U_B corresponding to states A and B of the system. From the law of conservation of energy for this closed system it is clear that

$$W = U_B - U_A$$

The difference in internal energy caused is denoted ΔU . The important point to note is that the work required to change the system from state A to state B is independent of the path, i.e. the exact sequence by which the work is done.

For a non-adiabatic process $\Delta U \neq W$ and the difference between these terms represents the heat flow (in or out) of the system which is denoted by Q .

The usual sign convention gives heat *into* a system as +ve Q and work done *on* a system also as +ve.

We can now state the first law of thermodynamics in a succinct form:

$$Q = \Delta U - W$$

Note that heat arises only with change of state of the system. Quantity of heat is not formally a function of the state of a body like temperature, pressure etc. This is not in accord with our common usage of the word heat as when we say heat is lost or gained by a body.

It is sometimes helpful (but not necessary) to think of internal energy in terms of an atomic view of the substance in question. The particles making up the substance (for example a gas or solid) can be thought of as having a combination of kinetic and potential energy which is affected by the state of the substance; temperature, pressure, volume etc. The internal energy of the body can then be interpreted as the sum of the potential and kinetic energies of all the particles constituting the body.

2. The Second Law of Thermodynamics

The second law relates to the observed phenomena that heat always flows spontaneously from a higher temperature to a lower one; never the reverse.

There are a number of different formulations, all more or less equivalent, due to Carnot, Clausius, Kelvin and others. In modern language we state it as:

2nd Law of Thermodynamics

In order to extract work from a system, heat must flow from a higher temperature to a lower temperature.

It is the emphasis on the direction of heat flow which distinguishes this law from the first law. It is fundamental to an understanding of heat engines (engines, refrigerators and heat pumps). There are a number of important developments from the second law. These are sometimes referred to in the text books as corollaries. They should help to make a rather abstract, and at first sight useless law, appear with the importance it deserves. We will deal with them in the following sub-sections.

2.1 The Heat Engine

Consider a heating coil through which an electric current is being passed and which is immersed in a liquid. Once steady state is reached, the state of the coil does not change in any way, and all of the electrical energy goes into heating the liquid. Similarly, when mechanical work is done to overcome friction, it too can be done in such a way that all the mechanical energy is converted to heat. In general the transformation of work (of any kind) into heat can be accomplished with 100% efficiency and can be continued indefinitely.

However, the opposite process, the continual conversion of heat into work, is never 100% efficient. A device which converts heat into work is called a **Heat Engine** (internal combustion engines and steam engines are examples). If it is to be useful, the engine must be able to do work continuously, and in order to do this it must work in a cycle.

In its simplest form we can consider a gas enclosed in a cylinder by a piston. If heat is applied to a gas, it expands and pushes back the piston. Thus the heat has been converted to work. The process stops however, as soon as the pressure of the gas becomes equal to the pressure outside the cylinder. Therefore, as part of a cycle, the gas must be returned to its original state. This is done by adding a “sink” to remove heat from the gas.

2.2 The Carnot cycle and the definition of thermodynamic efficiency

Carnot's paper which effectively solved the problem of heat engine design was written when he was only 28. The key idea was what we now call the Carnot cycle. It is the basis of all modern understanding of heat engines. It is so important that it is worth spending some time understanding it. The cycle is best understood in terms of a p-V diagram. This enables us to trace the cycle in terms of the changes in pressure and volume of the working fluid which we take as being a gas, although the approach itself, and the conclusions are general.

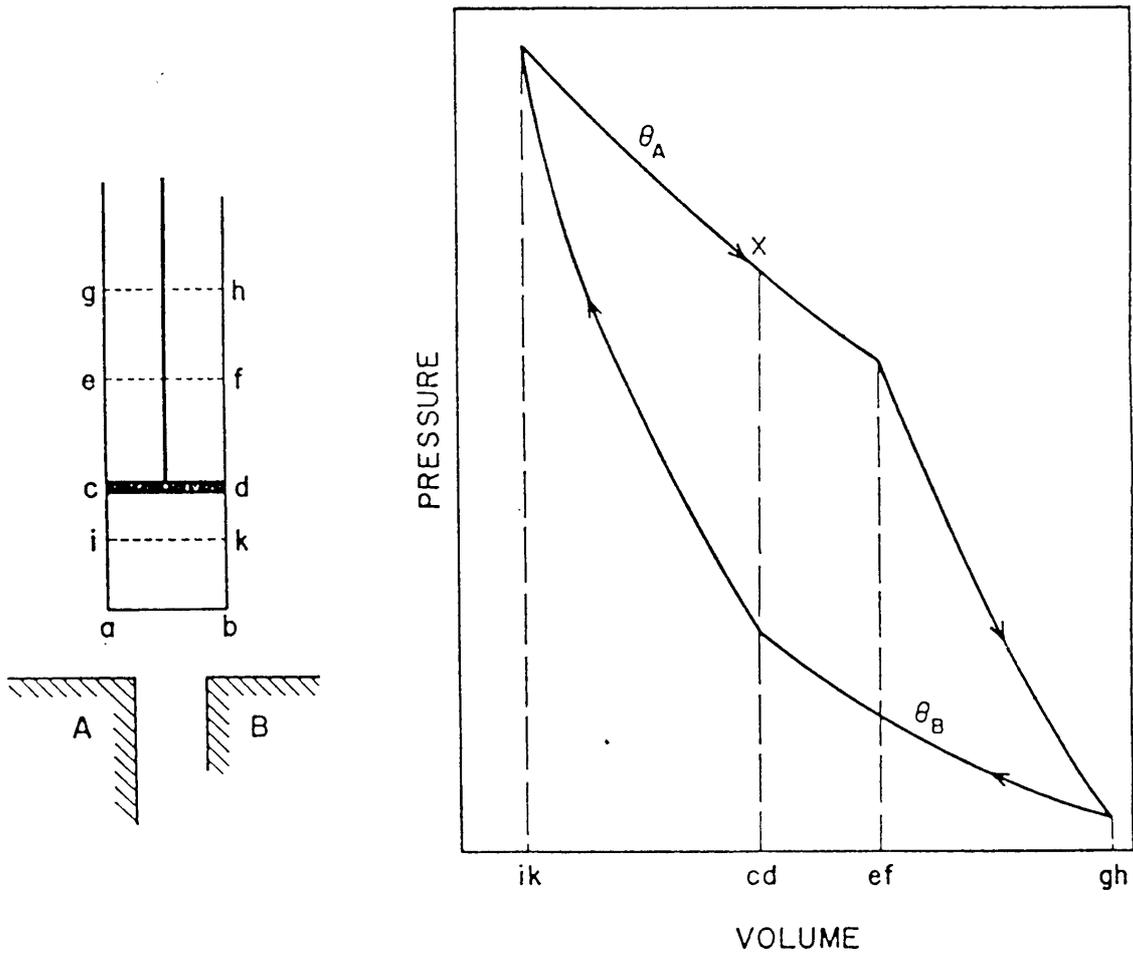


Figure 5: The Carnot Cycle

Following Carnot:

Let us imagine a gas, atmospheric air for example, enclosed in a cylindrical vessel $abcd$, Fig 1, furnished with a moveable diaphragm or piston cd ; in addition let there be two bodies, AB , each held at a constant temperature, that of A being higher than that of B ; let us now imagine the following series of operations:

1. Contact of the body A with the air enclosed in the space $abcd$, or with the wall of this space, a wall which we will suppose to conduct heat easily. Through this contact the air assumes the same temperature as the body A ; cd is the present position of the piston.
2. The piston rises gradually and takes the position ef . Contact is still maintained between the body A and the air, which is thus kept at a constant temperature during expansion. The body A furnishes the heat necessary to keep the temperature constant.
3. The body A is taken away and the air is no longer in contact with the body capable of giving it heat; the piston however continues to move and passes from the position ef to the position gh . The air expands without receiving heat, and its temperature falls. Let us imagine that it falls in this way until it becomes equal to that of the body B : at this stage of the piston stops and occupies the position gh .
4. The air is put into contact with body B ; it is compressed by the return of the piston as it is moved from the position gh to the position cd . The air however remains at a constant temperature because of its contact with the body B to which it gives up its heat.
5. The body B is removed and we continue to compress the air which, being now isolated, rises in temperature. The compression is continued until the air has acquired the temperature of the body A . During this time the piston passes from the position cd to the position ik .
6. The air is put back into contact with body A ; the piston returns from the position ik to the position ef ; the temperature stays constant.
7. The operation described under No. 3 is repeated, then successively the operations 4, 5, 6, 3, 4, 5, 6, 3, 4, 5 and so on.....

In terms of our definitions the two operations (3) and (5) are adiabatic, whilst the operations (1) (equivalent to (6)) and (4) are isothermal. By using these ideal processes for energy transfer the cycle has been carefully constructed so as to be the most efficient possible. No temperature gradients which would give rise to wasteful flows of heat (i.e. not doing work) are allowed.

The working substance (air in this case) produces a net amount of work during each cycle. This is clear from the p-V diagram. The work done *by* the air is $\int p dV$ which is the area of the cycle on the p-V diagram. The direction in which the cycle is followed determines whether work is done *by* the air or *to* the air. The other important point to note is that each step of the process is reversible and so the whole cycle is reversible. This fact is used to prove the statement made above that the cycle is the most efficient that can be designed. As such the Carnot cycle provides the definition of maximum efficiency for a heat engine.

Let us assume that the Carnot cycle is working between temperatures t_1 and t_2 , and that the heat taken in by the air at the higher temperature is Q_1 , and given out at the lower temperature is Q_2 . Since the working substance (air) is in exactly the same state at the end of the cycle as at the start $\Delta U = 0$. Thus the work done *by* the engine in one cycle is:

$$W = Q_1 - Q_2$$

This follows from the first law. The thermodynamic efficiency is defined as:

$$\eta = W/Q_1$$

It is the ratio of the work done per cycle to the heat taken in at high temperature.

For the Carnot cycle this is then:

$$\eta = (Q_1 - Q_2)/Q_1 = 1 - Q_2/Q_1$$

At this stage the ratio Q_2/Q_1 is a function of t_1 and t_2 . It can be shown that $Q_2/Q_1 = f(t_2)/f(t_1)$ and the choice of function f will lead to a definition of temperature scale. The Kelvin scale, K, is defined so that:

$$Q_1/Q_2 = T_1/T_2$$

This defines the ratio of the absolute temperatures but not the scale (or size) of the unit. By choosing the unit size for degrees K the same as for degrees C, the absolute temperature scale is completely defined. We can now state the Carnot efficiency as:

$$\eta = 1 - T_2/T_1$$

The greater the difference between the two working temperature as a fraction of the higher sink temperature the higher the efficiency. This is why engines are designed for the highest possible working temperatures that the materials will stand.

A Carnot engine working backwards is a refrigerator or heat pump.

2.3 Entropy

The first law of thermodynamics is concerned with energy; the second law is concerned with a quantity called entropy. As we shall see, all real processes occur in such a way that there is a net increase in entropy. Before we examine entropy in more detail, we can give an example to try and explain the concept of entropy.

Every time entropy increases the opportunity to convert some heat into work is lost forever. For example, there is an increase in entropy when hot and cold water are mixed. The warm water that results never separate itself into a cold layer and hot layer. There has been now loss of energy but some of the energy is no longer available for the conversion into work.

Rewriting one of the equations from the previous section we get

$$Q_1/T_1 - Q_2/T_2 = 0$$

This is generally true for a reversible cycle and motivates the definition of entropy as follows:

$$dS = dQ/T$$

Where dS is the entropy change corresponding to change in heat dQ . If we integrate over one complete (reversible) cycle we get

$$\oint \frac{dQ}{T} = \oint dS = 0$$

Note that although the integral of dQ depends on the path the integral of the ratio of dQ/T , i.e. dS is independent of the path. Some text books refer to dS therefore as being an exact differential. In general the change in entropy between any two arbitrary states depends only on those states and not on the path between them.

We can write an infinitesimal version of the first law informally as

$$dU = dW + dQ$$

If the changes are quasi-static and involve a change in volume dV at pressure p , then

$$dW = -pdV$$

Substituting for dW from the above equation and dQ from the definition of entropy we have

$$dU = TdS - pdV$$

This is the central equation of closed system thermodynamics. It can be used to investigate a whole range of phenomena including phase change transitions.

It is well known that 'entropy always increases'. This is easy to see now. Take the case of heat Q flowing from T_1 to T_2 . As a worst case assume the bodies at these temperatures are unaffected by the heat flow. Then the body at T_1 loses Q/T_1 in entropy while the other body gains Q/T_2 in entropy. Since Q always flows from higher to lower temperature (if $T_1 > T_2$) then

$$Q/T_2 > Q/T_1$$

The net change in entropy, $Q/T_2 - Q/T_1$, is thus always positive.

2.4 Gibbs and Helmholtz free energy

Two other path independent thermodynamic functions have also been found to be useful. These are due to Gibbs and Helmholtz. (NB entropy was due to Clausius).

The Helmholtz free energy is given by

$$A = U - TS$$

for changes at constant volume. For an isothermal change

$$dA = dU - TdS$$

The change in free energy dA is equal to the change in internal energy minus the 'unavailable' energy TdS .

The Gibbs free energy is given by

$$G = Q - TS$$

for a change at constant pressure.

Exergy is a trendy term seen in modern texts. It is in older texts referred to as availability. It is a measure of the maximum useful work which can be done by a system interacting with an environment which is at constant pressure and temperature. In other words it is the isothermal case of Gibbs free energy:

$$dG = Q - TdS$$

The maximum work is equal to the change in enthalpy minus the 'unavailable' energy.

FURTHER READING



G F C Rogers and Y R Mayhew, Engineering Thermodynamics Work and Heat Transfer, Third Edition, Longman, 1980.
