## Chapter 1: Introduction and revision

### 1.1 Thermodynamics

Thermodynamics is the science which defines the relationship between different forms of energy via characterisations of the various attributes of the enclosing system. This energy can take the form of work, heat, or the energy contained within a system. Engineering thermodynamics plays a major role in the consideration of power generation, air-conditioning, chemical reactions, cryogenics (low temperatures) and low pressure systems. In general, thermodynamic concepts can be applied over a whole range of sciences, including biological systems, and they govern the way in which energy can be transformed between its various forms.

The subject of Thermodynamics is closely related to Fluid Mechanics, but tends to take a broader view of the interaction between inputs and their effect on a system. Fluid mechanics is usually more concerned with the detailed distribution and structure of the flow. The principles of Thermodynamics were not fully defined until the middle of the 19th Century (1850's), so it is a relatively recent subject, and one of the last of the main engineering sciences to have reached maturity. Cardwell (1971) published an excellent discussion of the history of thermodynamics, showing the development of many of the fundamental ideas used today. Thermodynamics has maintained its importance through the ensuing period and it has and will make a major contribution in this century as countries develop and try to improve their standard of living. The major difficulties encountered in studying classical thermodynamics are philosophical rather than mathematical, and a good grounding in the basic principles of the subject is essential. This chapter will briefly reiterate the fundamentals of the subject to make the reader familiar with the vocabulary and symbols used in this book.

### 1.1.1 Macroscopic thermodynamics

There are two basic methods of studying thermodynamics, termed classical and statistical thermodynamics. Classical thermodynamics concentrates on the net changes affecting a system, without considering the detailed changes occurring within the system and the enclosing boundaries: it is also termed macroscopic thermodynamics. Statistical thermodynamics considers the detailed changes occurring to and within the molecules inside the system, and can be termed microscopic thermodynamics. Most simple engineering thermodynamics problems can be solved using macroscopic thermodynamics, and this book will concentrate in this area. However, some concepts of statistical thermodynamics will be used to explain certain phenomena (see Chapter 21).

Classical thermodynamics considers systems at, or close to, equilibrium: in fact Tribus (1961) referred to it as Thermostatics! Many of the simple applications of thermodynamics are covered under this restriction, although we will see that such an approach can result in misleading results (see Chapter 20). Notable cases which are not included in equilibrium situations are the production of pollutants (e.g., carbon monoxide, and oxides of nitrogen) in combustion processes along with a large number of industrially important physicochemical processes.

### 1.1.2 Laws of thermodynamics

There are four laws of thermodynamics, which have been developed from observations of large numbers of experiments.. These laws are termed axioms (self-evident truths), and are:

Zeroth Law of Thermodynamics: which defines the concept of temperature.
First Law of Thermodynamics: which defines the concept of energy.
Second Law of Thermodynamics: which defines the "quality" of energy, and the direction of processes and, even, time.

Third Law of Thermodynamics: which defines conditions at a temperature of absolute zero.
The first three laws listed can all be derived from macroscopic considerations; the Third Law requires some concepts from statistical thermodynamics.

It is possible, with hindsight, to obtain more general derivations for some of these laws \{Carathéodory (see Kestin (1976)), Tribus (1976) for entropy\}, but while these derivations are academically interesting and more general than the empirical ones they do not add any new data and or practically motivated applications.

### 1.2 Definitions

Thermodynamics introduces new concepts, and requires a new vocabulary based on a set of definitions. These will now be introduced.

### 1.2.1 System

A system is a collection of matter enclosed within prescribed boundaries.

## Closed system

A closed system is a prescribed and identifiable collection of matter enclosed within a prescribed boundary. There is no flow of matter across the boundary but energy exchanges can occur.

## Boundary

A system is separated from its surroundings by a boundary. The boundary of a closed system is not always fixed, and may move to contain the prescribed matter. The boundary always contains the same quantity of matter.

## Surroundings

The surroundings are anything not contained within the system boundaries. In general, the surroundings are vast compared to the system, and can usually be assumed to be unaffected by anything that happens to the system.

## Open system

An open system is defined by its boundaries, and there can be mass transfer across the boundaries: the matter contained within an open system will vary with time. The mass contained in the system can change in amount and composition. The space occupied by an open system is called a control volume, and the boundaries of an open system are referred to as control surfaces.

## Interaction between systems and their surroundings

Interactions between systems and their surroundings can only be examined at the boundaries. Hence, while the working fluid of a gas turbine might produce the power output through the detailed flow around the blades, the effect of this interaction can only be examined when the work output from the system crosses the boundary.

### 1.2.2 Properties

A property of a system is an observable characteristic of the system. Properties can be divided into two types:

- external or mechanical properties;
- internal or thermodynamic properties.


## A property is any quantity whose change is fixed by the end states, and is independent of the path between the end states.

## Mechanical properties

Mechanical properties are characteristic of the position or motion of the system in a gravitational field.
They are measured relative to external datums. Typical examples of mechanical properties are:

- velocity, height, kinetic energy, potential energy, momentum

These properties all contain mass, position, or time, or combinations of all three. These are sometimes called the mechanical co-ordinates of the system.

## Thermodynamic properties

Thermodynamic properties are characteristic of the matter within a system at equilibrium. The properties are measured by an observer at rest relative to the system; in the case of a moving system,
the thermodynamic properties are measured by an observer travelling at the same speed as the system. These are sometimes called the thermodynamic co-ordinates of the system.

Properties can be further divided into intensive, extensive, and specific properties.
Intensive properties: are independent of the size/mass of the system. Typical intensive properties are pressure, temperature, viscosity, height, velocity, etc.

Extensive properties: are dependent on the size/mass (or extent) of the system. Typical extensive properties are volume, surface area, kinetic energy, potential energy, etc.

Specific properties: are defined as the extensive property per unit mass. These will be introduced later.

### 1.2.3 State

The state of a system is a complete description of all the properties of the system, i.e. both the mechanical and thermodynamic properties. e.g., a simple system is defined by its volume, pressure, velocity and position.

A system is in the same state (e.g., after a series of processes) if, and only if, all the properties are identical in both instances.

## State point

The state of a system can be defined in a state space, which is depicted on a state diagram. The usual form of state diagram is two-dimensional, and each of the axes is an independent property. A state point is a point on the diagram representing the properties of the system at any instant. The state point is an equilibrium point, and A and B in fig 1.1 are examples.

### 1.2.3.1 Change of state

When the state of a system alters, the change of state is defined by the two end states. In fig. 1.1 the state changes from $\left(p_{1}, V_{1}\right)$ to $\left(p_{2}, V_{2}\right)$.

### 1.2.4 Some important properties

## Pressure (p)

Pressure is the force per unit area exerted by a system on its surface in the direction normal to that surface. Pressure is a continuum concept, and it is supposed that the number of molecules per unit volume is large - usually the case in typical engineering applications. However, at very low pressures (e.g. in space) the concept of pressure is more difficult to define and in some cases not even available.

It is usual to define pressure as positive if the force acts outwards from the system, and negative if the force acts inwards. The concept of "positive" and "negative" pressure is important when considering the work done by a system.

Pressure in thermodynamic systems is considered to act at the boundary of the system in the absence of gravitational, magnetic or electrical forces. Typical units of pressure are $\mathrm{N} / \mathrm{m}^{2}$, bar and $\mathrm{lb}_{\mathrm{f}} / \mathrm{in}^{2}$.

## Density ( $\rho$ )

Density is defined as mass per unit volume. Density is also a continuum concept. Typical units of density are kilograms per cubic metre denoted by $\mathrm{kg} / \mathrm{m}^{3}$.

## Specific volume (v)

Specific volume is the reciprocal of density and is defined as the volume per unit mass; this is also a continuum concept. Typical units of specific volume are cubic metres per kilogram, denoted by $\mathrm{m}^{3} / \mathrm{kg}$.


Fig. 1.1: Change of state from state points $\mathrm{A}\left(p_{1}, V_{1}\right)$ to $\mathrm{B}\left(p_{2}, V_{2}\right)$.
Note that four paths are shown on the diagram, and any one of these is a possible route between the two states. It is not possible to define the route at this stage.

## Temperature (t or T)

Temperature is a property introduced by thermodynamics: thermodynamic processes are driven by temperature or rather temperature differences. Temperature is a measure of how "hot" or "cold" a body is. However, in making that measurement it is important that the device used for measuring the temperature is in thermal (temperature) equilibrium with the body.

### 1.3 Thermal equilibrium and the Zeroth Law

If a system changes state slowly (compared to the reaction time of the system) it passes through a series of equilibrium states called a path. Such a path is shown on fig. 1.2(a).

### 1.3.1 Process

The path through a succession of equilibrium points on fig. 1.2(a) is called a process. Thus the process in fig. 1.2(a) is defined by the two end states and the path.


Fig. 1.2(a): Change of state from A to B, passing through a series of equilibrium points.


Fig. 1.2(b): A cyclic change of state from A to B to A , passing through a series of equilibrium points

### 1.3.2 Cycle

A cycle is a process whose end states are identical, and is depicted in fig. 1.2(b). The concept of a cycle is an extremely important one in thermodynamics, and many of the proofs in thermodynamics are derived by considering cycles.

### 1.3.3 Relationship between properties

The state of simple systems of constant mass and composition can be defined by two independent properties: this is referred to as the Two-property rule, or the Gibbs rule. Any other property can be evaluated from these two properties if the characteristics of the substance inside the system boundaries are known. Hence, two independent properties are sufficient to define the state of simple systems of constant mass.

### 1.3.4 Thermal equilibrium

Consider two systems, A and B, which are not at the same state, connected through a wall, which can be either a perfect insulator or a perfect conductor. If the systems do not change state with time, then the wall is an adiabatic one. If the systems spontaneously change state then the wall is a diathermal one, and the systems will ultimately reach a steady state: this steady state is called thermal equilibrium.

### 1.3.5 Zeroth Law of Thermodynamics

Two systems are in thermal equilibrium with each other if they are both in thermal equilibrium with a third system.

Systems in thermal equilibrium with each other are said to be at the same temperature.

### 1.4 Temperature scales

There are two different scales of temperature:

- The continuous scale of temperature is based on the Second Law of Thermodynamics and is independent of the thermometric substance; this will be introduced in the chapter 2.
- The discontinuous scales of temperature are defined as the International Temperature Scale (ITS-90). These are based on establishing a number of fixed points on the temperature scales and interpolating between them. The Celsius (or Centigrade) and Fahrenheit scales are the original ITS scales.


### 1.5 Interactions between systems and surroundings

The way a system can interact with its surroundings is through transfers across the system boundaries. In the case of a closed system there can be no mass flow across the system boundaries, and the only possible interactions are by two mechanisms:

- work
- heat

It will be shown that both of these are transfers of energy across the boundary.

### 1.5.1 Work - Thermodynamic definition

Work is done by a system when the sole effect on everything external to the system (the surroundings) would be the raising of a weight.

For engineers the main interest is in using systems to produce work, and hence the following definition is adopted for the sign convention of work:

- positive work: is done by a system on the surroundings
- negative work: is done by the surroundings on a system.

This sign convention is completely arbitrary and some engineering text books use the opposite convention, which is also used by physicists and chemists. While the convention is arbitrary it does have a significant effect on the equations of thermodynamics. It is important to use the sign convention consistently and correctly.

### 1.5.1.1 Negative work

Energy cannot be created or destroyed, so when a system does positive work then the surroundings must do an equal amount of negative work. Effectively, work can only be done when there is something to receive it - this is an important concept that will be returned to later.

### 1.5.1.2 Representation of work

Positive work will be represented by an arrow pointing out of the system, and negative work will be represented by an arrow pointing into the system. This is shown in fig. 1.3.


Fig. 1.3: Sign convention for work

### 1.5.1.3 Displacement work

Displacement work is an important feature of engines operating on thermodynamic principles, and this is often generated by a piston and a cylinder, as shown in fig. 1.4.

> The incremental piston, or displacement work, is $\mathrm{d} W=p \mathrm{~d} V$, and for a process in which the pressure varies with volume the work is $$
W=\int p \mathrm{~d} V
$$



Fig. 1.4: Displacement work in a piston - cylinder arrangement
In this case the pressure force on the piston was fully resisted by an equal and opposite force $F$. While the piston moves outwards causing the system to expand and do positive work, the resisting force $F$ could be associated with work being done on the surroundings which are contracting. Hence the surroundings are receiving work, which is equivalent to them doing negative work. The work done on the system is equal and opposite to the work done by the surroundings, and hence the net work done by the system plus surroundings is zero: energy has not been created or destroyed.

### 1.5.1.4 Unresisted expansion

Now consider the situation depicted in fig. 1.5: the system is at a pressure of $p_{1}$ and is separated from the surroundings, at a pressure of $p_{2}$, by a diaphragm. In this case $p_{1}>p_{2}$. If the diaphragm is burst then the system expands against the surroundings: when the system expands it can only do work against a reacting force. If the reacting force is not equal and opposite to the internal force in the system then the work done by the system is reduced to that which can be absorbed by the surroundings: in this case, $\int p_{2} \mathrm{~d} V$.


Fig. 1.5: System and surroundings with unequal pressures: $p_{1}>p_{2}$

If the surroundings of the system were a vacuum then $p_{2}$ is zero and the work done by the system in expanding against the vacuum would be zero. No work is done during an unresisted expansion.

### 1.5.2 Quasi-static processes

The rate of expansion is an important factor in assessing the work done. If the piston were moving very quickly, then the molecules of the gas in the system could not keep up with the piston motion, and hence they would not produce a pressure on the piston. Also, if the speed of the piston were lower than the speed of sound but still very rapid, it would create expansion waves in the cylinder and the pressure throughout the cylinder would not be uniform. For the work to be $\int p_{c} \mathrm{~d} V$ it is necessary that

- the pressure in the cylinder is uniform, which means that the piston speed must be low relative to the speed of sound;
- the speed of the piston is slow relative to the velocity of the molecules.

Such processes are referred to as quasi-static(semi-equlibrium) processes.
If processes are quasi-static then it is possible to plot the locus of the process on a state diagram, e.g. a pressure volume diagram. Fig. 1.6(a) shows a compression process on a $p$ - $V$ diagram and fig. 1.6(b) shows an expansion process.


Fig. 1.6: Compression and expansion work shown on $p$ - $V$ diagrams
The work done in the compression process is

$$
\begin{equation*}
W_{12}=\int_{V_{1}}^{V_{2}} p \mathrm{~d} V=-\int_{V_{2}}^{V_{1}} p \mathrm{~d} V \tag{1.3}
\end{equation*}
$$

If work is a property then it will be independent of the process and only depend on the end states. It is possible to show work on a $p-V$ diagram, where the work is the area under the line depicting the process. A number of different processes employing different thermodynamic/mechanical constraints on the system are shown on a $p$ $V$ diagram in fig. 1.7.


Fig. 1.7: Three work processes depicted on a $p-V$ diagram.
The work done by each process is the area under the curve, and it is obvious that $W=\int_{p} \mathrm{~d} V$ is different for all three processes. Hence, since work is dependent on the process and not only on the end states, it is not a property.

## Work is not a property of a system. <br> Work is a transitory phenomenon used to transfer energy. <br> Work exists only during the process that is causing it.

### 1.5.3 Heat Transfer

Heat transfer is another possible form of energy transfer across system boundaries. It is an interaction that occurs across the boundary due to temperature differences.

### 1.5.3.1 Definition of heat (transfer)

Heat (transfer) is the interaction between systems which occurs by virtue of temperature differences.

- heat interactions are associated with energy transfers
- heat interactions are transitory phenomena
- heat is energy usually being transmitted across a boundary
- heat is not a quantity of energy contained within a system
- if two bodies at different temperatures are brought into contact then heat is the energy transferred; the process ceases when the temperatures are equal (Zeroth Law)
- if the energy of a system is increased by heat interaction then the heat transfer is positive; if the energy is decreased then the heat transfer is negative. This is depicted in fig 1.8.


Fig 1.8: Definition of positive and negative heat interactions.
It should be noted that the direction of positive heat transfer is into the system, whereas positive work is out of the system. This is purely arbitrary and reflects the engineers' interest in the results of these transfer processes. Scientists use the positive direction into the system for both work and heat: some engineering thermodynamic textbooks do the same.

### 1.5.3.2 Unit of heat (energy)

The standard unit of heat is the unit of energy, viz. the Joule (J). In engineering practice the kilojoule (kJ), is often used because the joule is too small for convenience, but the kilojoule is not a rational unit. The Joule can be related to the calorie or kilocalorie.

1 kilocalorie is the quantity of energy required to raise the temperature of 1 kg of water by $1{ }^{\circ} \mathrm{C}$ if the water is at $15^{\circ} \mathrm{C}$.

The joule will be defined later, and is not based on the thermal capacity of a substance, but derives from the First Law of Thermodynamics.

## 1 kilocalorie (kcal) is equivalent to 4.1868 kJ

### 1.5.3.3 Heat (transfer) processes on a state diagram

Heat and work transfer processes both have similar effects on the changes of state. It is more difficult to see that the same change of state can be brought about by different heat transfer processes based on the different themodynamic constraints on the system, but this is the case. The effect of heat transfer processes on the state diagram is shown in fig 1.9.


Fig 1.9: Three heat transfer processes on a $p-V$ diagram.

The quantity of heat energy flowing into a system is dependent on the path followed during the process: hence heat is not a property of the system.

### 1.5.4 Relationship between heat and work

Both heat and work are transitory phenomena associated with interactions at the boundaries of systems. They only exist when they are taking place, and are not stored per se in the system.

### 1.5.4.1 The First Law of Thermodynamics

is a statement of the conservation of energy. It is based on the equivalence of heat and work, which was first stated by Joule in the 1840's. The First Law enables the concept of internal energy and enthalpy to be defined as thermodynamic properties.

## Statement of the First Law of Thermodynamics

When a system executes a cyclic process, the algebraic sum of the work transfers is proportional to the algebraic sum of the heat transfers

This can be written mathematically as:

$$
\begin{equation*}
\oint \delta W=\tilde{J} \oint \delta Q, \text { where } \oint \text { means integration around the cycle } \tag{1.4}
\end{equation*}
$$

which can be rearranged to give

$$
\begin{equation*}
\oint \delta W-\tilde{J} \oint \delta Q=\tilde{J} \oint \delta Q-\oint \delta W=0 \tag{1.5}
\end{equation*}
$$

In SI units the units of work and heat are both joules (J), and hence $\tilde{J}=1$. Thus eqn (1.5) becomes

$$
\begin{align*}
& \oint \delta W-\oint \delta Q=\oint \delta Q-\oint \delta W=0, \text { which can be rewritten as } \\
& \oint(\delta Q-\delta W)=0 . \tag{1.6}
\end{align*}
$$

In other systems of units $\tilde{J}$ is not unity, e.g. in Imperial units (foot, pound, sec) the value of $\tilde{J}=778 \mathrm{ft} \mathrm{lb} . / \mathrm{Btu}$, while in the cgs system (cm, gram, sec) the value of $\tilde{J}$ is $\mathbf{4 . 1 8 6 8} \mathrm{g} . \mathrm{cm} / \mathrm{cal}$. These other systems of units will not be used in this book, but the reader should be aware of them.

While eqn (1.6) shows the proportionality of heat and work around a cycle, it does not give any information about intermediate states around the cycle. However, it is possible to introduce the concept of internal energy.

### 1.5.5 Internal energy

Figure 1.10 shows three processes that cause the state of a system to change from 1 to 2 , or vice versa.


Fig 1.10: Heat and work processes on a state diagram
It is possible to define two cycles (1-A-2-B-1) and (1-A-2-C-1) from the processes shown on Fig 1.10. Applying the First Law of Thermodynamics to these two cycles it can be shown

$$
\begin{equation*}
\int_{\mathrm{B}}(\delta Q-\delta W)=\int_{\mathrm{C}}(\delta Q-\delta W) . \tag{1.7}
\end{equation*}
$$

Hence $\int(\delta Q-\delta W)$ is independent of the process, and is dependent only on the end states. This means that $\int(\delta Q-\delta W)$ is a thermodynamic property, and it is named INTERNAL ENERGY denoted by the symbol $\boldsymbol{E}$. The change in internal energy, E , in the process from 1 to 2 is
or

$$
\begin{align*}
& E_{2}-E_{1}=\int_{1}^{2}(\delta Q-\delta W)  \tag{1.8}\\
& \mathrm{d} E=\delta Q-\delta W \tag{1.9}
\end{align*}
$$

Equations 1.8 and 1.9 define the First Law in integrated or differential form. They both define the conservation of energy, which states that
the change in energy of a system is equal to the algebraic sum of the heat and work transfers to the system

Both eqns (1.8) and (1.9) relate the change in internal energy to the heat and work transfers. They do not define the datum level of internal energy.

### 1.5.5.1 Relationship between $E, Q$, and $W$

- the change in internal energy around a cycle is always zero;
- the net quantity of work $(\delta W)$ and heat $(\delta Q)$ transfers around a cycle will not necessarily be zero;
- the change of internal energy, $E_{2}-E_{1}$ has a significance as a quantity associated with the state of a system;
- Work, heat, and internal energy are all energy terms.
- Work and heat are both transitory energy transfers at the control surface of a system.
- Internal energy is the energy of the interior of the system.


### 1.5.5.2 Isolated systems

If a system executes a process in which no heat or work transfers occur then the system is said to be an isolated system. The internal energy of an isolated system is constant.

### 1.5.5.3 Energy of a system

The energy of a system was defined as $E$, without being specific about the form of this energy. Work transfer can bring about changes to many forms of energy: kinetic energy, potential energy, magnetic, capillary, electrical and thermal energy. In this analysis only kinetic, potential and thermal energy will be considered because these are the main forms of energy encountered by the mechanical engineer. The analysis can be expanded to include the other forms if necessary. Heat transfer can only, primarily, affect the thermal energy.

The change of internal energy, $\mathrm{d} E$, of a system of mass, $m$, is

$$
\begin{equation*}
E_{2}-E_{1}=m \frac{V_{2}^{2}}{2}-m \frac{V_{1}^{2}}{2}+m g h_{2}-m g h_{1}+m u_{2}-m u_{1} \tag{1.10}
\end{equation*}
$$

which is made up of three components:

$$
\begin{align*}
& \mathrm{d}(K E)=m \frac{V_{2}^{2}}{2}-m \frac{V_{1}^{2}}{2},  \tag{1.11}\\
& \mathrm{~d}(P E)=m g h_{2}-m g h_{1}, \tag{1.12}
\end{align*}
$$

and

$$
\begin{equation*}
\text { change of thermal energy }=m u_{2}-m u_{1} . \tag{1.13}
\end{equation*}
$$

The thermal energy ( $u$ ), which is based solely on the thermodynamic properties of the system, is termed the specific intrinsic internal energy. The term intrinsic, in this context, means "within" in the sense of a characteristic of the system. The properties defining specific intrinsic internal energy are usually temperature and pressure. The total energy of a moving system in a gravitational field is given by

$$
\begin{equation*}
E_{2}-E_{1}=m \frac{V_{2}^{2}}{2}-m \frac{V_{1}^{2}}{2}+m g h_{2}-m g h_{1}+m u_{2}-m u_{1} \tag{1.14}
\end{equation*}
$$

and hence, applying the First Law (eqn (1.9)), the net transfer of work and heat is

$$
\begin{equation*}
\delta Q-\delta W=m\left(u_{2}+\frac{V_{2}^{2}}{2}+g h_{2}\right)-m\left(u_{1}+\frac{V_{1}^{2}}{2}+g h_{1}\right) . \tag{1.15}
\end{equation*}
$$

### 1.5.5.4 Intrinsic internal energy, $U$ or $u$.

The intrinsic internal energy is the energy of the system based on the molecular motion inside the system. It is the energy of the system in the absence of motion, gravitational, electrical, magnetic, and capillary effects. The intrinsic energy of a system obeys the two-property rule, and is hence a function of any two independent properties.

The specific intrinsic internal energy is a specific property, defined by

$$
\begin{align*}
& u=u(T, v) \\
& u=u(p, T), \text { etc. } \tag{1.16}
\end{align*}
$$

and the intrinsic internal energy

$$
\begin{align*}
& U=U(m, T, v) \\
& U=U(m, p, T), \text { etc. } \tag{1.17}
\end{align*}
$$

The intrinsic internal energy is an extensive property.

### 1.5.5.5 Specific heat at constant volume, $c_{V}$

The specific heat at constant volume is a useful concept for single-phase pure substances. Typical substances of this type are substances in liquid or solid phases, and gases in the superheated phase. Hence, the specific heat at constant volume for oxygen, nitrogen, air etc., are commonly used, as is the specific heat of water, or other common liquids. The concept of the specific heat at constant volume can be seen from Fig 1.11, which shows the variation of specific intrinsic internal energy with temperature for a relatively complex substance in which the internal energy is a function of both temperature and volume. Most gases in the superheated region obey the
perfect gas law and the specific intrinsic internal energy is a function of temperature alone. The gas shown in Fig 1.11 might obey the van der Waals equation (see Chapter 8).


Fig 1.11: Constant volume lines (isochors) on a $u-T$ diagram
The specific heat at constant volume is defined as the rate of change of specific intrinsic internal energy at constant volume with temperature. This may be written mathematically as:

$$
\begin{equation*}
c_{v}=\left(\frac{\partial u}{\partial T}\right)_{v}=\left(\frac{\partial u}{\partial t}\right)_{v}=\left(\frac{\partial Q}{\partial T}\right)_{v} \tag{1.18}
\end{equation*}
$$

and is depicted in Fig 1.11 as the slope of an isochor. Fig 1.11 shows that the value of $c_{v}$ is, for a general substance, a function of both temperature and volume. The specific heat at constant volume is a property of the system because it is a derivative of the two properties. The units of $c_{v}$ in SI are $\mathrm{J} / \mathrm{kg} \mathrm{K}$, although in engineering it is usual to quote the values in $\mathrm{kJ} / \mathrm{kg} \mathrm{K}$. Equation (1.18) shows that the specific heat can be defined in terms of the discontinuous temperature scales ( $t$ - Celsius, or Fahrenheit) or the continuous temperature scales ( $T$ Kelvin, or Rankine). It has the same value for either scale because it is based on a temperature difference.

### 1.5.6 The First Law of Thermodynamics in the absence of kinetic and potential energy effects.

Many systems analysed in engineering thermodynamics are stationary relative to the Earth, which is used as a datum (e.g. a power station). If the kinetic and potential energy terms are removed from eqn (1.15) then the First Law equation becomes:

$$
\begin{equation*}
\delta Q-\delta W=m u_{2}-m u_{1} \tag{1.18}
\end{equation*}
$$

which in turn can be simplified to

$$
\begin{equation*}
\delta Q=\mathrm{d} U+\delta W \tag{1.19}
\end{equation*}
$$

Most of the applications of the First Law will be based on the formulations in eqns (1.18) and (1.19).

### 1.5.6.1 The First Law of Thermodynamics and the conversion of work to heat

The First Law contains no information on the direction of transferability of heat to work and work to heat. This means that work can be completely converted to heat, and also implies that heat can be completely converted to work. The First Law only states that energy can only be converted from one form to another. Fig 1.12 shows two situations that can be considered by the First Law.

## Perpetual motion machine of the first kind (PMM 1)

A perpetual motion machine of the first kind (PMM 1), shown in Fig 1.12a, is one which operates in a cycle and generates a work output without any other interaction with the surroundings. This is impossible by the First Law.

## Perpetual motion machine of the second kind (PMM 2)

A perpetual motion machine of the second kind (PMM 2), shown in Fig 1.12b, does not disobey the First Law, because the heat transfer to the cyclical system is transmuted into an equal and opposite work transfer. Hence, energy is conserved. It is not until the Second Law of Thermodynamics has been introduced that it can be shown that a PMM 2 is impossible.


Fig 1.12: (a) Perpetual motion machine (PMM 1) of the first kind
(b) Perpetual motion machine (PMM 2) of the second kind

### 1.5.6.2 Application of First Law of Thermodynamics to three general processes

### 1.5.6.2.1 Constant volume process

Two processes for a constant volume (isochoric) system have the same end states, one is brought about by work transfer and the other by heat transfer, and hence the change in internal energy is the same in both cases.

## (a) Heating process

In this process the system is taken from state 1 to state 2 by heat transfer to it. Since the system is a constant volume one, no work is done. Hence, from the First Law, eqn (1.19):

$$
\begin{equation*}
\delta Q=\mathrm{d} U . \tag{1.20}
\end{equation*}
$$

## (b) Work process

In this process the system is taken between the two end points, 1 and 2, by the application of work $(-W)$. The work has a negative sign because it is done on the system, and this is defined by the sign convention adopted. If the system is perfectly insulated the process is an adiabatic one, and the heat transfer, $\delta Q$, is zero. By the First Law:

$$
\begin{equation*}
0=\delta W+\mathrm{d} U \tag{1.21}
\end{equation*}
$$

Since the experiments both have the same end points the values of $\mathrm{d} U$ are the same in eqns (1.20) and (1.21). Hence,
the heat transfer to the system, $\delta Q$, is equal to the work transfer to the system, $-\delta W$.

### 1.5.6.2.2 Constant pressure process

It is easier to ensure that a system undergoes a constant pressure (isobaric) process than a constant volume one. This can be achieved by a piston cylinder arrangement of the type shown in Fig 1.4, but with the cylinder arranged vertically.
(a) Heating process

If the system is heated at constant pressure, the piston of mass $m$ will rise in the gravitational field. The potential energy of the piston will be increased, and work will have been done on the piston by the system. Applying the First Law (eqn (1.9)) gives:

$$
\delta Q=\mathrm{d} E+\delta W
$$

and if the whole system is not raised through the gravitational field this can be modified to eqn (1.19)

$$
\begin{equation*}
\delta Q=\mathrm{d} U+\delta W \tag{1.19}
\end{equation*}
$$

The first task is to define the pressure in the system ( $p$ ), which in this case is due to the pressure of the atmosphere - surroundings - $\left(p_{\mathrm{a}}\right)$ plus the effect of the weight. If the piston and the system are in static equilibrium then

$$
\begin{equation*}
p A=p_{\mathrm{a}} A+m g \tag{1.22}
\end{equation*}
$$

The work done by the system on the weight is

$$
\begin{equation*}
\delta W_{\mathrm{m}}=m g \mathrm{~d} L=\left(p-p_{\mathrm{a}}\right) A \mathrm{~d} L \tag{1.23}
\end{equation*}
$$

while the work done on the surroundings is

$$
\begin{equation*}
\delta W_{\mathrm{a}}=p_{\mathrm{a}} \mathrm{~d} V, \tag{1.24}
\end{equation*}
$$

because the pressure of the surroundings can be considered to remain constant. Hence, the total work done by the system is

$$
\begin{equation*}
\delta W=\delta W_{\mathrm{m}}+\delta W_{\mathrm{a}}=m g \mathrm{~d} L+p_{\mathrm{a}} \mathrm{~d} V=\left(p-p_{\mathrm{a}}\right) A \mathrm{~d} L+p_{\mathrm{a}} \mathrm{~d} V=p \mathrm{~d} V \tag{1.25}
\end{equation*}
$$

The First Law then becomes

$$
\begin{equation*}
\delta Q=\mathrm{d} U+p \mathrm{~d} V \tag{1.26}
\end{equation*}
$$

## (b) Work process

In this case the work done on the system is in the form of a paddle wheel stirring the fluid contained in the system. This is exactly the same as one of Joule's early experiments to evaluate the equivalence of heat and work. The work done on the system, in the absence of friction, is equivalent to the potential energy lost by the weight. The work done during the process is irreversible and can be denoted by the symbol $\delta W_{\mathrm{s}}$, where the suffix s indicates it is stirring, or shaft, work. The potential energy lost by the weight is absorbed by the fluid in the system through a viscous process and results in a rise of internal energy (and probably temperature) in the system. If the system is insulated from the surroundings, the process is adiabatic and $\delta Q=0$. Hence, applying the First Law (eqn (1.19)) gives

$$
\delta Q=\mathrm{d} U+\delta W
$$

but in this case, while $\delta Q=0$, the work term, $\delta W$, is made up of two components:

- the stirring work, $\delta W_{\mathrm{s}}$,
- the $p \mathrm{~d} V$ work done in raising the weight due to the change in properties of the substance, e.g. temperature.
Equation (1.19) then becomes

$$
\begin{equation*}
0=\mathrm{d} U+p \mathrm{~d} V-\delta W_{\mathrm{s}} \tag{1.27}
\end{equation*}
$$

which may be rewritten to give

$$
\begin{equation*}
\delta W_{\mathrm{s}}=\mathrm{d} U+p \mathrm{~d} V \tag{1.28}
\end{equation*}
$$

Since this was a constant pressure process it is possible to write eqn (1.28) as

$$
\begin{equation*}
\delta W_{\mathrm{s}}=\mathrm{d}(U+p V)=\mathrm{d} H . \tag{1.29}
\end{equation*}
$$

where $H$ is termed the enthalpy of the system. Enthalpy is a useful property when analysing constant pressure systems, and it will be shown later that it is a property closely related to flow processes and open systems.

If the end states of the two processes are the same, then the heat and work transfer processes are equivalent. Thus both the heat and work transferred to the system are equal to the change of enthalpy. Thus eqn (1.26) can be written

$$
\begin{equation*}
\delta Q=\mathrm{d} H . \tag{1.30}
\end{equation*}
$$

### 1.5.7 Enthalpy, $H$, and specific enthalpy, $h$.

Enthalpy is a property because it is defined as

$$
\begin{equation*}
H=U+p V, \tag{1.31}
\end{equation*}
$$

which is the sum of a property, $U$, and the product of two other properties, $p V$. This means that enthalpy must itself be a property. The specific enthalpy, $\boldsymbol{h}$, of a substance can be defined in a similar way to the specific internal energy, etc. and it is

$$
\begin{equation*}
h=\frac{H}{m}=\frac{U+p V}{m}=\frac{U}{m}+\frac{p V}{m}=u+p v . \tag{1.32}
\end{equation*}
$$

### 1.5.7.1 Specific heat at constant pressure, $c_{p}$

The specific heat at constant pressure is defined in a similar manner to that at constant volume, and all the restrictions outlined above apply to its use and definition. In this case the appropriate property diagram is that for constant pressure processes and the ordinate axis is now specific enthalpy, $h$, and not specific internal energy, $u$.

The specific heat at constant pressure is defined as the rate of change of specific enthalpy at constant pressure with temperature. It is also the quantity of heat which has to be added at constant pressure to unit mass of a substance to raise its temperature by a unit of temperature. The mathematical definition of $c_{p}$ is

$$
\begin{equation*}
c_{p}=\left(\frac{\mathrm{d} h}{\mathrm{~d} T}\right)_{p}=\left(\frac{\mathrm{d} h}{\mathrm{~d} t}\right)_{p}=\left(\frac{\delta Q}{\mathrm{~d} T}\right)_{p} \tag{1.33}
\end{equation*}
$$

Again, the value of $c_{p}$ can be obtained from either the continuous or discontinuous scales of temperature. The units of $c_{p}$ are the same as those of $c_{v}$, namely $\mathrm{J} / \mathrm{kg} \mathrm{K}$, or more commonly in engineering $\mathrm{kJ} / \mathrm{kg} \mathrm{K}$.

## Constant temperature processes

Constant temperature processes are referred to as isothermal processes. There are a number of isothermal processes encountered in common usage.

- boiling and condensing processes occur at constant temperature, and are accompanied by a change of phase of the working fluid: see Chapter 8 for more discussion.
- slow expansion and compression processes in equilibrium with constant temperature surroundings will be isothermal. A good example of such a process is that performed in the Boyle's Law experiment to prove $p V=c$, for a perfect gas.
- isothermal processes require heat or work transfer to or from the surroundings. They are not adiabatic.


## Constant internal energy processes

A constant internal energy process occurs when $\mathrm{d} U=0$. This can occur if the following circumstances exist:

- heat and work transfers are both equal to zero: i.e. $\delta Q=0 ; \delta W=0$.
- heat and work transfers are equal and opposite, so that $\delta Q-\delta W=0$.

An example of a constant internal energy system is the expansion of an insulated system against a vacuum.

### 1.5.8 Application of the First Law of Thermodynamics to open systems

The First Law of Thermodynamics for Closed Systems was derived in Section 1.5.4. This can be extended to open systems: the following analysis is a simplified approach to the derivation, and more rigorous ones, which give the same result are possible. Having derived the First Law of Thermodynamics it will be used to examine some engineering applications.

It was previously shown in section 1.5 .4 that the first law for a closed system (eqn (1.19)) is

$$
\delta Q=\mathrm{d} U+\delta W
$$

where $\mathrm{d} U$ is the intrinsic internal energy. If the whole system has kinetic (KE) and potential energy (PE) then eqn (1.9) gives
where

$$
\delta Q=\mathrm{d} E+\delta W
$$

At this stage it is necessary to reconsider the definitions of closed and open systems.
A closed system: is a quantity of matter contained within prescribed boundaries, i.e. it has a fixed mass.
An open system: is defined by its boundaries, or control surface, i.e. it has variable mass.

### 1.5.8.1 Unsteady flow energy equation

The equations of the First Law applied to an open system will be derived by considering a pseudo-flow situation. The diagrams in Fig 1.13 show a system at time $t=0$ and $t=\delta t$.


Time, $t=0$


Time, $t=\delta t$

Fig 1.13: Flow entering the boundaries of an open system
During time, $\delta t$, a mass, $\delta m_{\mathrm{i}}$ enters the system at boundary 1: this element of mass has the following energy terms associated with it:
i. specific intrinsic internal energy, $u_{\mathrm{i}}$, due to molecular motion - related to the temperature and pressure of the substance;
ii. specific kinetic energy, $\frac{V_{i}^{2}}{2}$, due to the gross velocity of the element.
iii. specific potential Energy, $g z_{i}$, due to elevation above a datum.

In addition to these terms, the element of mass has associated with it the work required to "push" it across the system boundary at 1 . This work is
iv. specific flow energy, and is a form of energy which has not been discussed up till now. It can be understood by consideration of Fig 1.14, which depicts the pipe at the entry to the system


Fig 1.14: Mass element at entry to the open system
Figure 1.14 clearly shows that work equal to $\delta m_{\mathrm{i}} p_{\mathrm{i}} v_{\mathrm{i}}$ is done on the element $\delta m_{\mathrm{i}}$ to 'push' it into the system this assumes that $p_{\mathrm{i}}$ remains constant over the interval of time $\delta t$.

Hence the element, $\delta m_{\mathrm{i}}$, introduces energy equal to

$$
\begin{equation*}
\delta m_{\mathrm{i}}\left(u_{\mathrm{i}}+p_{\mathrm{i}} v_{\mathrm{i}}+\frac{V_{\mathrm{i}}^{2}}{2}+g z_{\mathrm{i}}\right) \quad \text { into the system. } \tag{1.34}
\end{equation*}
$$

Applying the principle of conservation of energy to the system, the change in energy in the system $\delta E_{\mathrm{cv}}$ is

$$
\begin{equation*}
\delta E_{\mathrm{cv}}=\delta E_{\mathrm{i}}-\delta E_{\mathrm{e}}+\delta Q-\delta W \tag{1.35}
\end{equation*}
$$

where $\quad E_{\mathrm{cv}} \quad=$ internal energy in control volume,
$E_{\mathrm{i}} \quad=$ energy introduced by inflowing element,
$E_{\mathrm{e}} \quad=$ energy withdrawn by outflowing element,
$Q \quad=$ heat transfer to system,
$W \quad=$ work transfer from system.
By a similar analysis to that performed above it is apparent that the outflowing energy, taken by an element of mass, $\delta m_{\mathrm{e}}$, is

$$
\begin{equation*}
\delta m_{\mathrm{e}}\left(u_{\mathrm{e}}+p_{\mathrm{e}} v_{\mathrm{e}}+\frac{V_{\mathrm{e}}^{2}}{2}+g z_{\mathrm{e}}\right) \tag{1.36}
\end{equation*}
$$

The internal energy of the system, $E_{\mathrm{cv}}$, is given by

$$
\begin{equation*}
E_{\mathrm{cv}}=\left(U+\frac{\bar{V}^{2}}{2}+g Z\right)_{\mathrm{cv}} \tag{1.37}
\end{equation*}
$$

and the change of internal energy is $\delta E_{\mathrm{cv}}=\delta\left(U+\frac{\bar{V}^{2}}{2}+g Z\right)_{\mathrm{cv}}$
Hence eqn (1.35) becomes:
$\delta Q-\delta W=\delta\left(U+\frac{\bar{V}^{2}}{2}+g Z\right)_{\mathrm{cv}}-\delta m_{\mathrm{i}}\left(u_{\mathrm{i}}+p_{\mathrm{i}} v_{\mathrm{i}}+\frac{V_{\mathrm{i}}^{2}}{2}+g z_{\mathrm{i}}\right)+\delta m_{\mathrm{e}}\left(u_{\mathrm{e}}+p_{\mathrm{e}} v_{\mathrm{e}}+\frac{V_{\mathrm{e}}^{2}}{2}+g z_{\mathrm{e}}\right)$
Giving further consideration to the flow energy term $p_{i} v_{i}$, it can be seen that this is the product of two properties and is hence itself a property of the substance. It also has the units of energy, and because it always occurs in conjunction with the internal energy, $u$, in flow processes it is convenient to define another property

$$
\begin{equation*}
h=u+p v \tag{1.40}
\end{equation*}
$$

$h$ is called as the specific enthalpy of a substance. This was also introduced in Section 1.5.4 by consideration of a closed system undergoing a process at constant pressure. The enthalpy, $\boldsymbol{H}$, of a system is given by

$$
\begin{equation*}
H=m h \tag{1.41}
\end{equation*}
$$

where $\quad m=$ mass of the system.
Thus eqn (1.39) becomes

$$
\begin{equation*}
\delta Q-\delta W=\delta\left(U+\frac{\bar{V}^{2}}{2}+g Z\right)_{\mathrm{cv}}-\delta m_{\mathrm{i}}\left(h_{\mathrm{i}}+\frac{V_{\mathrm{i}}^{2}}{2}+g z_{\mathrm{i}}\right)+\delta m_{\mathrm{e}}\left(h_{\mathrm{e}}+\frac{V_{\mathrm{e}}^{2}}{2}+g z_{\mathrm{e}}\right) \tag{1.42}
\end{equation*}
$$

Now, the average rate of change of properties over the step is given by

$$
\begin{equation*}
\frac{\delta Q}{\delta t}-\frac{\delta W}{\delta t}=\frac{\delta}{\delta t}\left(U+\frac{\bar{V}^{2}}{2}+g z\right)_{\mathrm{cv}}-\frac{\delta m_{\mathrm{i}}}{\delta t}\left(h_{\mathrm{i}}+\frac{V_{\mathrm{i}}^{2}}{2}+g z_{\mathrm{i}}\right)+\frac{\delta m_{\mathrm{e}}}{\delta t}\left(h_{\mathrm{e}}+\frac{V_{\mathrm{e}}^{2}}{2}+g z_{\mathrm{e}}\right) \tag{1.43}
\end{equation*}
$$

In the limit $\delta t \rightarrow 0$, eqn (1.43) can be written, with $\frac{\mathrm{d}}{\mathrm{d} t}(x)=\dot{x}$.

$$
\begin{equation*}
\dot{Q}-\dot{W}=\frac{\partial}{\partial t}\left(U+\frac{\bar{V}^{2}}{2}+g z\right)_{c v}-\dot{m}_{\mathrm{i}}\left(h_{\mathrm{i}}+\frac{V_{\mathrm{i}}^{2}}{2}+g z_{\mathrm{i}}\right)+\dot{m}_{\mathrm{e}}\left(h_{\mathrm{e}}+\frac{V_{\mathrm{e}}^{2}}{2}+g z_{\mathrm{e}}\right) \tag{1.44}
\end{equation*}
$$

Equation (1.44) may be simplified to

$$
\begin{equation*}
\dot{Q}-\dot{W}=\frac{\partial}{\partial t}(E)_{\mathrm{cv}}-\dot{m}_{\mathrm{i}}\left(h_{\mathrm{i}}+\frac{V_{\mathrm{i}}^{2}}{2}+g z_{\mathrm{i}}\right)+\dot{m}_{\mathrm{e}}\left(h_{\mathrm{e}}+\frac{V_{\mathrm{e}}^{2}}{2}+g z_{\mathrm{e}}\right) \tag{1.45}
\end{equation*}
$$

Equation (1.45) is called the Unsteady flow energy equation (USFEE). It is unsteady because the conditions existing in the control volume may be functions of time, i.e. $\frac{\partial}{\partial t}(E)_{\mathrm{cv}} \neq 0$.

### 1.5.8.2 Steady Flow Energy Equation

The steady flow energy equation is a particular case of the USFEE, and may be derived from eqn (1.45) by making the following assumptions:

- $\dot{m}_{\mathrm{e}}=\dot{m}_{\mathrm{i}}$;
- all velocities, enthalpies and elevations remain constant with time;
- $\frac{\partial}{\partial t}(E)_{\mathrm{cv}}=0$.

Then

$$
\begin{equation*}
\dot{Q}-\dot{W}=\dot{m}\left(h_{\mathrm{e}}-h_{\mathrm{i}}+\frac{V_{\mathrm{e}}^{2}-V_{\mathrm{i}}^{2}}{2}+g\left(z_{\mathrm{e}}-z_{\mathrm{i}}\right)\right) \tag{1.46}
\end{equation*}
$$

These assumptions mean that to an observer there appears to be no change in the state of the system with the passage of time, even though the fluid inside the system is continuously changing.

### 1.5.8.3 Applications of Steady Flow Energy Equation

## (a) Throttling process

Throttling processes occur commonly in engineering, when a fluid is passed from a high pressure to a lower one. An example of a throttling process is the induction system of a petrol engine, when the power output (or speed) of the engine is reduced by fitting a valve in the inlet manifold. Other examples are valves fitted in pipes to control the flow of fluid along the pipe; a stop-cock in a water main might act as a throttle when it is not fully open. A typical throttling process is shown schematically by Fig 1.15.


Fig 1.15: Schematic diagram of throttle valve
The control volume of the throttle is defined by the control surfaces at 1 and 2, and the pipe-work of the system. The flow through the throttle valve can be considered to be steady, and hence it obeys the Steady Flow Energy Equation (eqn 1.46), giving

$$
\dot{Q}-\dot{W}=\dot{m}\left(h_{\mathrm{e}}-h_{\mathrm{i}}+\frac{V_{\mathrm{e}}^{2}-V_{\mathrm{i}}^{2}}{2}+g\left(z_{\mathrm{e}}-z_{\mathrm{i}}\right)\right)
$$

There is no shaft or $p \mathrm{~d} V$ work done in the throttle, and hence $\dot{W}=0$. It can be assumed that the heat losses (or gains) to the fluid passing through the throttle are negligible compared to the energy contained in the fluid itself, giving $\dot{Q}=0$. Also, the change of potential energy of the flow passing through the throttle is small compared to the changes in the other properties, which enables eqn (1.46) to be reduced to

$$
\begin{equation*}
h_{2}+\frac{V_{2}^{2}}{2}=h_{1}+\frac{V_{1}^{2}}{2}=h_{0} . \tag{1.47}
\end{equation*}
$$

The term $h_{0}=h+\frac{V^{2}}{2}$ is called the stagnation enthalpy of the fluid. It is the enthalpy of the fluid if it were brought to rest. The enthalpy, $h$, in a flowing fluid is termed the static enthalpy, and is measured by an observer travelling with the fluid. When the fluid is brought to rest the kinetic energy is turned into thermal
energy, and the observer would see a rise in the values of the property being measured, e.g. temperature, enthalpy: these are called the stagnation properties.

In many cases the velocity of the fluid does not change significantly across the throttle, and eqn (1.47) can be simplified to

$$
\begin{equation*}
h_{2}=h_{1} \tag{1.48}
\end{equation*}
$$

Hence,

## the stagnation enthalpy remains constant across a throttle

if the change in velocity across the throttle is low the static enthalpy is constant across a throttle

### 1.5.8.3.1 Perfect gas flowing through a throttle

The enthalpy of a perfect gas is defined by $h=c_{\mathrm{p}} T$, and hence when a perfect gas flows through a throttle, from eqn (1.47)

$$
\begin{equation*}
c_{p} T_{02}=c_{p} T_{01} \tag{1.49a}
\end{equation*}
$$

Since, $c_{p}$ is a constant

$$
\begin{equation*}
T_{02}=T_{01} \tag{1.49b}
\end{equation*}
$$

which can be written

$$
\begin{equation*}
T_{2}+\frac{V_{2}^{2}}{2}=T_{1}+\frac{V_{1}^{2}}{2} \tag{1.49c}
\end{equation*}
$$

Thus, when a perfect gas flows through a throttle the stagnation temperature remains constant. If the change in velocity across the throttle is small, then eqn (1.49c) may be written as

$$
\begin{equation*}
T_{2}=T_{1} \tag{1.50}
\end{equation*}
$$

Hence, when the velocity terms are negligible, the static temperature across the throttle is constant. This is not surprising because the energy (enthalpy) of the gas is proportional to temperature, and the energy (enthalpy) does not change.

> The stagnation temperature of a perfect gas does not change when it passes through a throttle If the velocity change across the throttle is small - the static temperature of a perfect gas does not change when it passes through a throttle

### 1.5.8.3.2 Steam (or any non-perfect gas) flowing through a throttle

The static (or more correctly, the stagnation) enthalpy of steam travelling through a throttle remains constant. Hence, the effect of throttling the steam can be examined by considering the way in which the enthalpy of steam varies with pressure. Figure 1.16 has been plotted from the 'steam tables'(Rogers and Mayhew (1994)) and shows the saturated liquid and saturated vapour enthalpy lines as a function of pressure.


Fig 1.16: Variation of enthalpy on the saturated liquid and vapour lines with pressure

## for steam

It can be seen from this diagram that a constant enthalpy line drawn for a change of pressure might cross into the two-phase saturated liquid + saturated vapour region. An enlarged portion of Fig 1.16 is shown in Fig 1.17, and two isenthalpic processes are shown on that diagram.

The horizontal lines shown in Fig 1.17 are isenthalpic lines; the actual flow through the valve does not follow this line, but the end states of the processes defining the flow through the throttle will be on this line. It is possible to consider two processes on this diagram. First, consider a process that is defined by points 4 and 3 . In this case the fluid will go from state 4 to state 3 , because $p_{4}>p_{3}$. In undergoing this process the steam will pass from inside the liquid + vapour region to the saturated vapour line. If $p_{4}=30 \mathrm{bar}$, and $p_{3}=10 \mathrm{bar}$, and if the state at 3 is dry saturated, then $h_{3}=2778 \mathrm{~kJ} / \mathrm{kg}$. Since the throttling process is isenthalpic $h_{4}=h_{3}=2778$ $\mathrm{kJ} / \mathrm{kg}$. Thus the dryness fraction or quality at 4 is

$$
x_{4}=\frac{h_{4}-h_{\mathrm{f}, 30}}{h_{\mathrm{g}, 30}-h_{\mathrm{f}, 30}}=\frac{2778-1008}{2803-1008}=0.986 .
$$

The temperature at 4 is the saturation temperature at 30 bar, thus $t_{4}=233.8^{\circ} \mathrm{C}$, whereas that at point 3 is the saturation temperature of 10 bar , i.e. $t_{3}=179.9^{\circ} \mathrm{C}$. In this case the throttling process has increased the dryness of the steam, and the temperature of the steam has lowered from 233.8 to $179.9^{\circ} \mathrm{C}$. This is in direct contrast to the throttling of a perfect gas, and has occurred because the steam can contain energy in two ways: it can contain it as a result of its temperature and also its phase (i.e. liquid or vapour).


Fig 1.17: Enlargement of saturated vapour line from Fig 1.16
Examination of figs 1.16 and 1.17 shows that the enthalpy against pressure diagram exhibits a maximum value of $2803 \mathrm{~kJ} / \mathrm{kg}$ between pressures of about 26 and 34 bar . Point 4 on the diagram was carefully chosen to be in the middle of this range. Consider another isenthalpic process, this time starting on the saturated vapour line, with pressure $p_{2}=65 \mathrm{bar}$, and enthalpy, $h_{2}=2779 \mathrm{~kJ} / \mathrm{kg}$. This enthalpy value is close enough to that of point 3 to be considered the same. Hence, a process from 2 to 4 will be isenthalpic, but in this case the dryness fraction will have decreased from 1 to 0.986 . This means that there is a pressure, and hence temperature, for steam (and all real gases) beneath which the gas can be made drier by throttling. This point is defined by the inversion pressure, and inversion temperature. The effect is known as the Joule - Thomson effect, and this characteristic of gases is used in liquefaction processes, which are discussed in more detail in Chapter 18. Note that a perfect gas cannot exhibit such an effect.

### 1.6 Concluding remarks

This chapter has summarised the basic definitions of thermodynamics. It has also introduced the concepts of work and heat - and most importantly emphasised that these forms of energy transfer. Work and heat are transitory phenomena that exist only when a system interacts with its surroundings. However, the net effect of
work and heat transfers is to change the energy of the system. The chapter has also introduced the concepts of open and closed systems, and derived forms of the energy conservation equation for both types of system. This chapter provides the building blocks of engineering thermodynamics up to the First Law: the Second Law is introduced in Chapter 2.

## Problems

P1.1.


Property, $X$
Fig P1.1: Cycle of events made up of four processes.

Process 12: $\delta \mathrm{Q}=+10 \mathrm{~J} \quad \delta \mathrm{~W}=-18 \mathrm{~J}$
Process 23: $\delta \mathbf{Q}=+100 \mathrm{~J} \quad \delta \mathrm{~W}=0 \mathrm{~J}$
Process 34: $\delta \mathrm{Q}=-20 \mathrm{~J} \quad \delta \mathrm{~W}=+70 \mathrm{~J}$
Process 41: $\delta \mathrm{Q}=-10 \mathrm{~J} \quad \delta \mathrm{~W}=+28 \mathrm{~J}$

Calculate the values of $U_{\mathrm{n}}-U_{1}$, the net work, the net heat transfer and the heat supplied for the cycle.

P1.2. In the system shown in fig P1.2, the piston has negligible weight and the initial spring force is zero. The gas is heated until the volume is doubled and the final pressure is 5 bar. Calculate the work done and find how much work is done on the spring.


Fig P1.2.
[100kJ; 150kJ]
P1.3. A spherical balloon has a diameter of 0.3 m and contains air at a pressure of 1.5 bar. The diameter of the balloon increases to 0.33 m due to heating and during this process the pressure is proportional to the diameter. Calculate the work done by the air during the process.

P1.4. A spherical balloon has a diameter of 0.3 m and contains air at a pressure of 1.5 bar. The diameter of the balloon increases to 1.0 m due to heating and during this process the pressure is proportional to the diameter. Calculate the work done by the air during the process.

P1.5. A cylinder contains 3 kg of saturated steam at 20 bar . The steam is heated until the temperature becomes $500^{\circ} \mathrm{C}$, the pressure remaining constant. Determine the energy added and the work done by the steam during the process.
[2004kJ; 456kJ]
P1.6. Steam at the critical state is contained in a rigid vessel. The vessel cools until the pressure is 27.5 bar. Calculate the final quality.

P1.7. A rigid vessel is initially divided into two parts A and B by a thin partition. Part A contains 1 kg of dry saturated steam at 3.5 bar and part B contains 2 kg of steam at 7 bar with dryness 0.8 . The partition is removed and the pressure in the vessel after some time is found to be 5 bar. Find:
a. the volume of the vessel and the state of the steam at 5 bar;
b. the amount of heat transfer from the steam to the vessel and the surroundings.
[0.9610m $\left.{ }^{3} ; 0.8541 ;-98 \mathrm{~kJ}\right]$
P1.8. The cylinder shown in Fig P1.8 contains 5 kg of steam at 14 bar quality 0.8 . When the cylinder is empty there is no force in the spring. Heat is transferred until the volume is $150 \%$ of the initial volume. Determine the final pressure, work done and heat transfer.


Fig P1.8
[21bar; 494kJ; 4870kJ]
P1.9. Tank A contains 1 kg of saturated Freon- 12 vapour at $20^{\circ} \mathrm{C}$. The valve is then opened slightly and the Freon flows into the cylinder so that the piston rises against a constant external pressure of 2 bar. Heat is transferred during the process to keep the temperature constant throughout the process at $20^{\circ} \mathrm{C}$. Calculate the heat transfer. [Assume for superheated Freon-12 at 2 bar, $t=20^{\circ} \mathrm{C} ; v=0.0969 \mathrm{~m}^{3} / \mathrm{kg}$, and $h=202.27$ $\mathrm{kJ} / \mathrm{kg}$ ]


Fig P1.9

P1.10. An insulated bottle is initially evacuated, i.e. it contains a vacuum, and then the stopper is removed allowing atmospheric air to fill the bottle. Evaluate the final specific internal energy in a bottle when the air has just filled it, i.e. the pressure has just reached the ambient value.

Comment: This is a relatively complex problem in unsteady gas dynamics if the processes between the removal of the stopper and the quiescent end state are considered in detail. In the flow processes pressure waves will travel into the bottle and be reflected; these will cause the atmospheric air to start flowing into the bottle. The waves will ultimately die out due to the flow interactions at the neck of the bottle and fluid friction, and finally a steady state will be reached. The great strength of the approaches of thermodynamics is that they allow the final state to be evaluated without any knowledge of gas dynamics.

$$
\left[u_{2}=\left(u_{\mathrm{in}}+p_{\mathrm{atm}} v_{\mathrm{in}}\right)=h_{\mathrm{in}}\right]
$$

P1.11. Filling a bottle which already contains some fluid. The analysis adopted above may be applied to a bottle which is not initially evacuated, i.e. contents are at $p_{1} \neq 0$. Evaluate the final temperature in the bottle when the pressure reaches the ambient value.

$$
\left[T_{2}=\kappa T_{a} /\left\{\frac{p_{1}}{p_{a}}\left\{\frac{\kappa T_{a}}{T_{1}}-1\right\}+1\right\}\right]
$$

P1.12. Discharge from a bottle. Problems P1.10 and P1.11 have dealt with filling a bottle, and shown how this can be considered to be a closed system problem. A similar approach can be applied to a bottle discharging to the surroundings. Evaluate the mass remaining in the bottle when the pressure reaches the ambient value.

$$
\left[m_{1}=\left\{\frac{\left(h_{\mathrm{exh}}-u_{1}\right)}{\left(h_{\mathrm{exh}}-u_{2}\right)}\right\}\right]
$$

P1.13. A tank containing saturated steam at 3.5 bar has a volume of $0.4 \mathrm{~m}^{3}$. A valve is opened and steam flows into the tank from a steam main where the state is $15 \mathrm{bar}, 300^{\circ} \mathrm{C}$, until the pressure in the tank becomes 15 bar.

Calculate the mass of steam that flows into the tank and the final state assuming no heat transfer takes place.
[1.4kg; 15 bar; $345^{\circ} \mathrm{C}$ ]
P1.14. An insulated tank having a volume of $0.8 \mathrm{~m}^{3}$ contains dry saturated steam at 60 bar. Steam is allowed to flow out of the tank through a valve until the pressure becomes 30 bar. Calculate the mass of steam that is withdrawn, assuming that the contents remain as a homogeneous mixture of liquid and vapour at all times and that this mixture flows out of the tank.
[Hint: Examine the variation of $h_{f}-u_{f}$ and $h_{g}-u_{g}$ range of the steam tables].
[11.23kg]

