

# **THERMODYNAMIC SYSTEMS**

## **Introduction**

The word thermodynamics is made up from two words of Greek origin .

Thermo, meaning hot, or heat and dynamics, the study of matter in motion.

Thus, thermodynamics is the study of heat related to matter in motion.

Applied thermodynamics deals with the relationships between heat, work, and the properties of a system.

The first part of these notes deals with some fundamental details such as units and basic definitions.

## **Units**

### **System of units**

The system of units used throughout is the International System (SI).

This system has six basic units, each given a special symbol, all other units are derived from these basic units. (Some of these derived units also have special names and special symbols.)

### **Rules for writing units**

- ❖ No upper case letters except for name of person
- ❖ No full stop required
- ❖ No plural endings
- ❖ No double prefix

The basic units are:

Quantity	Name of unit	Symbol
Mass	kilogramme	kg
Length	metre	m
Time	second	s
Thermodynamic temperature	kelvin	K

### **Mass**

The mass of a substance can be said to be the amount of matter it contains.

Mass is constant and has the same value at sea-level, in space, or on another planet, where a kilogramme of steel would still be a kilogramme of steel.

### **Force**

The unit of force is the Newton (N), and it is defined as the force necessary to give 1 kg an acceleration of  $1 \text{ m/s}^2$ , i.e.

$$1 \text{ N} = 1 \text{ kg} \times 1 \text{ m/s}^2$$

### **Weight**

The weight of a body is defined as the force exerted on the body when acted on by the acceleration due to gravity, i.e.  $\text{weight} = \text{mass} \times \text{local acceleration due to gravity} = mg$ .

The value of  $g$  varies from place to place on the earth's surface and so a standard value of  $9.80665 \text{ m/s}^2$  has been adopted. For many engineering problems it is sufficiently accurate to take a value of  $9.81 \text{ m/s}^2$

## Multiples and sub-multiples

These are formed by means of the following prefixes.

Prefix	Symbol	Factor by which the unit is multiplied		
Tera	T	$10^{12}$	=	1 000 000 000 000
<b>giga</b>	<b>G</b>	<b><math>10^9</math></b>	=	<b>1 000 000 000</b>
<b>mega</b>	<b>M</b>	<b><math>10^6</math></b>	=	<b>1 000 000</b>
<b>kilo</b>	<b>k</b>	<b><math>10^3</math></b>	=	<b>1 000</b>
hecto	h	$10^2$	=	100
deca	da	$10^1$	=	10
deci	d	$10^{-1}$	=	0.1
<b>centi</b>	<b>C</b>	<b><math>10^{-2}</math></b>	=	<b>0.01</b>
<b>milli</b>	<b>m</b>	<b><math>10^{-3}</math></b>	=	<b>0.001</b>
<b>micro</b>	<b><math>\mu</math></b>	<b><math>10^{-6}</math></b>	=	<b>0.000 001</b>
nano	n	$10^{-9}$	=	0.000 000 001
pico	p	$10^{-12}$	=	0.000 000 000 001
femto	f	$10^{-15}$	=	0.000 000 000 000 001
atto	a	$10^{-18}$	=	0.000 000 000 000 000 001

Units in bold are used in preference to the others

## Definitions

Since thermodynamics relates heat, work, and the properties of matter, it is necessary to give some strict definitions in order to obtain a satisfactory conception of these relationships.

## System

The idea of a system is important, problems cannot exist without one because you need to decide what should be included.

A system can therefore be broadly defined as a region containing matter whose behaviour is under investigation.

## Boundary

This region under investigation must be enclosed by a boundary line, which may be a real physical surface or an imaginary line.

The boundary takes no part in the change or process, it only determines what is taking part in the process.

The boundary may be open or closed, and can be elastic or fixed, but what is very important is that all mass and energy transfers are said to take place across the boundary and are calculated at the boundary.

## Surroundings

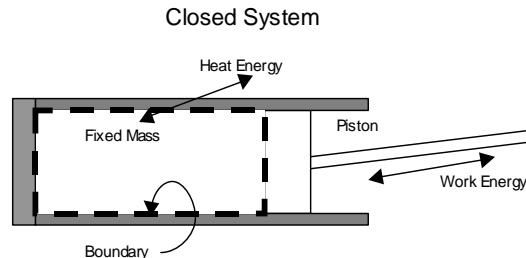
The term “surroundings” usually refers to everything outside the boundary line which may be affected by changes within the system.

The surroundings themselves may form another system.

## Closed systems

The system is said to be closed when only heat energy and work energy cross the boundary, there is no mass transfer hence this remains constant within the system. Since there is no fluid flow across the boundary any process which the system undergoes is called a “**non – flow**” process.

A typical closed system would be a piston in a cylinder such as that shown below.



If the boundary remains fixed only heat energy can enter or leave the system across the boundary, the process then takes place at constant volume.

If the boundary were to expand or contract then work transfer can take place as well as heat transfer and the system undergoes a process which can be called a Polytropic Process.

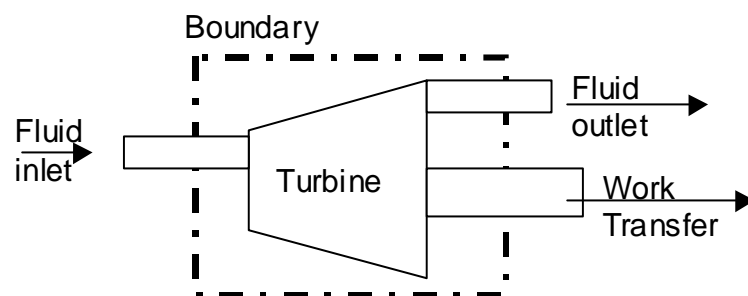
## Open system

The system is said to be open when there are, one or more openings in the boundary through which fluid may flow.

Heat and work energy transfers take place as before, however there is now also a mass transfer across the boundary, any process undergone by the system is now called a **flow process**.

If the mass of substance entering per unit time is constant and equal to the mass leaving per unit time, then the mass of the system- remains constant; the system is termed a **steady-flow** system and the process a **steady-flow process**.

A typical open system would be a turbine.



## Properties and States

A system requires a working fluid, which can be either a gas, vapour, liquid or a mixture of all three. Thus before the process can be studied, it is necessary to know certain characteristics or properties of the working fluid.

### Property

A property is any characteristic which defines the exact state of the working fluid examples are, pressure, volume, temperature, enthalpy, internal energy, entropy,. The changes in these properties are used to determine any energy transfers associated with the change.

It is not always physically possible to observe or measure all these properties; for instance, enthalpy, internal energy and entropy are determined mathematically from expressions involving other properties.

### Intensive properties

Properties that are independent of mass, such as pressure and temperature.

### Extensive properties

Properties that are mass dependent thus specific values are often quoted.

Volume  $\text{m}^3$  or specific volume  $\text{m}^3/\text{kg}$ , Internal energy kJ or specific internal energy kJ/kg.

## 2-Property Rule

The 2-property rule states that in general when any two properties of a fluid are specified, every other property will have a definite value and the complete state of the fluid will be determined.

This rule is not strictly true, for two reasons.

1. The rule applies only to pure fluid, however, within limitations all working fluids obey the rule and therefore may be treated as pure fluids.

Air is not a pure fluid, the limitation in this case is that it must be in the gaseous phase. Fortunately, the air used in heat engines generally is gaseous.

2. The rule does not apply unless the two properties are independent properties.

If the pressure and temperature of a system consisting of unit mass of steam is given, the state of the system is not completely specified, since the temperature depends on the pressure the properties are not independent

Therefore, another independent property would be required.

## State

State is the term used to give a complete specification of the system. When a system is in a particular state, all the properties have definite values (fixed by virtue of the system being in that state). The term does not mean the physical aspect of the system, for example if it is solid, liquid or gaseous.

## Process

A process occurs when a system changes its state, and the path of the process is a series of state points through which the system has passed.

A process is said to be cyclic if all the properties of the system have the same values at the end of the process as they had at the beginning.

## Datum for properties

Changes in properties are usually more important than absolute values and hence the datum for properties may be varied to suit the nature of the system and processes involved.

For example, properties of ;

Water and Steam are calculated with 0°C as datum.

Refrigerants are calculated with -40°C as datum.

Gases are generally calculated with -273°C as datum.

## Working substance

All systems require some substance so that the various operations required can be carried out.

The working substances ;

Are usually fluids which can be readily expanded or compressed.

Take part in energy transfer.

Can receive or reject heat energy.

Can be the means by which work is done.

The distinction between fluids such as a superheated vapour and a gas is not rigid, however at very high degrees of superheat an isothermal line on a p-v diagram tends towards the shape of a hyperbola (i.e.  $Pv = \text{constant}$ ).

An idealised substance called a perfect gas is considered to have an equation of state in the form  $Pv/T = \text{constant}$  and this equation is satisfied when an isothermal line is in the shape of a hyperbola thus all substances tend towards a perfect gas at very high levels of superheat.

Fluids such as oxygen and nitrogen that are considered gasses have high levels of superheat at normal atmospheric conditions, the critical temperatures being -119°C and -147°C respectively.

The critical temperatures of Ammonia and Water Vapour are 130°C and 374.15°C respectively hence at normal atmospheric conditions these fluids exist as liquids.

In general working fluids are considered to be either “Real” or “Ideal”

“**Real**” fluids are vapours or vapour mixtures such as steam or refrigerants their properties are obtained from tables

“**Ideal**” fluids are generally gasses such as air and their properties are calculated using the equations of state.

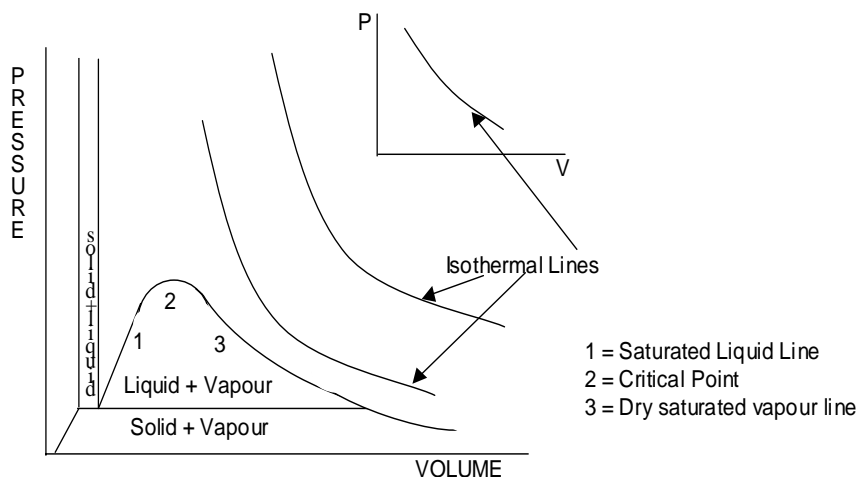
This distinction is important particularly when dealing with steam air mixtures such as exist in condensers.

## State diagrams for gases

The most usual way of illustrating changes of state of a closed system is on a pressure-volume state diagram, however we could also show the change of state on a Temperature-Entropy diagram.

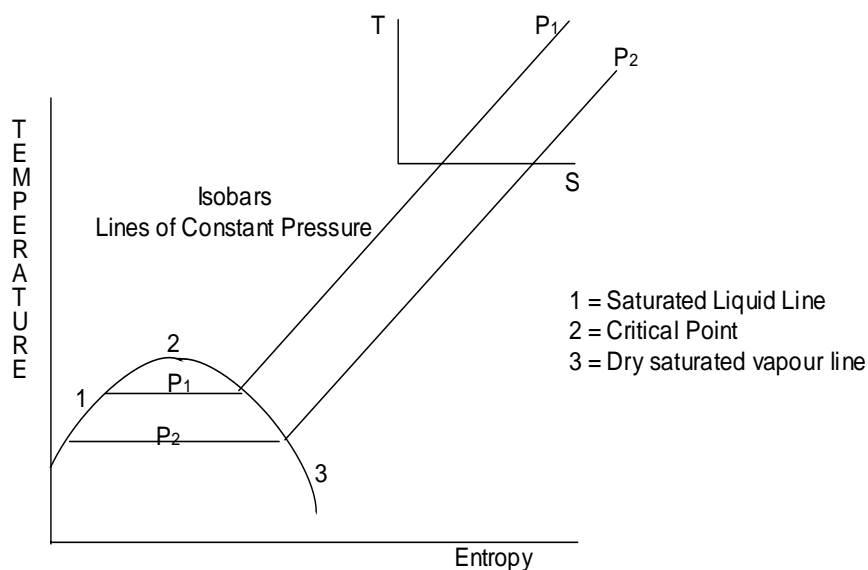
A pressure- volume diagram for a real substance, showing the solid, liquid and gaseous phases is shown below.

The upper right part of the diagram well above the critical pressure and temperature is the region which is normally associated with the so-called permanent gases, and shows the usual form of  $p$ - $v$  diagram for a gas. If the gas is considered perfect, then the solid and liquid phase regions have no meaning.



When state changes occur in an open system, for example a gas turbine plant, a Temperature- Specific entropy state diagram would be used rather than a  $p$  $v$  diagram although we could use both if required.

A  $T$ - $s$  diagram for a real substance would only cover the lower left hand corner of the diagram below, the typical  $T$ - $s$  diagram for a gas appears in the upper-right region of this diagram.



Pressure –Volume and Temperature – Entropy diagrams will be used extensively throughout the following sections.

## **Heat “Q”**

Is a transient quantity, it describes the energy transfer process through a system boundary resulting from temperature difference between one body and another. The heat, having been transferred, will then disperse into other forms of energy such as internal energy or work, the dispersal being a function of the system employed.

Thus heat is not a property.

Unit of heat = Joule or rate of heat transfer = Joule/second = Watt

## **Work “W”**

If a system exists in which a force at the boundary of the system is moved through a distance, then work is done by or on the system.

Note that as soon as the force ceases then, any work being done will also cease.

Work is also a transient quantity and is therefore not a property. Unit of work = Joule

## **Power “P”**

Is the rate at which work is being done.

Thus Power = work done/unit time Joule/second (J/s) or Watt (W).

## **S.T.P and N.T.P.**

**Standard Temperature and Pressure** (STP) is a standard condition used for reference purposes being a pressure of  $101.325 \text{ kN/m}^2$  and a temperature of  $0^\circ\text{C}$

**Normal Temperature and Pressure** (NTP) refers to atmospheric conditions of a normal day, namely a pressure of  $101.325 \text{ kN/m}^2$  and a temperature of  $15^\circ\text{C}$  and is also used for reference purposes.

# THE LAWS OF THERMODYNAMICS

## The laws of thermodynamics are:

Statements of thermodynamic behaviour.

Natural laws which are based on observable phenomena,

Designated as laws because, they have never been shown to be contradicted.

## THE ZEROth LAW

The concept of this law was developed after the first, second and third laws of thermodynamics.

The law is concerned with thermal equilibrium while the other laws refer to work and energy transfers, plus the possibility of temperature difference, so they are involved with change.

Thus the law involved with thermal equilibrium should logically precede the other laws.

This law States:

If two bodies are separately in thermal equilibrium with a third body then they must be in thermal equilibrium with each other.

Thermal equilibrium means there is no change of state and hence the Zeroth law implies that all bodies if in thermal equilibrium, will be at the same temperature.

As an example, this situation arises when taking a temperature using a thermometer.

When the thermometer is steady it is assumed that the fluid, the glass container and the body whose temperature is being measured, are all at the same temperature, so they are in thermal equilibrium.

## THE FIRST LAW OF THERMODYNAMICS

This is based on the principle of conservation of energy and establishes a relationship between heat and work for a fixed mass system of the form

$$\text{work transfer (W)} = \text{heat transfer (Q)}$$

This relationship is a statement of the first law of thermodynamics.

### Consider a Thermodynamic Cycle

Here, a working fluid is taken through a series of processes and is returned to its original state thus its final properties are the same as its original properties.

If work is transferred during this cycle then, since there is no overall change in the fluid properties, all the work energy must have been transferred as heat energy

The first law implies that, in a cycle, there must be heat transfer for there to be work transfer.

For example, an engine, which could provide work transfer without heat transfer would break the first law because it would create energy and contradict to the principle of conservation of energy.

An engine, which could provide work transfer without heat transfer would run forever, it would have perpetual motion!



## THE GENERAL ENERGY EQUATION

The first law of thermodynamics is based on the principle of energy conservation, but we must identify the energy involved,

### Potential energy

This is related to position (height) relative to a defined datum.

$$\text{Potential energy} = mgz$$

### Kinetic energy

This is related to velocity relative to a fixed point, this is the mechanical energy of the system mass.

$$\text{Kinetic energy} = \frac{1}{2} mc^2$$

### Internal energy

This is the energy possessed by the molecules due to their movements or vibrations.

$$\text{Internal energy } U = mc_v(T_2 - T_1)$$

### Flow energy

This is the energy which is required to carry out a mass transfer across the boundary of an open system, it cannot be stored in the system but because it is always present when a flow process occurs, it is usual to consider that it is contained within the system and link it to the internal energy to form a new property called enthalpy. Flow energy is determined in terms of a work transfer and can be considered to be the work required to push the fluid into and out of the system.

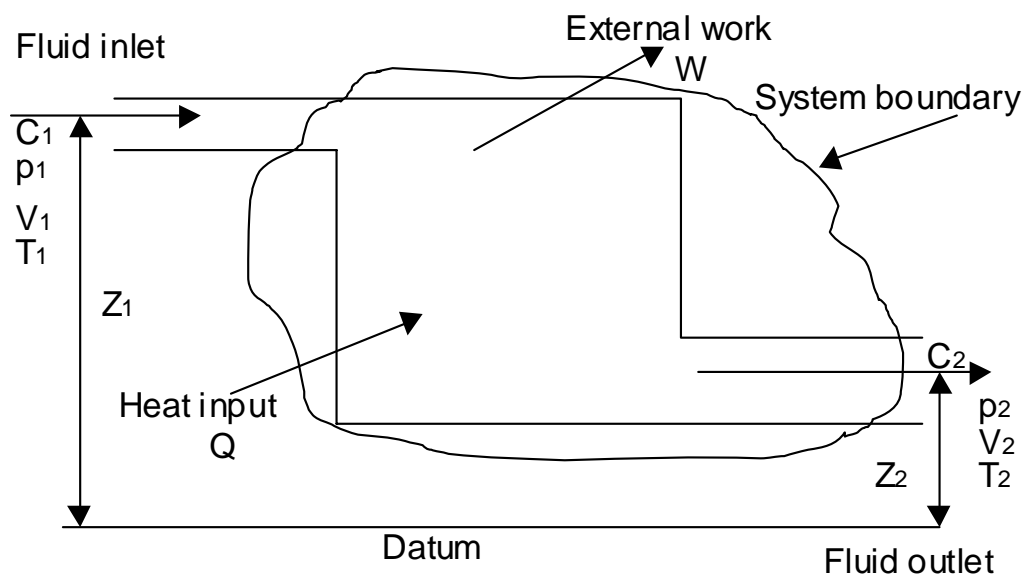
Therefore the energy of the system is increased by  $p_1 V_1$  at inlet and decreased by  $p_2 V_2$  at outlet.

### Work and Heat

During its passage through the system the substance could take in a quantity of heat and do external work.

### Open System

The diagram below represents an open system in which a steady flow process is taking place, remember that the mass entering the system is the same as the mass leaving the system.



At entry to the system the working substance possess, potential, kinetic and internal energy, it will also do flow work to enter the system.

During its passage through the system the working substance could take in a quantity of heat and do external work.

At exit from the system the working substance possess, potential, kinetic and internal energy, it will also do flow work to leave the system.

In the above diagram

$P \text{ N/m}^2$  = Fluid pressure

$V \text{ m}^3/\text{s}$  = Volume flow rate

$T \text{ K}$  = Fluid Temperature

$C \text{ m/s}$  = Fluid velocity

$Z \text{ m}$  = Height above datum at which properties are measured

Suffix; 1 refers to inlet conditions and 2 refers to inlet conditions

From the First Law

Sum of the input energy = Sum of the output energy

Potential + Kinetic + Internal + Flow + Heat = Potential + Kinetic + Internal + Flow + Work

$$9.81mZ_1 + \frac{mc_1^2}{2} + U_1 + p_1V_1 + Q = 9.81mZ_2 + \frac{mc_2^2}{2} + U_2 + p_2V_2 + W$$

This is usually referred to as **THE STEADY FLOW ENERGY EQUATION (SFEE)**

### Enthalpy (H)

At this point we can introduce another property of the working substance called Enthalpy it is the sum of internal energy and flow work.

$$H = U + pV$$

Since internal energy and volume can be expressed in terms of unit mass then enthalpy can also be expressed in terms of unit mass.

$$h = u + pv$$

The SFEE becomes

$$9.81mZ_1 + \frac{mc_1^2}{2} + H_1 + Q = 9.81mZ_2 + \frac{mc_2^2}{2} + H_2 + W$$

or

$$9.81Z_1 + \frac{c_1^2}{2} + h_1 + Q = 9.81Z_2 + \frac{c_2^2}{2} + h_2 + W$$

where heat and work are expressed in terms of unit mass

In many flow processes the potential energy components are negligible while the entry and exit velocities are similar.

The equation then reduces to

$$H_1 + Q = H_2 + W \quad \text{or} \quad Q = W + (H_2 - H_1)$$

The steady-flow energy equation is a further statement of the first law.

## Closed System

Consider now a closed system such as a piston in a cylinder which does not execute a cycle.

If a process is carried out on a substance in a closed system such that there is both heat and work transfer, it is not necessarily the case that the algebraic sum of these energy transfers is zero.

Now, the principle of conservation of energy states that Energy in = Energy out thus, if the heat and work transfers are not equal, any energy difference must have been added to the substance or have been lost from the substance.

Since this is a non-flow process, the flow energy and kinetic energy terms in the general energy equation do not exist while the potential energy can be ignored as before.

The general energy equation reduces to

$$U_1 + Q = U_2 + W$$
$$Q = W + (U_2 - U_1)$$

This is generally referred to as the **NON FLOW ENERGY EQUATION**  
**NFEE**

The non-flow energy equation, it is another statement of the first law of thermodynamics.

These equations will be used in flow and non flow processes all that is required is to remember the general equation and include the terms we have the information for.

If we do not have the information or have not been asked for information then leave the term out and see what is left.