# **Chapter 2: The Second Law and Equilibrium**

The First Law of Thermodynamics (Chapter 1) states that energy cannot be created or destroyed: it can simply be transformed from one form of energy to another. It was shown that work could be transformed completely into heat. The Second Law of Thermodynamics relates to the transformation of heat into work, and it will be shown that it is not possible to completely transform heat to work. In its simplest form for engineers, the Second Law is useful for considering the thermal efficiency of heat engines. In a more general form, the Second Law introduces the concept of the "quality" of energy.

This law was postulated by Sadi Carnot in 1824 (Mendoza (1960)), which is remarkable because at this stage the law which became known as the First Law of Thermodynamics had not been "discovered". Carnot introduced the idea of the heat engine operating in a cycle, and these have remained important concepts through to the present day.

# 2.1 Thermal efficiency

The concept of efficiency was introduced early in the history of mechanics, because it was obvious that the work input and work output terms were both forms of energy. The definition of mechanical efficiency is:

Efficiency, 
$$\eta = \frac{\text{Work output}}{\text{Work input}}$$
 (2.1)

It was not possible to derive a similar relationship for thermal efficiency until Joule showed the equivalence between heat and work in 1848. Then thermal efficiency could be stated as

Thermal efficiency,  $\eta_{\text{th}} = \frac{\text{Useful work output}}{\text{Thermal energy input, for a heat engine operating in a cycle}}$  (2.2)

# 2.2 Heat engine

The derivation of the Second Law of Thermodynamics is based on a special thermodynamic device called a heat engine.

A *heat engine* is a continuously operating thermodynamic system across the boundaries of which only heat and work flow: it is a closed system as indicated in Section 1.2.1.

The term *continuously operating* means that the heat engine operates in a *cycle*, and that a number of integral cycles is/are performed.

The strict definition of the heat engine means that not all thermodynamic engines which produce work output are heat engines. Those that are included in the strict definition are steam turbines, closed cycle gas turbines, refrigerators and heat pumps, and the operating portion of the Stirling engine. Surprisingly, petrol and diesel engines, and aircraft gas turbines do not obey the rigid definition of the heat engine - because the air and fuel which are used for combustion cross the system boundaries.

# 2.3 Second Law of Thermodynamics

Two statements of the Second Law will be given here. The first is the Kelvin-Planck statement which says:

It is impossible to construct an engine which will operate in a complete cycle and produce no other effects than to transfer heat with a single reservoir and raise a weight (i.e. do work)

This gives directionality to processes which obey the First Law. For example, consider fig 2.1(a) in which work is transferred completely to heat - this is possible by the First Law and obeys both this and the Second Law. Such an experiment could be simply the rubbing of a block on a frictional surface, when all the work is converted into a temperature rise. Fig 2.1(b) depicts a situation where all the heat transferred through the system is converted to work: this is impossible when it is considered by the Second Law.



Fig 2.1: Conversion of work to heat and heat to work.

The device shown in fig 2.1(b) was called a perpetual motion machine of the second kind (PMM2) in Chapter 1. These machines do not violate the conservation of energy defined in the First Law, but they violate the Second Law. Devices which violate the conservation of energy are called perpetual motion machines of the first kind and denoted PMM1. Many proposed, unsuccessful inventions are of the PMM2 variety.

The other statement of the Second Law, attributed to Clausius, states

# It is impossible to construct a system which will operate in a cycle and transfer heat from a cooler to a hotter body without work being done on the system by the surroundings.

Both of these are statements of the Second Law, and are equally valid.

It is possible to derive six corollaries of the Second Law, and these will simply be stated here, but will be referred to during this chapter, and form the basis of reasoning in many of the other chapters.

#### **Corollary 1:**

It is impossible to construct a heat engine to work between two heat reservoirs which has an efficiency which exceeds that of a reversible engine operating between the same two reservoirs.

#### **Corollary 2:**

All reversible heat engines operating between the same two heat reservoirs have the same thermal efficiency.

#### **Corollary 3:**

A temperature scale may be defined which is independent of the thermometric substance.

#### **Corollary 4:**

This is often referred to as the Clausius lnequality and defines a relationship for the net heat transfer of a cyclic process.

#### Whenever a system executes a complete cyclic process {i.e. a cycle}

 $\oint_{cvcle} \frac{\mathrm{d}Q}{T} \leq \mathbf{0}$ 

#### **Corollary 5**

This corollary defines the property *entropy*, which is the property associated with the Second Law of Thermodynamics. Entropy is a measure of the transformation brought about by a process, and is also an indicator of the direction of a process.

 $\int_{\text{cycle}} \frac{dQ_R}{T} = \mathbf{0} \text{ for any reversible, cyclic process. Hence, } \int \frac{dQ_R}{T} \text{ is a property of any reversible process between a reference state 0 and any other state 1. This property is called$ *entropy* $.}$ 

#### **Corollary 6:**

This is an important concept which shows that the degree of disorder in the universe will increase. If there is an increase in the order of a part of the universe, then it is accompanied by a decrease in the order of the remainder of the universe.

The entropy of an isolated system increases, or in the limit remains constant.

# 2.4 The Concept of the Heat Engine: derived by analogy with other devices.

Fig 2.2 shows schematic diagrams of two different types of engine, viz. hydraulic, and thermodynamic: it is also possible to develop a similar analogy with an electrical machine, and this will be left for the reader (see Winterbone (1977)). Considering first the hydraulic machine; the power output of the machine is directly related to the head of water across it, neglecting kinetic and frictional effects. The maximum power obtainable from the machine is limited by the maximum head of water achievable in nature; in practice this is the height above mean sea level. Hence the power produced is the difference between the energy carried by the water before the engine  $(mgh_1)$  and that after the engine  $(mgh_2)$ . The water flowrate, mg, is the same for both sides of the machine, hence the power is  $mg(h_1 - h_2)$  and the efficiency is



Fig 2.2 Comparison of different types of engine

The maximum efficiency that can be achieved from such a machine occurs when the receiving reservoir is at mean sea level,  $h_0$ . The efficiency would then be 100 per cent. In practice both kinetic and frictional effects reduce the efficiency achieved.

Considering now the thermodynamic machine or heat engine: the energy flowing into the machine can be defined as  $\dot{Q}_1$  and that leaving as  $\dot{Q}_2$  then, by the First Law, the power output,  $\dot{W} = \dot{Q}_1 - \dot{Q}_2$ . This equation is not comparable to eqn (2.3), and the flow quantity is not conserved. By analogy with the hydraulic engine, the obvious forcing potential for a thermodynamic machine is temperature, T, in which case the flow quantity would have to be  $\dot{Q}/T$ , which would give the power output equal to the product of the flow of energy per unit potential and the potential difference. Hence,

$$\dot{W} = \frac{\dot{Q}_1}{T_1} (T_1 - T_2) = \dot{Q} \frac{T_1 - T_2}{T_1}$$
(2.4)

This expression is the usual one for the power output of a reversible heat engine and it can be seen to be similar to the expression for the power of hydraulic machine. This is a convenient linear equation for the calculation of the power of a heat engine; other equations could be developed based on more complex temperature scales but these would not fit the general pattern. The linear scale of absolute temperature has the added advantage of similarity to the temperature scale of a perfect gas. The results of this analogy are summarised in Table 2.1.

	Hydraulic machine	Thermodynamic machine
"Forcing" quantity	Head of water	Temperature difference
	$(h_1 - h_2)$	$(T_1 - T_2)$
"Flowing" quantity	Weight flow rate	Entropy flow rate
	ṁg	$\dot{s} = \dot{Q}/T$
Work output rate	$\dot{m}g(h_1-h_2)$	$\dot{s}(T_1 - T_2)$
Efficiency	$h_1 - h_2$	$T_1 - T_2$
	$\eta =$	$\eta = \overline{T_1}$
		1

Table 2.1: A comparison of parameters defining power output and efficiency for engines

# 2.5 The Absolute Temperature Scale

The scales of temperature introduced early in the history of thermodynamics were "discontinuous" ones based on the melting or freezing of water, or other substances (see section 1.4). With the discovery of Charles' (Gay-Lussac's) Law, which suggested that the volume of a gas became zero at some temperature, the concept of an absolute zero of temperature evolved. Attempts had been made to evaluate this absolute zero by experiments with various gases, but it was not until Carnot showed that the amount of work that could be obtained from a given flow of heat for the same temperature difference decreased as the temperature increased that it was possible to introduce the concept of absolute temperature from consideration of the reversible heat engine.

Clapeyron applied this approach to a simplified Carnot cycle with an infinitesimal temperature difference between the isothermal lines, and assumed the working fluid obeyed the perfect gas law. He showed that

$$\dot{W} = rac{\dot{Q}\delta T}{T}$$

where *T* is called the absolute temperature. An interesting discussion of this work is given in Fox (1986).

The weakness of Clapeyron's derivation was that it relied upon the definition of a perfect gas, but then Kelvin realised that the absolute scale of temperature could be defined in terms of the reversible heat engine, and would be independent of the working fluid. This must be the case, or reversible heat engines operating between the same two temperature reservoirs with different working fluids would have different efficiencies, which would violate the 1st and 2nd corollaries.

The efficiency of a heat engine is defined by the equation  $\eta = 1 - Q_C/Q_H$ , where the heat flow terms are for the hot (H) and cold (C) reservoirs. If it is possible to define the heat flow terms ( $\dot{Q}$ ) as functions of temperature (T) then  $\eta = 1 - f(T_C)/f(T_H) = f(T_C, T_H)$ . Now it is possible to propose temperature to be any monotonic function of heat flow, but the simplest one is that derived by Kelvin, and described below.

(2.5)

Kelvin defined a scale such that the same quantity of work is produced by a unit fall (1°)in temperature irrespective of the temperature level. This means that  $\dot{Q}/T$  must be constant irrespective of the absolute temperature, *T*. Hence

$$\frac{\dot{Q}}{T} = \text{const} = \frac{\dot{Q}_0}{T_0} = \frac{\dot{Q}_1}{T_1} = \text{etc.}$$

This scale can be conceptualised by the series of heat engines shown in fig 2.3.





This relationship between temperature and heat flow gives the efficiency as

$$\eta = 1 - \frac{Q_{\rm C}}{Q_{\rm H}} = 1 - \frac{T_{\rm C}}{T_{\rm H}} = \frac{T_{\rm H} - T_{\rm C}}{T_{\rm H}}$$
(2.6)

This is one of the most well-known and important results of the Second Law of Thermodynamics.

The maximum value of efficiency is achieved when  $T_{\rm C} = 0$ , when  $\eta = 100\%$ . An engine of this type was discussed in Chapter 1, where it was shown that it would be a Perpetual Motion Machine of the Second kind, denoted a PMM2. Such a device has never been built, and would violate the Second Law of Thermodynamics. This conclusion leads to the Kelvin-Planck statement of the Second Law.

# 2.6 Entropy

Table 2.1 shows that the "thermodynamic flow" quantity to be considered in heat engines has the value of  $\dot{Q}/T$ . This quantity is conserved in a reversible engine; and is referred to as the 'entropy' flow rate. Mendoza (1960) quotes Carnot as writing 'The production of motive power is then due in steam engines not to an actual consumption of caloric, but to its transportation from a warm body to a cold body, that is, to its re-establishment of equilibrium - an equilibrium considered as destroyed by any cause whatever, by chemical action such as combustion, or by any other'. If the word 'caloric' in this sentence is replaced by 'entropy' it agrees exactly with the analogy drawn; whether this is a result of liberal interpretation or what Carnot actually meant is debatable.

If the heat engine is "irreversible" there is a production of entropy as the energy passes through the machine. There is no tangible analogue between this entropy production and the flow of 'energy' in the hydraulic machine. A direct consequence of this is the Clausius Inequality which has no counterpart in any other field of physical science.

The measurement of the performance of an ideal heat engine has been shown to be very similar to that of a hydraulic machine. This similarity has been used to develop the concept of efficiency as a temperature ratio and also to introduce the property 'entropy'. The analogies drawn are by no means perfect and must not be extrapolated too far but they do permit a more tangible understanding of heat engines and entropy.

A more rigorous definition can be derived by application of the Second Law to a system executing a cycle. Consider the system shown in fig 2.4, and the processes involved in transferring the energy from the reservoir at temperature,  $T_0$ .



Fig 2.4: Heat being transferred from a hot reservoir to a system by means of a reversible heat engine

- 1. Heat energy,  $\delta Q_0$ , is transferred from the reservoir at  $T_0$  to system A, which receives it at temperature T via the reversible heat engine. It is assumed that the engine performs a number of cycles in transferring the energy (so that no energy is stored in the engine).
- 2. The engine rejects heat,  $\delta Q$ , during this process, and this is transferred to system A at temperature *T* while producing a work output of  $\delta W_{\rm R}$ .
- 3. If system A and the heat engine are combined into another system, called system B, then the work output of system B can be considered.
- 4. If it is assumed that system B executes one cycle, then applying the First Law to system B gives

$$\oint_{\text{system B}} (\delta Q - \delta W) = 0. \tag{2.6}$$

It can be seen by considering system B that it constitutes a system which is producing work, but only transferring heat from a single reservoir. This is impossible by the Second Law, and hence the net work output of system B must be less than zero – in other words, work must be done on system B. This means

$$\oint_{\text{ystem B}} \left( \delta W + \delta W_{\text{R}} \right) \le 0 \tag{2.7}$$

Now, for a reversible engine

$$\oint \delta W_{\rm R} = \oint \eta_{\rm R} \delta Q_0 = \frac{\eta_{\rm R}}{1 - \eta_{\rm R}} \oint \delta Q \tag{2.8}$$

and substituting  $\eta_{\rm R} = 1 - \frac{T}{T_0}$ , gives  $\oint \delta W_{\rm R} = \left(1 - \frac{T}{T_0}\right) \left(\frac{T}{T_0}\right) \oint \delta Q = \oint \left\{\frac{T_0}{T} \delta Q - \delta Q\right\}$ (2.9)

If the system A has undertaken a cycle then there has been no change in the internal energy of the system, and hence  $\oint_{\text{system A}} \delta W = \oint_{\text{system A}} \delta Q$ . Hence, the work output of system B is given by

$$\oint (\delta W + \delta W_{\rm R}) = \oint \left( \left\{ \frac{T_0}{T} \delta Q - \delta Q \right\} + \delta Q \right) = \oint \frac{T_0}{T} \delta Q \le 0$$
(2.10)

The significance of this equation is that, for a system executing a cycle, the cyclic integral of the work output is less than, or in the limit equal to, the cyclic integral of the heat transfer. Since  $T_0$  is constant in eqn (2.10) it is possible to take it out of the integral sign and then

$$\oint \frac{\delta Q}{T} \le 0. \tag{2.11}$$

This is called the *Clausius Inequality* 

The significance of the inequality sign is that:

for reversible processes 
$$\oint \frac{\delta Q}{T} = 0.$$
 (2.12)

 $\oint \frac{\delta Q}{T} < 0.$ 

while, for irreversible processes



. . . .. ..

Fig 2.5: Two reversible cycles made up of reversible processes A, B, and C.

Let the heat transfer along the reversible processes be denoted by the symbol  $\delta Q_{\rm R}$ , where the suffix R denotes that the process is reversible.

(2.13)

From the Clausius Inequality,  $\oint_{1-A-2-B-1} \frac{\delta Q_R}{T} \leq 0$ , for cycle 1-A-2-B-1. If the cycle is operated in the reverse direction, then  $\oint_{1-B-2-A-1} \frac{\delta Q'_R}{T} \leq 0$ , where the heat transfer in the reverse direction is denoted by the symbol  $\delta Q'_R$ . But these two cycles are the reverse of each other, and hence  $\delta Q_R = -\delta Q'_R$ . This means that for the reversed cycle, 1-B-2-A-1,  $\oint_{1-B-2-A-1} \frac{\delta Q_R}{T} \geq 0$ . The only way in which the Second Law can be obeyed is if

$$\oint \frac{\delta Q_{\rm R}}{T} = 0.$$

A similar analysis can be performed in which the cycles are now 1-A-2-C-1, and the same result will be achieved. Now, the cycles are made up of individual processes, and hence

$$\oint_{1-A-2-B-1} \frac{\delta Q_R}{T} = \int_{1-A-2} \frac{\delta Q_R}{T} = \int_{2-B-1} \frac{\delta Q_R}{T} = 0$$
(2.14)

And

$$\oint_{1-A-2-C-1} \frac{\delta Q_{R}}{T} = \int_{1-A-2} \frac{\delta Q_{R}}{T} = \int_{2-C-1} \frac{\delta Q_{R}}{T} = 0$$
(2.15)

These equations can only be obeyed if  $\int_{2-B-1} \frac{\delta Q_R}{T} = \int_{2-C-1} \frac{\delta Q_R}{T}$ , which means that  $\int \frac{\delta Q_R}{T}$  independent of the path of the process, and is dependent only on the end states. Hence  $\int \frac{\delta Q_R}{T}$  is a property of the system.

$$\int \frac{\delta Q_{\rm R}}{T}$$
 is called the *ENTROPY* of the system,

and is denoted by the symbol S, while specific entropy is s.

The change of entropy between states 1 and 2 is  $S_2 - S_1 = \int_1^2 \frac{\delta Q_R}{T}$  (2.16)

#### 2.6.1 The significance of entropy

- 1. Entropy is evaluated from *reversible processes*.
- 2. Entropy can be used with irreversible processes.
- 3. The factor 1/T is the integrating factor that turns  $\delta Q_{\rm R}$  from an indefinite integral into a definite one.
- 4. Entropy is a measure of the order or disorder of a system. For example, consider the gas mixtures shown in figs 2.6(a) and (b). In fig 2.6(a) the molecules of oxygen and nitrogen are well mixed, as they are in the atmosphere. This is a relatively disordered state because if an attempt was made to take an oxygen molecule from the container then the probability would be about one in four. However, if the mixture in fig 2.6(a) was processed to separate the oxygen and nitrogen molecules and these were placed in separate containers, as shown in fig 2.6(b), then the probability of finding an oxygen molecule is increased it is simply necessary to go to the left-hand container. The separation process has probably been achieved by a liquefaction and distillation process, and hence significant work has been required to separate the gases. If the barrier between the containers is removed the gases will spontaneously mix again, and the entropy of the system will increase. *The mixing process is irreversible*.



Fig 2.6: A container filled with air (a mixture of oxygen and nitrogen) (a) molecules mixed as in air (b) molecules after separation process

#### 2.6.2 Evaluation of entropy change for an irreversible process

The change of entropy for an irreversible process must be evaluated by considering the change of entropy for a reversible process (or processes) that achieves the same two end states. A good example of such a process occurs in a throttling process - which is an unresisted expansion, see fig 2.7. The steady flow energy equation (eqn (1.46)) can be applied to the throttle to give:

$$\dot{Q} - \dot{W_S} = \dot{m_2} \left( h_2 + \frac{v_2^2}{2} + gz_2 \right) - \dot{m_1} \left( h_1 + \frac{v_1^2}{2} + gz_1 \right)$$

A control surface has been drawn around the throttle, and it can be assumed that there is no heat transfer across that surface ( $\dot{Q}$ =0), i.e. the throttle is an adiabatic device. Also, there is no shaft work done on the throttle, and hence  $\dot{W}_S = 0$ . If it is assumed that the velocities entering and leaving the throttle are small, and that the elevation changes are negligible, then

$$h_2 = h_1 \tag{2.17}$$

Hence, the throttling process is isenthalpic. So far no information has been elicited about the change of entropy. There might be a temptation to assume that this is zero because the heat transfer is zero. However, this would not be true because the process is an irreversible one and  $S_2 - S_1 = \int_1^2 \frac{\delta Q_R}{T}$ , which is based on a reversible process and *this process is not reversible*.





It is necessary to try to define a reversible process which will bring the fluid at 2 back to state 1. The first, obvious, effect of passing the fluid through the throttle is that the pressure is reduced. The pressure can be increased from  $p_2$  to  $p_1$  by passing the gas through a reversible, adiabatic pump in which the heat transfer is zero, as depicted in fig 2.7b The effect of this is to raise the pressure, but it will also increase the temperature. Hence, although the pressure has been restored to  $p_1$  the temperature is too high. The temperature can be reduced by passing the fluid through a heat exchanger, and if it is reversible the heat transferred will be  $-\delta Q_R$ . In this way the gas can be restored to state 1, but in doing this heat has had to be transferred from the gas - hence, during the reverse process the entropy has been reduced. This means that the entropy of the fluid was increased during the forward process. Hence, the entropy of fluid increases as it passes through a throttle.

# 2.6.3 Entropy change as envisaged by Clausius

Clausius suggested that the change of entropy could be considered to be made up of two terms

$$dS = \frac{d(IE)}{T} + dZ$$
(2.18)

where d(IE) is the change of "internal heat" of the system  $=\delta Q - \delta W_S$ , and dZ is the change in disgregation of the molecules of the system i.e. a measure of the molecular spacing.

In a cyclic process

 $\int dZ = 0$ , because the initial and final molecular spacings are the same  $\int d(IE) = 0$ , because this is a cyclic change of a property Hence  $\int dS = 0$  for a cyclic process; i.e. the entropy is the same at the state point at the beginning and end of the cycle.

For a throttle,

 $\int dZ > 0, \text{ and } \int d(IE) = 0$ Hence  $\int dS > 0$  due to the change in molecular spacing.

For a constant volume heating process,

 $\int dZ = 0$ , because the molecular spacings cannot change  $\int d(IE) > 0$ , because this is a change of a property Hence  $\int dS = \int \left(\frac{d(IE)}{T}\right) > 0$ 

# 2.6.4 Entropy changes for pure substances

Assume that the internal energy of the substance is changed: the heat transfer can be evaluated from the First Law (eqn (1.19) as

 $\delta Q = dU + \delta W$ For a reversible process, e.g. a fully resisted expansion,

 $\delta W = p dV$ And  $dQ_{\rm R} = T dS$ 

Hence

$$TdS = dU + pdV \tag{2.19}$$

Also, 
$$H = U + pV$$
, giving  $dH = dU + pdV + Vdp$ , and  
 $TdS = dH - Vdp$  (2.20)

Specific entropy is the entropy per unit mass, hence the specific entropy, s = S/m, and  $ds = \frac{du + pdv}{T} = \frac{dh - vdp}{T}$ (2.21) Since this is a relationship between the properties u, p, T, u, and h it is possible to evaluate the entropy of a fluid at any state defined by two independent properties. Also, since entropy is a property it can be used as a co-ordinate in a state diagram. In fact, a very useful diagram in thermodynamic analysis is the temperature - entropy (T - s) diagram.

#### 2.6.4.1 Temperature - entropy diagram for a pure substance

In these diagrams entropy is usually used as the abscissa {i.e. the x - axis} of the diagram. A T - s diagram for a substance which changes phase is depicted in fig 2.8 Two constant pressure lines are shown on the diagram. At the lower pressure the fluid is first heated as a liquid until it reaches the saturated liquid line. At this point further heating does not raise the temperature it simply provides the latent heat of evaporation. On reaching the saturated vapour line, the temperature then rises as the fluid is heated. At the higher pressure, which is above the critical pressure, the fluid does not go through an evaporation process, and passes from the liquid to vapour phase without addition of latent heat.



Specific entropy, s



# 2.7 Representation of Heat Engines

A heat engine which operates in a cyclical manner can be represented diagrammatically as shown in fig 2.9.



Fig 2.9: Schematic representation of a heat engine (a) direct heat engine (b) reversed heat engine

The direct heat engine, fig 2.9a, receives heat (energy) from the high temperature reservoir at temperature,  $T_1$ , and rejects it to the low temperature reservoir at temperature,  $T_2$ . The reversed heat engine, fig 2.9b, receives heat from the low temperature reservoir at  $T_2$ , and pumps it to the high temperature reservoir at  $T_1$ .

Examples of some things which can act as reservoirs are the sea and the atmosphere which have very large masses relative to the individual engines. Another, different form of example might be the flame in a boiler, which appears to be a reservoir because energy is supplied at the same rate as it is being withdrawn, and a third which acts as a cold reservoir for steam turbine power plant is the condenser water. Of course, while these reservoirs are appropriate for most considerations, they are affected by the sum of all the heat and work transfers from the world's power stations, and hence might change slowly over time - man-made global warming.

#### 2.7.1 Efficiency of a heat engine

Carnot derived the efficiency of a heat engine in terms of temperature ratio in the early 1800's. However, it was not until the First Law had been stated in 1848 that it was possible to relate directly the heat and work associated with a heat engine. Watt and his contemporaries evaluated the efficiency of their engines by measuring the power output per bushel of coal - this did not take into account the variation in the quality of the coal when making the measurements.

The efficiency of a direct heat engine, often referred to as the thermal efficiency,  $\eta_{th}$ , is defined as the ratio of useful work to the heat supplied.

Thermal efficiency, 
$$\eta_{\text{th}} = \frac{\text{Net work}}{\text{Heat supplied}}$$
 (2.22)

This can be defined, in terms of fig 2.10, as

$$\eta_{\rm th} = \frac{W_{\rm S}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$
(2.23)

While this definition is useful for evaluating the thermal efficiency of a direct heat engine which is used to produce shaft power, it is not appropriate when considering a reversed heat engine which uses power to pump energy between two reservoirs.

Consideration of eqn (2.23) will show that this definition will result in an efficiency of greater than 100% - obviously not a useful concept. A more general, non-technical, definition is

Using this definition it is possible to define the "efficiency" of reversed heat engines: normally called the coefficient of performance. First, it is apparent that the reversed heat engine could deliver two desirable outputs - what you want. It could take energy from the cold reservoir, or it could deliver energy to the hot reservoir. The first device is called a refrigerator, while the second is called a heat pump.

The coefficient of performance of a refrigerator is designated  $\beta$ , where this is defined as

Coefficient of performance, 
$$\beta = \frac{\text{Heat transferred from cold reservoir}}{\frac{Q_2}{W_S} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}}$$
 (2.25)

The coefficient of performance of a heat pump is designated  $\beta$  ', where this is defined as

Coefficient of performance, 
$$\beta' = \frac{\text{Heat transferred to hot reservoir}}{\frac{Q_1}{W_S} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}}$$
 (2.26)

The coefficient of performance of a heat pump can be related to that of a refrigerator by the simple equation

$$\beta' = 1 + \frac{Q_2}{W_S} = 1 + \beta \tag{2.27}$$

If the "engines" shown in fig 2.10 operate between the same two temperature reservoirs, then it is possible for the heat engine to drive the reversed heat engine, i.e. the heat pump, and return the universe (the system + surroundings) to its original state. This means that

$$W_{\rm S}|_{\rm E_{\rm R}} = -W_{\rm S}|_{\exists_{\rm R}}$$
  
Now  $W_{\rm S}|_{\rm E_{\rm R}} = \eta_{\rm R}Q_1$ , and  $-W_{\rm S}|_{\exists_{\rm R}} = Q_1/\beta'_{\rm R}$   
Thus  $\eta_{\rm R} = 1/\beta'_{\rm R}$  (2.28)



Fig 2.10: Reversible heat engines (a) a reversible direct heat engine (b) a reversible reversed heat engine

#### 2.7.2 Engine with thermal efficiency of 100%

The efficiency of a heat engine is defined in eqn (2.23) as

$$\eta_{\rm th} = \frac{w_{\rm S}}{q_{\rm 1}} = \frac{q_{\rm 1} - q_{\rm 2}}{q_{\rm 1}} = 1 - \frac{q_{\rm 2}}{q_{\rm 1}} = 1 - \frac{T_{\rm 2}}{T_{\rm 1}}$$

The efficiency of a heat engine can be 100% if  $Q_2 = 0$ . This would modify the diagram of a heat engine to that shown in fig. 2.11(b), which would be a PMM2 and violate the Kelvin-Planck statement of the Second Law.



Fig 2.11: Heat engine with thermal efficiency of 100%

#### 2.7.3 Reversible heat engine.

The concept of reversible processes is a very important one, and will be introduced here. Consider the system and processes shown in fig 2.12. If the piston moves outwards without any frictional forces acting on it, and if there is no heat transfer from the system to the surroundings, or vice versa, then the expansion process will cool the gas down because the working fluid is doing work against the surroundings. If the

surroundings then do work on the piston to return it to its original position, then the state of the system will be returned to its initial value. The second process (compression) has reversed the effects of the first process (expansion): the processes are reversible.



Fig 2.12: Expansion against a piston.

Consider another example where heat is transferred to an adiabatic system though an infinitesimal temperature gradient, i.e. a conduction process. The heat transfer will take a very long time, but the thermal resistance to the process will be small. If the temperature of the surroundings is decreased by an infinitesimal amount then the heat transfer could easily go the other direction, and after an equally long time the system could be returned to its original state. Again, these heat transfer processes would have been reversible.

It is possible to define a cycle made up of such processes, and because each of the processes in the cycle is reversible then the cycle will be reversible. A heat engine could execute such a cycle, and this heat engine would be called a reversible heat engine. A reversible cycle might be like that shown in fig 2.13. Since all the processes in fig 2.13 are reversible, then an engine operating on this cycle can work with equal "efficiency" in either direction, i.e. it could operate either as an engine or a heat pump or refrigerator. Reversible engines can be depicted as in fig 2.10.



Toporty

Fig 2.13: A reversible cycle

# 2.8 Reversibility and irreversibility {1st corollary of Second Law}

As stated previously, the Second Law defines the direction of energy transfer during a process. All real processes are irreversible, due to friction, turbulence, mixing, electrical resistance, etc. However, it is useful to postulate what would happen in reversible processes, because these will give a yard-stick at which to aim when designing engines. This is similar to neglecting friction at bearings when assessing the operation of a mechanism.

#### 2.8.1 Reversible processes

A reversible process is one which can be taken from its initial state to another state, and then back to the initial state without any change to either the system or the surroundings. This means that the cycle has no

net effect on the universe, and there is no way of knowing it has happened after it has been completed. There are no completely reversible processes due to small intrinsic losses, however some processes approach reversibility. Examples of these are:

- frictionless motion of solids (no friction between mating surfaces)
- extension of springs (no hysteresis losses in the materials)
- slow adiabatic compression or expansion of gases (so that no pressure waves are set up in the gas)
- slow isothermal compression or expansion of gases (so that no temperature gradient is required to transfer the heat into or out of the system)
- electrolysis (with no resistance in the electrolyte)

The requirement to achieve reversibility is given in brackets after the process: it can be seen that these requirements will never be met in real systems.

#### 2.8.2 Irreversible processes

In reality all the processes have some losses, which might be friction, heat losses, hysteresis, etc.. Hence, all real processes are irreversible. This does not mean that it is impossible for a system to perform a cycle made up of irreversible processes but simply that the surroundings will have been altered by the cycle having been performed. A number of common irreversible processes will be listed.

- friction between solids, or in fluids
- unresisted expansions
- heat transfer across finite temperature differences
- combustion because the fuel and air are turned into carbon dioxide and water
- mixing of unlike, and miscible fluids
- hysteresis processes (internal friction in metals, hysteresis in electrical systems
- plastic deformation of materials
- electrical resistance to current flow (production of heat through  $I^2R$  losses)

# 2.9 Equilibrium

Most texts on thermodynamics restrict themselves to dealing exclusively with equilibrium thermodynamics. This book will also focus on equilibrium thermodynamics but the effects of making this assumption will be explicitly borne in mind. The majority of processes met by engineers are in thermodynamic equilibrium, but some important processes have to be considered by non-equilibrium thermodynamics. Most of the combustion processes that generate atmospheric pollution include non-equilibrium effects, and carbon monoxide (CO) and oxides of nitrogen (NOx) are both the result of the inability of the system to reach thermodynamic equilibrium in the time available.



Fig 2.14 The four types of equilibrium for a mechanical system

There are four kinds of equilibrium, and these are most easily understood by reference to simple mechanical systems shown in Fig 2.14. Here a marble is placed on a number of different surfaces, and the effect of a perturbation is considered: the result is then related to systems in similar thermodynamic states.

- (i) Stable equilibrium: marble in bowl (depicted in fig 2.14a): For stable equilibrium  $\Delta E$ )<sub>S</sub> > 0 and  $\Delta S$ )<sub>E</sub> < 0, where  $\Delta$  indicates the sum of terms in the Taylor's series (see footnote<sup>1</sup>). In this case any deflection results in motion back to the stable condition.
- (ii) Neutral equilibrium: marble in trough (depicted in fig 2.14b):  $\Delta E$ )<sub>S</sub> = 0 and  $\Delta S$ )<sub>E</sub> = 0 along the trough axis. The marble is in equilibrium at any point along the axis.
- (iii) Unstable equilibrium: marble sitting on top of an upturned bowl (depicted in fig 2.14c)  $\Delta E$ )<sub>S</sub> < 0 and  $\Delta S$ )<sub>E</sub> > 0; any movement causes the marble to move farther from its 'equilibrium'position.
- Metastable equilibrium: marble in higher of two 'troughs' (depicted in fig 2.14d): Relatively small variations of position will take the marble over the local maxima, and then it will be in an unstable state.

Hence the following statements can be derived for certain classes of problem [see Hatsopoulos and Keenan (1972)]:

(i)	Stable equilibrium:	$dS_E = 0$ and $\Delta S_E < 0$
(ii)	Neutral equilibrium:	$dS_E = 0$ and $\Delta S_E = 0$
(iii)	Unstable equilibrium:	$dS$ <sub>E</sub> = 0 and $\Delta S$ <sub>E</sub> > 0

#### 2.9.1 Equilibrium of a thermodynamic system

The type of equilibrium in a mechanical system can be judged by considering the variation in energy due to an infinitesimal disturbance. If the energy (potential energy) increases then the system will return to its previous state, if it decreases it will not return to that state. A similar method for examining the equilibrium of thermodynamic systems is required. This will be developed from the Second Law of Thermodynamics and the definition of entropy.



Fig 2.15: Heat transfer between two blocks

Consider a system comprising two identical blocks of metal at different temperatures (see fig 2.15), but connected by a conducting medium. From experience the block at the higher temperature will transfer 'heat' to that at lower temperature. If the two blocks together constitute an isolated system the energy transfers will not affect the total energy in the system. If the high temperature block is at an temperature  $T_1$  and the other at  $T_2$  and if the quantity of energy transferred is  $\delta Q$  then the change in entropy of the high temperature block is:

#### <sup>1</sup> The difference between $\Delta S$ and dS

Consider the Taylor's series

 $\Delta S = \frac{dS}{dx}\Delta x + \frac{1}{2}\frac{d^2S}{dx^2}\Delta x^2 + \frac{1}{6}\frac{d^3S}{dx^3}\Delta x^3 + \dots \cong dS + \frac{1}{2}\frac{d^2S}{dx^2}\Delta x^2$ Thus dS is the first term only of the Taylor's series, and dS would equal zero at the top of the bowl in fig 2.15c, but  $\Delta S = dS + \frac{1}{2}\frac{d^2S}{dx^2}\Delta x^2$  would not be zero because the second derivative  $\frac{d^2S}{dx^2}$  is not zero.

$$\mathrm{d}S_1 = -\frac{\delta Q}{T_1} \tag{2.29}$$

and that of the lower temperature block is:

$$\mathrm{d}S_2 = +\frac{\delta Q}{T_2} \tag{2.30}$$

Both eqns (2.29) and (2.30) contain the assumption that the heat transfers from block 1, and into block 2 are reversible. If the transfers were irreversible then eqn (2.29) would become

$$\mathrm{d}S_1 > -\frac{\delta Q}{T_1} \tag{2.29a}$$

and eqn (2.30) would be

$$\mathrm{d}S_2 > +\frac{\delta Q}{T_2} \tag{2.30a}$$

Since the system is isolated the energy transfer to the surroundings is zero, and hence the change of entropy of the surroundings is zero. Hence the change in entropy of the system is equal to the change in entropy of the universe and is, using eqns (2.29) and (2.30):

$$dS = dS_1 + dS_2 = -\frac{\delta Q}{T_1} + \frac{\delta Q}{T_2} = \delta Q \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(2.31)

Since  $T_1 > T_2$ , then the change of entropy of both the system and the universe is

$$dS = \frac{\delta Q}{T_2 T_1} (T_1 - T_2) > 0$$

The same solution, viz. dS > 0, is obtained from eqns (2.29a) and (2.30a). The previous way of considering the equilibrium condition shows how systems will tend to go towards such a state. A slightly different approach, which is more analogous to the one used to investigate the equilibrium of mechanical systems, is to consider the two blocks of metal to be in equilibrium and for heat transfer to occur spontaneously (and reversibly) between one and the other. Assume the temperature change in each block is  $\delta T$ , with one temperature increasing and the other decreasing, and the heat transfer is  $\delta Q$ . Then the change of entropy, dS, is given by

$$dS = \frac{\delta Q}{T + \delta T} - \frac{\delta Q}{T - \delta T} = \frac{\delta Q}{(T + \delta T)(T - \delta T)} (T - \delta T - T - \delta T)$$
  
$$= \frac{\delta Q}{T^2 + \delta T^2} (-2\delta T) \approx -2\delta Q \frac{\delta T}{T^2}$$
(2.32)

This means that the entropy of the system would have decreased. Hence maximum entropy is obtained when the two blocks are in equilibrium and are at the same temperature. The general criterion of equilibrium according to Keenan (1963) is:

For stability of any system it is necessary and sufficient that, in all possible variations of the state of the system which do not alter its energy, the variation of entropy shall be negative.

This can be stated mathematically as:

$$\Delta S)_E < 0 \tag{2.33}$$

It can be seen that the statements of equilibrium based on energy and entropy, viz.  $\Delta E$ )<sub>S</sub> > 0 and  $\Delta S$ )<sub>E</sub> < 0, are equivalent by applying the following simple analysis. Consider the marble at the base of the bowl, as shown in fig 2.14(a): if it is lifted up the bowl its potential energy will be increased. When it is released it will oscillate in the base of the bowl until it comes to rest as a result of "friction", and if that "friction" is used solely to raise the temperature of the marble then its temperature will be higher after the process than at the beginning. A way to ensure the end conditions, i.e. the initial and final conditions, are identical would be to cool the marble by an amount equivalent to the increase in potential energy before releasing it. This cooling is equivalent to lowering the entropy of the marble by an amount  $\Delta S$ , and since the cooling has been undertaken to bring the energy level back to the original value this proves that  $\Delta E$ )<sub>S</sub> > 0 and  $\Delta S$ )<sub>E</sub> < 0.

Equilibrium can be defined by the following statements:

- (i) if the properties of an isolated system change spontaneously there is an increase in the entropy of the system;
- (ii) when the entropy of an isolated system is at a maximum the system is in equilibrium;
- (iii) if for all the possible variations in state of the isolated system there is a negative change in entropy then the system is in stable equilibrium.

These conditions may be written mathematically as:

- (i)  $\Delta S$ <sub>E</sub> > 0, spontaneous change (unstable equilibrium)
- (ii)  $\Delta S$ <sub>E</sub> = 0, equilibrium (neutral equilibrium)
- (iii)  $\Delta S$ )<sub>*E*</sub> < 0, criterion of stability (stable equilibrium)

# 2.10 Helmholtz energy (Helmholtz function)

There are a number of ways of obtaining an expression for Helmholtz Energy, but the one based on the Clausius derivation of entropy gives the most insight.

In the previous section the criteria for equilibrium were discussed and these were derived in terms of  $\Delta S$ <sub>*E*</sub>. The variation of entropy is not always easy to visualise, and it would be more useful if the criteria could be derived in a more tangible form related to other properties of the system under consideration. Consider the arrangements in figs 2.16(a) and (b). Figure 2.16(a) shows a System A, which is a general system of constant composition in which the work output,  $\delta W$ , can be either shaft or displacement work, or a combination of both. Figure 2.16(b) is a more specific example in which the work output is displacement work, pdV; the system in fig 2.16(b) is easier to understand.

In both arrangements, System A is a closed system {i.e. there are no mass transfers} which delivers an infinitesimal quantity of heat,  $\delta Q$ , in a reversible manner to the heat engine  $E_R$ . The heat engine then rejects a quantity of heat  $\delta Q_0$  to a reservoir, e.g. the atmosphere, at temperature  $T_0$ .



Fig 2.16: Maximum work achievable from a system

Let dE, dV and dS denote the changes in internal energy, volume and entropy of the system, which is of constant, invariant composition. For a specified change of state these quantities, which are changes in properties, would be independent of the process or work done. Applying the First Law of Thermodynamics (eqn 1.9) to System A gives

$$\delta W = -dE + \delta Q \tag{2.34}$$

If the heat engine  $(E_R)$  and system A are considered to constitute another system, system B. Then, applying the First Law of Thermodynamics to system B gives

$$\delta W_{\rm net} = \delta W + \delta W_{\rm R} = -dE + \delta Q_0 \tag{2.35}$$

where  $\delta W + \delta W_R$  = net work done by the heat engine and system A. Since the heat engine is internally reversible, and the entropy flow on either side is equal, then

$$\frac{\delta Q_0}{T_0} = \frac{\delta Q}{T} \tag{2.36}$$

and the change in entropy of system A during this process, because it is reversible, is  $dS = \frac{\delta Q_R}{\tau}$ ,

Hence 
$$\delta W_{\text{net}} = -dE + T_0 dS = -d(E - T_0 S)$$
, because  $T_0$  is constant. (2.37)

The expression  $E - T_0 S$  is called the HELMHOLTZ ENERGY or HELMHOLTZ FUNCTION. In the absence of motion and gravitational effects the energy, E, may be replaced by the intrinsic internal energy, U, giving

$$\delta W_{\rm net} = -d(U - T_0 S) \tag{2.38}$$

The significance of  $\delta W_{net}$  will now be examined. The changes executed were considered to be reversible and  $\delta W_{net}$  was the net work obtained from system B (i.e. system A + heat engine  $E_R$ ). Thus  $\delta W_{net}$  must be the maximum quantity of work that can be obtained from the combined system. The expression for  $\delta W_{net}$  is called the change in the Helmholtz Energy, where the Helmholtz Energy is defined as:

$$F = U - TS \tag{2.39}$$

Helmholtz Energy is a property which has the units of energy, and indicates the maximum work that can be obtained from a system. It can be seen that this is less than the internal energy, U, and it will be shown that the product TS is a measure of the unavailable energy.

#### 2.11 Gibbs Energy

In the previous section the maximum work that can be obtained from system B, comprising system A and heat engine  $E_R$  was derived. It was also stipulated that system A could change its volume by  $\delta V$ , and while it is doing this it must perform work on the atmosphere equivalent to  $p_0 \delta V$ , where  $p_0$  is the pressure of the atmosphere. This work detracts from the work previously calculated and gives the **maximum useful work**,  $\delta W_{\mu}$  as:

$$\delta W_u = \delta W_{\text{net}} - p_0 dV \tag{2.40}$$

if the system is in pressure equilibrium with surroundings,

$$\delta W_u = -d(E - T_0 S) - p_0 dV = -d(E + p_0 V - T_0 S)$$
 because  $p_0$  is constant.

Hence,  $\delta W_u = -d(H - TS)$  (2.41) The quantity H - TS is called the **Gibbs Energy**, **Gibbs Potential**, or the **Gibbs function**, *G*.

Hence, 
$$\boldsymbol{G} = \boldsymbol{H} - \boldsymbol{T}\boldsymbol{S}$$
 (2.42)

Gibbs Energy is a property which has the units of energy, and indicates the maximum useful work that can be obtained from a system. It can be seen that this is less than the enthalpy, H, and it will be shown that the product TS is a measure of the unavailable energy.

#### 2.11.1 The use and significance of the Helmholtz and Gibbs Energies

It should be noted that the definitions of Helmholtz and Gibbs energies, eqns (2.39) and (2.42), have been obtained for systems of invariant composition. The more general form of these basic thermodynamic relationships, in differential form, is

$$dU = TdS - pdV + \sum \mu_i dn_i$$
  

$$dH = TdS + Vdp + \sum \mu_i dn_i$$
  

$$dF = -SdT - pdV + \sum \mu_i dn_i$$
  

$$dG = -SdT + Vdp + \sum \mu_i dn_i$$
  
(2.43)

The additional term,  $\sum \mu_i dn_i$ , is the product of the chemical potential of component, i, and the change of the amount of substance (measured in moles) of component i. (The chemical potential of a substance has the same numerical value as the specific Gibbs energy of the substance, and is introduced in Section 12.2 when dissociation is discussed. It is used extensively in the later chapters where it can be seen to be the driving force of chemical reactions). Obviously if the amount of substance of the constituents does not change then this term is zero. However, if there is a reaction between the components of a mixture then this term will be non-zero and must be taken into account.

#### 2.11.2 Helmholtz Energy

- (i) the change in Helmholtz Energy is the maximum work that can be obtained from a closed system undergoing a reversible process whilst remaining in temperature equilibrium with its surroundings;
- (ii) a decrease in Helmholtz Energy corresponds to an increase in entropy, hence the minimum value of the function signifies the equilibrium condition;
- (iii) a decrease in entropy corresponds to an increase in *F*; hence the criterion  $dF)_T > 0$  is that for stability. This criterion corresponds to work being done on the system;
- (iv) for a constant volume system in which  $\delta W = 0$ , dF = 0
- (v) for reversible processes  $F_1 = F_2$ ; for all other processes there is a decrease in Helmholtz energy.
- (vi) the minimum value of Helmholtz Energy corresponds to the equilibrium condition.

#### 2.11.3 Gibbs Energy

- (i) The change in Gibbs Energy is the maximum useful work that can be obtained from a system undergoing a reversible process whilst remaining in pressure and temperature equilibrium with its surroundings;
- (ii) the equilibrium condition for the constraints of constant pressure and temperature can be defined as:
  - 1.  $dG_{p,T} < 0$  spontaneous change
  - 2.  $dG_{p,T} = 0$  equilibrium
  - 3.  $dG_{p,T} > 0$  criterion of stability;
- (iii) the minimum value of Gibbs energy corresponds to the equilibrium condition.

# 2.12 Gibbs energy and phases

An extremely important feature of Gibbs energy is that it defines the interaction of co-existing phases (see Atkins (1994)). Fig 2.17 is a typical p-v-T diagram for H<sub>2</sub>O (water). All stable equilibrium states of H<sub>2</sub>O are represented by points on the surface of the diagram: any points that are not on the surface would be in unstable or metastable equilibrium. If the p-v-T diagram is viewed from the right, normal to the p-v plane, the phase diagram for H<sub>2</sub>O is seen: this is shown in fig 2.18. This diagram shows the phase boundary lines where the changes between the various phases take place, and it can be used to analyse what happens to water as it is cooled at constant pressure from superheated steam (at A) to ice (at E). Experience tells us that the steam will start to condense at B, on the saturated vapour line; it will remain as a liquid (water) as it passes through point C, with the temperature reducing, until it becomes a saturated liquid at point D. Further cooling at constant pressure will result in a reduction in temperature and solid H<sub>2</sub>O (ice) will form.

An interesting question is how many properties are required to define the state of the system when a number of components, C, in a number of different phases, P, are present. This problem was solved by Gibbs, and

his Phase Rule states that for a system at equilibrium the number of degrees of freedom, D, (equal to the number of independent intensive properties) is



Fig 2.17 *p-v-T* surface for H<sub>2</sub>O (a substance that expands on freezing)

Most mechanical engineering problems only deal with multiple phase mixtures of single components, e.g.  $H_2O$ . Hence, for the regions shown in fig 2.18, where there is a single component present (steam, water, ice) P = 1, and C = 1, eqn (2.44) gives D = 2. This means that it is necessary to have two independent properties, e.g. p and T, to define the state of the substance.



Fig 2.18 Phase diagram for H<sub>2</sub>O

If the substance is changing phase, i.e. from water to steam, on one of the boundary lines then P=2, and D=1: hence, the state of the substance can be defined by a single property during the phase change because p and T are not independent properties in this region. Another characteristic of phase change which comes

(2.44)

from Gibbs energy (or, more correctly, chemical potential) is that the Gibbs energy of both phases are equal during the phase change process. This means that in fig 2.18, as shown at the phase boundaries, the specific Gibbs energy is equal for both phases.

# 2.13 Examples of different forms of equilibrium met in thermodynamics

Stable equilibrium is the most frequently met state in thermodynamics, and most systems exist in this state. Most of the theories of thermodynamics are based on stable equilibrium, which might be more correctly named "thermostatics" (Tribus(1961)). The measurement of thermodynamic properties relies on the measuring device being in equilibrium with the system. For example, a thermometer must be in thermal equilibrium with a system if it is to measure its temperature, which explains why it is not possible to assess the temperature of something by touch because there is heat transfer either to or from the fingers - the body "measures" the heat transfer rate. A system is in a stable state if it will permanently stay in this state without a tendency to change. Examples of this are a mixture of water and water vapour at constant pressure and temperature, the mixture of gases from an internal combustion engine when they exit the exhaust pipe; and many forms of crystalline structures in metals. Basically, stable equilibrium of mixtures of elements and compounds is defined by the state of maximum entropy or minimum Gibbs or Helmholtz energy; this is discussed in Chapter 12. The concepts of stable equilibrium can also be used to analyse the operation of fuel cells and these are considered in Chapter 21.

Another form of equilibrium met in thermodynamics is metastable equilibrium. This is where a system exists in a "stable" state without any tendency to change until it is perturbed by an external influence. A good example of this is met in combustion in spark-ignition engines, where the reactants (air and fuel) are induced into the engine in a pre-mixed form. They are ignited by a small spark and convert rapidly into products, releasing many thousands of times the energy of the spark used to initiate the combustion process. Another example of metastable equilibrium is encountered in the Wilson "cloud chamber" used to show the tracks of  $\alpha$  particles in atomic physics. The Wilson cloud chamber consists of super-saturated water vapour which has been cooled down below the dew-point without condensation - it is in a metastable state. If an  $\alpha$ -particle is introduced into the chamber it provides sufficient perturbation to bring about condensation along its path. Other examples include explosive boiling which can occur if there are not sufficient nucleation sites to induce sufficient bubbles at boiling point to induce normal boiling, and some of the crystalline states encountered in metallic structures.

Unstable states cannot be sustained in thermodynamics because the molecular movement will tend to perturb the systems and cause them to move towards a stable state. Hence, unstable states are only transitory states met in systems which are moving towards equilibrium. The gases in a combustion chamber are often in unstable equilibrium because they cannot react quickly enough to maintain the equilibrium state, which is defined by minimum Gibbs or Helmholtz energy. The "distance" of the unstable state from the state of stable equilibrium defines the rate at which the reaction occurs; this is referred to as rate kinetics, and will be discussed in Chapter 14. Another example of unstable "equilibrium" occurs when a partition is removed between two gases which are initially separated. These gases then mix due to diffusion, and this mixing is driven by the difference in chemical potential between the gases; chemical potential is introduced in Chapter 12 and the process of mixing is discussed in Chapter 20. Some thermodynamic situations never achieve stable equilibrium, they exist in a steady state with energy passing between systems in stable equilibrium, and such a situation can be analysed using the techniques of irreversible thermodynamics developed in Chapter 20.

# 2.13.1 Significance of the minimum Gibbs energy at constant pressure and

#### temperature

It is difficult for many mechanical engineers to readily see the significance of these Gibbs and Helmholtz energy. If systems are judged to undergo change while remaining in temperature and pressure equilibrium with their surroundings then most mechanical engineers would feel that no change could have taken place in the system. However, consideration of eqns (2.43) shows that, if the system were a multi-component mixture, it would be possible for changes in Gibbs (or Helmholtz) energies to take place if there were

changes in composition. For example, an equilibrium mixture of carbon dioxide, carbon monoxide and oxygen could change its composition by the carbon dioxide breaking down into carbon monoxide and oxygen, in their stoichiometric proportions; this break down would change the composition of the mixture. If the process happened at constant temperature and pressure, in equilibrium with the surroundings, then an increase in the Gibbs Energy, G, would have occurred; such a process would be depicted by figure 2.17. This is directly analogous to the marble in the dish, which was discussed in Section 2.9.



Fig 2.19: Variation of Gibbs Energy with chemical composition, for a system in temperature and pressure equilibrium with the environment

The formation of equilibrium mixtures by dissociation is considered in much more depth in Chapter 12, where the combustion processes in engines are evaluated. Dissociation and equilibrium are the driving forces in the formation of pollution from all combustion processes.

# 2.14 Concluding remarks

This chapter has revised the important features resulting from the Second Law of Thermodynamics, and probably introduced some new ideas relating to equilibrium. The concepts of the heat engine and Carnot cycle have been introduced, and these will be returned to in Chapters 3 and 6: they also introduced reversibility, and the Carnot efficiency. A new property, entropy, has been developed and this will be used throughout this book to analyse a broad range of thermodynamic situations. Entropy is probably the most useful property in thermodynamics because it often enables complex problems to be analysed philosophically without resorting to complex numerical calculations.

Having developed these ideas it was possible to define thermodynamic equilibrium in terms of Helmholtz and Gibbs energies. These concepts will become essential when analysing the more complex problems developed in the later chapters. It was also shown that Gibbs energy can define equilibrium in multicomponent and multi-phase mixtures, although we will limit ourselves to the latter in this book.

#### Problems

Problems P2.1 to P2.5 are revision problems and are relatively easy. The remainder relate to equilibrium in the later part of the chapter.

- P2.1 A mass of 10 kg of water at 0°C is brought into contact with a large heat reservoir at 100°C.
  - (a) When the water has reached 100°C what has been:
    - (i) the change of entropy of the water;
    - (ii) the change of entropy of the reservoir;
    - (iii) the change of entropy of the universe?
  - (b) If the water had been heated from 0°C to 100°C by first bringing it into contact with a reservoir at 30°C and then a reservoir of 100°C, what would have been the change in the entropy of the universe?

#### [Pick the date] [THE SECOND LAW AND EQUILIBRIUM]

(c) Explain how the water could have been heated to give no change in the entropy of the universe.

[13.11kJ/kgK; -11.26kJ/kgK; 1.85kJ/kgK; 1.070kJ/kgK; infinite number of reservoirs]

- P2.2. A system contains a fluid at a temperature of 70°C and 1 bar. It undergoes a reversible process during which the temperature of the system remains constant. Given that the heat transfer to the fluid during the process is 100 kJ, evaluate:
  - (a) the increase in entropy.
  - (b) if the system has a mass of 2.31 kg. Evaluate the increase in specific entropy of the system.
  - (c) If a second fluid system, identical to the first one undergoes an irreversible isothermal process from the same initial state to the same final state as above; and the heat transfer to the fluid in this irreversible process is 180 kJ; evaluate the increase in entropy of the fluid.

[0.2915kJ/K; 0.1262kJ/kgK; 0.2915kJ/kgK]

P2.3 Calculate the gain in entropy when 1 kg of water at 30°C is converted into steam at 150°C and then superheated to 300°C, with the process taking place at constant pressure.

Take  $c_{p(\text{water})} = 4.2 \text{ kJ/kg K}$ ,  $c_{p(\text{steam})} = 2.1 \text{ kJ/kg K}$ ,  $h_{\text{fg}} = 2600 - 1.5 t$ , where t = temperature in °C. [7.6533kJ/kgK]

P2.4 A mass of a liquid, *m*, at temperature,  $T_1$ , is mixed with an equal mass of the same liquid at temperature,  $T_2$ . The system is thermally insulated. Show that the change of entropy of the Universe is:

$$2mc_p \ln\left(\frac{(T_1+T_2)/2}{\sqrt{T_1T_2}}\right)$$

and prove that this is necessarily positive.

[Hint: Do not specifically consider the mixing of the fluids.].

P2.5 A substance has the following physical properties at a certain pressure:

Saturation temperature,  $t_s = 76^{\circ}$ C;  $h_{fg} = 61.1$ kJ/kg  $c_{p(liquid)} = 0.21$ kJ/kgK;  $c_{p(vapour)} = 0.14 + 0.00036T$  kJ/kgK, where *T*=temperature in K

Determine the enthalpy and entropy of superheated vapour at 150°C assuming these properties are zero for the fluid in liquid state at -40°C.

[106.10kJ/kg; 0.31348kJ/kgK]

- P2.6. Determine the criteria for equilibrium for a thermally isolated system at (a) constant volume; (b) at constant pressure. Assume that the system is:
  - (i) constant, and invariant, in composition;
  - (ii) variable in composition.
- P2.7. Determine the criteria for isothermal equilibrium of a system at (a) constant volume, and (b) constant pressure. Assume that the system is:
  - (i) constant, and invariant, in composition;
  - (ii) variable in composition.

#### [Pick the date] [THE SECOND LAW AND EQUILIBRIUM]

P2.8. A system at constant pressure consists of 10 kg of air at a temperature of 1000 K. This is connected to a large reservoir which is maintained at a temperature of 300 K by a reversible heat engine. Calculate the maximum amount of work which can be obtained from the system. Take the specific heat at constant pressure of air,  $c_p$ , as 0.98 kJ/kg K

[3320.3 kJ]

- P2.9. A thermally isolated system at constant pressure consists of 10 kg of air at a temperature of 1000 K and 10 kg of water at 300K, connected together by a heat engine. What would be the equilibrium temperature of the system if
  - (a) the heat engine has a thermal efficiency of zero;
  - (b) the heat engine is reversible?

{Hint: consider the definition of equilibrium defined by the entropy change of the system.}

Assume

for water : 
$$c_v = 4.2 \text{ kJ/ kg K};$$
  
 $\kappa = c_p / c_v = 1.0;$   
for air :  $c_v = 0.7 \text{ kJ/ kg K};$   
 $\kappa = c_p / c_v = 1.4.$   
[432.4 K; 376.7 K]

P2.10. A thermally isolated system at constant pressure consists of 10 kg of air at a temperature of 1000 K and 10 kg of water at 300 K, connected together by a heat engine. What would be the equilibrium temperature of the system if the maximum thermal efficiency of the engine is only 50%?

Assume

for water : 
$$c_v = 4.2 \text{ kJ/ kg K};$$
  
 $\kappa = c_p / c_v = 1.0;$   
for air :  $c_v = 0.7 \text{ kJ/ kg K};$   
 $\kappa = c_p / c_v = 1.4.$   
[385.1 K]

P2.11. Show that if a liquid is in equilibrium with its own vapour and an inert gas in a closed vessel, then

$$\frac{\mathrm{d}p_v}{\mathrm{d}p} = \frac{\rho_v}{\rho_l}$$

where  $p_v$  is the partial pressure of the vapour, p is the total pressure,  $\rho_v$  is the density of the vapour,  $\rho_l$  is the density of the liquid.

P2.12. An incompressible liquid of specific volume  $v_l$ , is in equilibrium with its own vapour and an inert gas in a closed vessel. The vapour obeys the law

$$p(v-b) = \Re T$$

Show that

$$\ln\left(\frac{p_{\nu}}{p_0}\right) = \frac{1}{\Re T} \left\{ \left(p - p_0\right) \nu_{\ell} - \left(p_{\nu} - p_0\right) b \right\}$$

where  $p_0$  is the vapour pressure when no inert gas is present, and p is the total pressure.

P2.13.(a) Describe the meaning of the term thermodynamic equilibrium. Explain how entropy can be used as a measure of equilibrium and also how other properties can be developed which can be used to assess the equilibrium of a system.

If two phases of a component coexist in equilibrium (e.g. liquid and vapour phase H<sub>2</sub>O) show that

$$T\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{l}{v_{\mathrm{fg}}}$$

where

T = temperature, p = pressure, l = latent heat, and  $v_{fg}$  = difference between liquid and vapour phases

Show the significance of this on a phase diagram.

(b) The melting point of tin at a pressure of 1 bar is 505K, but increases to 508.4K at 1000 bar. Evaluate

- (i) the change of density between these pressures, and
- (ii) the change in entropy during melting.

The latent heat of fusion of tin is 58.6 kJ/kg.

[254100 kg/m<sup>3</sup>; 0.1157 kJ/kg K]

P2.14. Show that when different phases are in equilibrium the specific Gibbs energy of each phase is equal.

Using the following data, show the pressure at which graphite and diamond are in equilibrium at a temperature of 25 °C. The data for these two phases of carbon at 25 °C and 1 bar are given in the following table:

	Graphite	Diamond
Specific Gibbs energy, $g / (kJ/kg)$	0	269
Specific volume, $v / (m^3/kg)$	$0.446 \times 10^{-3}$	$0.285 \times 10^{-3}$
Isothermal compressibility, $k / (bar^{-1})$	$2.96 \times 10^{-6}$	0.158 × 10 <sup>-6</sup>

It may be assumed that the variation of kv with pressure is negligible, and the lower value of the solution may be used.

[17990 bar]

P2.15. Van der Waals equation for water is given by

$$p = \frac{0.004619T}{v - 0.0016891} - \frac{0.017034}{v^2}$$

where p = pressure (bar), v = specific volume (m<sup>3</sup>/kmol), T = temperature (K).

Draw a *p-v* diagram for the following isotherms: 250°C, 270°C, 300°C, 330°C, 374°C, 390°C.

Compare the computed specific volumes with Steam Table values and explain the differences in terms of the value of  $p_c v_c / \Re T_c$ .