Thermodynamics

What is “Thermodynamics” and why is it important in Engineering?

The study of the conversion of heat into useful work (and vice versa) and has implications for energy conversion processes in general. For example in the generation, transmission and use of electrical energy, involving the conversion of heat into work and work into heat.

It is governed by the properties of matter and the transfer of energy in the forms of work and heat. This is intrinsic to the use of fluids in engineering....

Fundamentally:

• It is an experimentally based science.
• Its laws cannot be “proven”.
• Nobody has yet managed to disprove them.

Reminders and notation

Work (J) = force (N) × distance (m)

Power (W) = work (J) / time (s) = rate of doing work

Pressure (Pa or bar) = force (N) / area (m²)

1 N/m² = 1 Pa, 1 bar = 10⁵ N/m² 1 atmosphere=1.013 bar

Absolute pressure: actual pressure (includes atmospheric pressure)

Gauge pressure: pressure relative to atmospheric pressure (measured)

$$P_{\text{abs}} = P_{\text{gauge}} + P_{\text{atmos}}$$

$$P_{\text{vac}} = P_{\text{atmos}} - P_{\text{abs}}$$

Molecular unit: Unit of the number of molecules is the “Mole”, defined as equal to the number of atoms in 0.012kg of C₁₂ (carbon). More usual to use kmole, i.e. equivalent to the number of atoms in 12kg of C₁₂.

Actual mass (m), number of moles (n), molecular mass (M) related by:

$$n = \frac{m}{M}$$
Temperature and scales

Temperature (°C or K): a measure of “hotness” or “coldness”

Thermometer: a device for recording temperature, the basis is comparative.

Celsius scale: defined by freezing and boiling points of water, somewhat dependent on pressure.

Absolute scale: defined by thermodynamic arguments, lowest possible value is 0 K, the size of unit is same as Celsius.

\[
273.15 \text{ K} = 0 \degree \text{C} \\
0 \text{ K} = -273.15 \degree \text{C}
\]

Zeroth Law of Thermodynamics

Coined by Fowler and Guggenheim in 1939 is also called the "Equilibrium Principle". Joseph Black first stated a similar principle in the 18th century when justifying the existence of thermometers, also defined by Maxwell as "when two bodies are placed in thermal communication neither of them loses or gains heat, the two bodies are said to have equal temperatures of the same temperature [and] are then said to be in thermal equilibrium". The Zeroth Law is generally stated as:

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

Thermodynamic systems

**System**: the quantity of matter or region in space chosen for study

**Surroundings**: the region outside the system

**Property**: any characteristic of a system

**Thermodynamic properties**: those which define TD state of the system

- Intensive properties: those independent of the size of a system
  - e.g. pressure $p$, temperature $T$, density $\rho$
- Extensive properties: those dependent on the size of a system
  - e.g. mass $m$, volume $V$, energy

Thermodynamic relations that are applicable to closed and open systems are very different. Therefore, it is extremely important that we recognise the type of system we have before we start analysing it.
Thermodynamic systems

1. Closed system: (control mass)
   - No mass may cross the boundary.
   - Energy may cross the boundary.
   - Boundary shape may change – may be deformable.

2. Open system (Control volume):
   - Mass may cross the boundary.
   - Energy may cross the boundary.
   - Boundary is usually a fixed region of space.

3. Isolated system: No mass or energy may cross the boundary.

State: A system condition defined by a set of thermodynamic properties.

In a given state, all the properties of a system have fixed values.

Thermodynamics deals with equilibrium states

Equilibrium: a state of balance, requiring the system to have
- uniform temperature
- constant pressure
- constant chemical composition

Process: any change that a system undergoes from one equilibrium state to another.

Reversibility: When a process can be reversed and the system returned to its original state through the same set of equilibrium states without leaving any net effect on the system or the surroundings.

Irreversibility: When the system cannot be returned through the same equilibrium states to the original state – usually due to heat transfer from source to sink.

Property diagram: The variations of properties during a process are best studied and understood with the help of property diagrams.

Cycle: Series of processes connected such that the system returns to its original state.
Series of processes connected so that the system returns to original state.
- A cycle may consist of two or more processes.
- A cycle may be reversible or irreversible.

Steam power plant – conceptual model

Pressure – volume property diagram

**Thermodynamic systems: work**

*Work*: energy transfer at a boundary associated with the action of a force. If no force exists then no work is done. Definition: $W = F \Delta x$

**Example 1. Fixed boundary work**

$N$ turns of shaft work

$W = F \Delta x = FN \pi r$

$= \text{torque} \times \text{rotation}$

Electrical work

$W_i = IV$

The normal definition of energy transfer in thermodynamics is relative to the system. In this sense, the system does the work and work out is positive. In the above example, if the shaft work is inwards (to move the fluid in the system), then that is negative.

**Example 2. Moving boundary work**

Add weight, piston falls, gas is compressed.

$W = F \Delta x = p dA x = p dV$

If the weight added is infinitesimally small, then

$dW = pdV$

Adding a succession of weights, the total work is

$W = \int pdV$

The area under the line representing the process on a pressure-volume property diagram is quantitatively representative of the work done during the process.
Work done during a cycle

The work done during a cycle is equal to the sum of the integrals for the work done in each process making up the cycle:

\[ W = \int pdV = \int_1^2 pdV + \int_2^3 pdV + \int_3^4 pdV \]

For an individual process, the area under the curve on a \( p-V \) diagram represents the work.

The individual processes in a cycle form an enclosed area on the \( p-V \) diagram; this area represents the NET work during the cycle.

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Thermodynamic systems: heat

**Heat:** Heat is a form of energy crossing the boundary of a system under the action of a temperature difference.

There cannot be any heat transfer between two systems that are at the same temperature – zeroth law in reverse.

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The First Law of Thermodynamics
The first law of Thermodynamics

What is the 1st Law of Thermodynamics?

Energy can be neither created nor destroyed, it can only change forms (Conservation of energy)

In terms of the concepts discussed here:

During an interaction between a system and its surroundings, the amount of energy gained by the system must be exactly equal to the amount of energy lost by the surroundings.

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1st law for a cycle

Cycle: series of processes, after which the system is returned to its initial state. In general, both work and heat transfer take place.

The energy of the system at the end of the cycle must be the same as at the beginning. During the cycle:

net transfer of heat = net transfer of work

\[-q_1 + q_2 = W_1 - W_2\]

Equivalently: \[\int dq = \int dw\] or \[q_{net} = w_{net}\]

True for all closed systems even if \(q_{net}\) and \(w_{net}\) are approximately zero.

Important: Sign convention: heat in is positive, work out is positive

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Temperature–entropy diagram

In a reversible cycle: \[\int dv = \int dq\]

Also: \[w_{net} = \int p\,dv\]

Therefore: \[q_{net} = w_{net} = \int p\,dv\]

Significance: the amount of heat transferred can be determined even though we know nothing about the heating and cooling processes.

Another diagram can be drawn whose area is equal to \(q_{net}\). By definition \(q = \int (c_p T)\), therefore temperature could form one coordinate. The other coordinate is called ENTROPY.

Symbol for entropy is \(S\) (kJ/K or specific entropy \(s\) (kJ/kgK) and \[\frac{dS}{T} = \frac{q}{T}\]
Temperature–entropy diagram

There is no easy conceptual model for entropy and entropy is not a conserved property, except for ideal Carnot Cycles.

Entropy is somehow associated with disorder in the matter studied.

Fluids at a high temperature are highly active, highly disordered therefore have a high entropy.

\[ S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}} \]

Engineers are usually interested in entropy changes rather than absolute values.

More on this later.

Temperature–entropy diagram

Therefore:

For a cycle

\[ Q = \int T \, ds \]

For a process

\[ q = \int T \, ds \]

The heat transferred is represented by the area on the T-s graph.

For an isothermal process:

\[ \Delta S = \frac{q}{T} \]

\[ \Delta S = \frac{Q}{T} \]

1st Law for a process

Energy conservation still holds:

Energy in – energy out = energy stored

\[ q - w = \Delta e \]

where

\[ \Delta e = \sum \Delta KE + \sum \Delta PE + \Delta U \]

In most cases (close systems):

\[ \Delta KE = \Delta PE = 0 \]

Therefore for closed systems:

\[ q - w = \Delta e \]
**Fluid Properties, equations & definitions**

**Pure substance**: a substance that has a fixed chemical composition

- A pure substance does not have to be a single chemical element or compound. Homogeneous mixtures can be regarded as a pure substance.
- A mixture of oil and water is not a pure substance.
- A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same.

**Phase**: There are three principal phases: Solid, Liquid and Vapour/Gas

Relation between fluid properties is usually complicated, values are often listed in tables or drawn on charts.

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**Compressible fluids**

**Equation of state**: Functional relation between properties which defines its thermodynamic state. e.g. \( p = f(T,v) \)

**Perfect gas**: well above the saturation state and tend to obey two laws

- Boyle’s law: \( pv = \text{constant} \) at constant \( T \)
- Charles’ law: \( \frac{T}{p} = \text{constant} \) at constant \( p \)

We can generalise the equation of state by observing that for both of these equations to be true, the relationship between temperature, pressure and volume must be that given by the following definition.
The equation of state for a perfect gas

For a perfect gas: \( \frac{pV}{T} = \text{constant} = R \) or \( pv = RT \)

\( R \) is called the gas constant but is a different constant for different gases i.e. a material property

With total volume rather than specific, the equation can also be written as

\[ pv = mRT \quad \text{or} \quad pv = nR_0T \]

where \( m \) is the mass, \( n \) the number of moles and \( R_0 \) is the universal gas constant related to \( R \) by

\[ R = \frac{R_0}{M} \]

where \( M \) is the molecular mass (\( \mu = nM \))

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A perfect gas in diagram form

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Non-flow processes in closed systems

Constant Volume:

\[ Q = \Delta U - W = \Delta U \]

\[ Q = \Delta U \]

Constant Pressure:

\[ Q - W = \Delta U \Rightarrow Q = \Delta U + W = \Delta U + p\Delta V \]

or \( Q = \Delta H \) with enthalpy defined as \( H = U + pV \)

or specific enthalpy \( h = u + pv \)

\[ \Delta h = \Delta u + p\Delta v \]
Non-flow processes in closed systems

**Constant Temperature:** (isothermal)
\[ \Delta U = 0 \Rightarrow Q - W = \delta U \]
\[ Q = W \]

**Adiabatic:** (no heat flow)
\[ Q = 0 \]
\[ -W = \Delta U \]

**Polytropic:** (both heat & work flow)
\[ Q - W = \Delta U \]
or
\[ q - w = \Delta u \]

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Specific heats of gases

Specific heat is defined as "the heat required to raise unit mass by one degree"

For example:

\[ m = 1 \text{ kg} \]
\[ \Delta T = 1 \text{oC} \]

Specific heat = \( 5 \text{ kJ/kg\oC} \)

\[ Q = 5 \text{ kJ} \]

Solids and liquids are effectively incompressible and the specific heats are approximately constant as temperature changes.

For **gases**, there are two important processes and an associated specific heat: constant volume \( (C_v) \) and constant pressure \( (C_p) \)

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**Constant volume process**

Definition:
\[ C_v = \frac{\delta q}{\delta T} - \frac{dq}{dT} \]

For a constant volume process, 1st law is
\[ q - w = \Delta u \]

A perfect gas is one whose behaviour conforms to
\[ pV = mRT \]

A further requirement of a perfect gas is that
\[ u = f(T) \]
only.

For many gases the function is linear, i.e.
\[ u = aT \]
Constant volume process

Therefore the specific heat is

\[ C_v = \frac{\Delta u}{\Delta T} = \frac{du}{dT} \]

Conclusion: the specific heat for a constant volume process, \( C_v \), is a constant.

If \( u \) and \( T \) are properties, then \( C_v \) must also be a property and its use is not restricted to constant volume process.

Internal energy can be written as

\[ du = C_v dT \]

1st law for a constant volume process:

\[ q = \Delta u = C_v (T_2 - T_1) \]

Constant pressure process

Definition, as before:

\[ C_p = \frac{\Delta h}{\Delta T} = \frac{dh}{dT} \]

\[ q - w = \Delta u \Rightarrow q = \Delta u + w = \Delta u + \int pdv = \Delta u + p\Delta v = \Delta (u + pv) = \Delta h \]

In this case

\[ C_p = \frac{\Delta h}{\Delta T} = \frac{\Delta h}{\Delta T} \]

Since \( h = u + pv = u + RT \) for a perfect gas, then \( h = f(T) \) only

\[ f_1(T) \quad f_2(T) \]

Similarly, we can have \( h = C_p T \) and \( q = \Delta h = C_p (T_2 - T_1) \)

Relation between specific heats

Since

\[ dh = du + pdv \]

and for a perfect gas we have \( dh = C_p dT \), \( du = C_v dT \) and \( pv = RT \)

then

\[ dh = C_p dT + RdT \]

\[ C_p dT = C_v dT + RdT \]

Hence

\[ C_p - C_v = R \]
Isothermal process

Temperature is constant, therefore \( pv = \text{constant} \)

If the process proceeds through a series of equilibrium states, then

\[
\mathbf{w} = \int \mathbf{pdv} = \int \frac{\mathbf{K}}{\mathbf{T}} \, d\mathbf{v} = \mathbf{K} \ln \left[ \frac{\mathbf{v}_2}{\mathbf{v}_1} \right] \quad \text{or} \quad \frac{1}{\mathbf{v}} = \ln \mathbf{v}
\]

Isothermal process

Since \( \mathbf{pv} = \mathbf{K} \Rightarrow \mathbf{p}_1 \mathbf{v}_1 = \mathbf{p}_2 \mathbf{v}_2 = \mathbf{K} \)
hence

\[
\mathbf{w} = \mathbf{p}_1 \mathbf{v}_1 \ln \left[ \frac{\mathbf{v}_2}{\mathbf{v}_1} \right]
\]

Substituting in 1st law gives:

\[
\mathbf{q} = \mathbf{w} = \mathbf{p}_1 \mathbf{v}_1 \ln \left[ \frac{\mathbf{v}_2}{\mathbf{v}_1} \right]
\]

The heat transferred in a reversible isothermal process is equal to the work done for a perfect gas.

\[
\mathbf{q} = \mathbf{w} = \mathbf{RT} \ln \left[ \frac{\mathbf{p}_2}{\mathbf{p}_1} \right] \quad \Rightarrow \quad \frac{\mathbf{p}_1 \mathbf{v}_1}{\mathbf{p}_2} = \frac{\mathbf{p}_2 \mathbf{v}_2}{\mathbf{p}_1}
\]

Adiabatic process

Relation between pressure and volume in a reversible adiabatic process:

\( \mathbf{pv}^\gamma = \mathbf{K} \)

The reversible work will be:

\[
\mathbf{w} = \int \mathbf{pdv} = \int \frac{\mathbf{K}}{\gamma - 1} \, d\mathbf{v} = \mathbf{K} \left[ \frac{\mathbf{v}_2^{\gamma - 1} - \mathbf{v}_1^{\gamma - 1}}{\gamma - 1} \right]
\]

Substituting \( \mathbf{p}_1 \mathbf{v}_1^\gamma \) and \( \mathbf{p}_2 \mathbf{v}_2^\gamma \) for \( \mathbf{K} \) gives

\[
\mathbf{w} = \frac{\mathbf{p}_1 \mathbf{v}_1^\gamma - \mathbf{p}_2 \mathbf{v}_2^\gamma}{\gamma - 1}
\]
Adiabatic process

Substituting into 1st law, with \( q = 0 \), gives:

\[
-\frac{p_2 V_2 - p_1 V_1}{1 - \gamma} = u_2 - u_1
\]

And for a perfect gas:

\[
R \left( T_2 - T_1 \right) = C_v \left( T_2 - T_1 \right)
\]

\[
\frac{p_2}{p_1} = \frac{T_2}{T_1} = \left( \frac{V_2}{V_1} \right)\gamma
\]

Therefore:

\[
\gamma = \frac{C_v}{C_p}
\]

Polytropic process

A general expansion or compression process in which both heat and work cross the boundary, including a change in temperature.

The relation between \( p \) and \( v \) is:

\[
pv^n = \text{constant}
\]

where \( n \) is the index of expansion or compression.

\( n = 0 \) constant pressure process

\( n = 1 \) constant temperature process

\( n = \gamma \) adiabatic process
**Polytropic process**

The reversible work will be:

\[ w = \int p\,dv = \int \frac{C_p}{v} \, dv = \left[ \frac{p_v}{1-n} \right] \]

substituting into 1st law gives the heat:

\[ q - \frac{p_v v_2 - p_v v_1}{1-n} = u_2 - u_1 \]

and for a perfect gas:

\[ q = C_v(T_2 - T_1) + \frac{R}{1-n}(T_2 - T_1) \]

Similarly to the adiabatic process, useful ratios can be derived:

\[ \frac{T_2}{T_1} = \left[ \frac{V_2}{V_1} \right]^{n-1} \quad \frac{p_2}{p_1} = \left[ \frac{V_2}{V_1} \right]^{-n} \]

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**Three basic phases summary**

In reality, the behaviour of a material on a property diagram requires a complicated description.

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The Second Law of Thermodynamics and Heat Engines
Heat Engines and Cycles

Most power plants work on thermodynamic cycles. Analysis of power plants is important part of engineering thermodynamics.

Examples of cyclic devices:
- Power station boiler/turbine set
- Heat pumps
- Domestic fridge
- Generator or aircraft gas turbine
- Otto and diesel engine

Energy Conservation:

\[ Q - W = \Delta U \]

For a cyclic device

\[ \int \Delta U = 0 \Rightarrow \int dW = \int dQ \]

Hence

\[ W_{net} = Q_{in} - Q_{out} \]

Thermal efficiency:

\[ \eta = \frac{W_{net}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} \]

Some cycles

Steam power plant:
Some cycles

Gas turbine cycle:

- $p = \text{const}$
- $pv^{\gamma} = \text{const}$

Heat engines

Heat engines differ considerably from one to another, but can all be characterised by the following:

- They receive heat from a High Temperature source.
- They convert part of this heat to work.
- They reject the remaining waste heat to a Low Temperature sink.
- They operate on a cycle.

Heat engines and other cyclic devices usually involve a fluid to and from which heat is transferred while undergoing a cycle.

This fluid is called the working fluid.

The Second Law of Thermodynamics

Thermal energy reservoirs:

- A hypothetical body with a relatively large thermal energy capacity (mass-specific heat) that can supply or absorb finite amounts of energy as heat without undergoing any significant change in temperature.
- A reservoir that supplies energy in the form of heat is called a source and one that absorbs energy in the form of heat is called a sink.

The first law of Thermodynamics – energy conservation, no process is known to have taken place in violation of the 1st law, therefore a process must satisfy the 1st law to occur.

Question: Will a process actually take place if it satisfies the 1st law?

The 2nd law of Thermodynamics is a law based on the observation of physical processes and has implications for the direction of energy flow.

A process can occur only when it satisfy both the 1st and 2nd laws of TD.
The Second Law of Thermodynamics

The Kelvin-Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce an equivalent amount of work.

A heat engine must exchange heat with a low temperature sink as well as a high temperature source in order to keep operating.

Alternative statement:

No heat engine can have a thermal efficiency of 100%.

Illustration

Why must heat be rejected, why is it not possible to convert all the heat energy into work?

Consider the following cycle:

A gas in a cylinder, at 30°C, is to be heated to raise its temperature allowing it to expand and to work by raising a weight placed on the piston.

The heat is transferred from a thermal reservoir at 100°C, raising the temperature of the gas to 90°C.

Illustration

As the gas is heated the temperature rises and its pressure increases.

Eventually the pressure equals that exerted by the weight on the piston and on further heating the gas expands lifting the weight. When the piston reaches the top the weight is removed.

Note that in order for the gas to expand it was necessary to raise its temperature, thus not all the heat transferred went in raising the weight, some went in increasing its internal energy.
In order to return the piston to the bottom, and thus complete the cycle, it is necessary to cool the gas so that it contracts.

Can we return some of the thermal energy back to the original reservoir? No, because heat will not flow from a lower to a higher temperature. To reject heat, a low temperature thermal reservoir is necessary.

To complete the cycle some heat had to be rejected to return the gas to its original state. As a result, $W$ cannot equal $Q_{in}$ and the efficiency cannot be 100%.

What is the best efficiency we can achieve? The answer depends on the processes involved:

**Reversible and Irreversible processes**

Reversible process: a process which can be reversed without leaving any trace of its existence either on the system or the surroundings.

A reversible process is an idealisation and does not exist in nature, but they are still useful in that they represent the limiting case of real processes and can be used to give a measure of how “good” a real process is.

**Examples of reversible processes**

- Relative motion without friction
- Extension or compression of a spring
- Frictionless adiabatic expansion or compression
- Isothermal expansion or compression
Irreversible processes

Irreversible processes: any process that is not reversible must therefore be an IRREVERSIBLE process.

Friction is not the only factor which can cause irreversibility of the system.

Some examples of irreversible processes
- Relative motion with friction
- Finite temperature differences in heat transfer

In order to achieve maximum efficiency, all processes in a cycle must be reversible.

The Carnot Cycle

During the cyclic operation of a heat engine work is done on the working fluid in one part of the cycle and by the working fluid in another part of the cycle. The difference between these is the net work output. The efficiency depends on how these processes are carried out. The net work that can be produce will be maximised by using processes that absorb the least amount of work and produce the maximum amount of work, i.e. by using reversible process.

The most well known reversible cycle is the Carnot Cycle, proposed by Sadi Carnot in 1842.

The Carnot Cycle

The Carnot cycle consists of two reversible adiabatic processes and two reversible isothermal processes.

\[ \int dW = \int dQ \]

Since the Carnot cycle is a reversible cycle the efficiency must be the maximum possible for the given source and sink temperatures.
Reversible Carnot Cycle

Since all the processes for the Carnot heat engine are reversible then the cycle can be reversed.

Typical devices which use the reversible Carnot cycle are refrigerators & heat pumps. In this case work is done on the system which produces a flow of heat from a cold source to a high temperature sink.

Corollaries of the 2\textsuperscript{nd} law

1. The efficiency of an IRREVERSIBLE engine is always LESS than that of a REVERSIBLE engine operating between the SAME temperature reservoirs.

2. The efficiency of ALL REVERSIBLE engines operating between the SAME temperature reservoirs is the SAME.

The Absolute Temperature Scale

The efficiency of a reversible heat engine must be independent of the working fluid and dependent only on some property of the thermal reservoirs. It must be the temperatures that determine the efficiency, i.e.

\[ \eta = \text{function}(T_c, T_h) \]

where \( T_c \) and \( T_h \) are the temperatures of the sink and source on a scale to be defined.

We can derive this function by examining the relationship between \( \dot{Q} \) and \( T \) in the Carnot cycle. This derivation is also related to the definition of the absolute temperature scale.
The efficiency can also be expressed in terms of heat flows:
\[ \eta = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} \]
\[ \eta(T_f, T_i) = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} \]

then
\[ \frac{Q_{\text{out}}}{Q_{\text{in}}} = 1 - \eta(T_f, T_i) = \Psi(T_f, T_i) \]

where the function \( \Psi \) has yet to be specified. Kelvin made the arbitrary choice of the simplest function:
\[ \Psi(T_f, T_i) = \frac{T_f}{T_i} \]

where \( T \) is the symbol for temperature on the Kelvin scale.

Carnot efficiency
We start with the Carnot cycle and the definition of efficiency.
\[ Q_{\text{in}} = \int p \, dv = RT_i \int_{v_1}^{v'} \frac{1}{v} \, dv = RT_i \ln \left( \frac{v'}{v_1} \right) \]
\[ Q_{\text{out}} = \int p \, dv = RT_f \int_{v_1}^{v'} \frac{1}{v} \, dv = RT_f \ln \left( \frac{v'}{v_1} \right) \]
\[ q = \frac{W_{\text{net}}}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{1}{T_f} \ln \left( \frac{v'}{v_1} \right) / \ln \left( \frac{v_2}{v_1} \right) \]

Need volumes in terms of temperature.
\[ \frac{p v^{\gamma+1}}{v^\gamma} = K = \frac{p T}{v^\gamma} \]
\[ \frac{p v}{v^\gamma} = RT \]
\[ T v^\gamma = K \]
\[ \Rightarrow T v_1^\gamma = T v_2^\gamma \]
\[ T v_1^\gamma = T v_2^\gamma \]
\[ \Rightarrow \frac{v_2}{v_1} = \frac{v_1}{v_1} \]
\[ \Rightarrow \frac{v_2}{v_1} = \frac{v_1}{v_1} \]
\[ q = \frac{W_{\text{net}}}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{1}{T_f} \ln \left( \frac{v'}{v_1} \right) / \ln \left( \frac{v_2}{v_1} \right) = 1 - \frac{T_f}{T_1} \]
### Carnot efficiency

The Carnot efficiency can be expressed as:

\[
\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} = 1 - \frac{T_{\text{sink}}}{T_{\text{source}}}
\]

Therefore, in a reversible heat engine, the ratio of heat flows is equal to the ratio of **absolute temperatures** of the thermal reservoirs.

Also:

\[
\frac{Q_2}{T_2} = \frac{Q_1}{T_1}
\]

i.e. entropy out = entropy in

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### Absolute temperature

This relation defines the Absolute Temperature scale, i.e. a temperature scale independent of any substance. Absolute temperatures can accurately determined using conventional comparative instruments such as the constant volume ideal gas thermometer.

**Note:**

We must always reject some heat to a low temperature reservoir (2nd law), this means that absolute zero temperature can never be achieved.

i.e. \( Q_{\text{out}} > 0 \) then \( T_2 > 0 \)

\[
T_1 = T_2 \frac{Q_{\text{out}}}{Q_1}
\]

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### Summary

The Carnot efficiency in terms of heat and absolute temperatures:

1st law: heat and work are interchangeable.

2nd law: work is wholly convertible, heat is not.

**POSSIBLE**

\[\begin{array}{c}
E \rightarrow W \\
Q \end{array}\]

**IMPOSSIBLE**

\[\begin{array}{c}
E \rightarrow W \\
Q \end{array}\]

Work is more valuable than heat!
The Third Law of Thermodynamics and Free Energy

Entropy and the 2nd Law

The second law can be written to give a more quantifiable view of entropy in terms of changes in entropy. From before,

There is a state function $S$, called entropy, the change of which from state A to state B is given by:

$$\Delta S = \int_{A}^{B} \frac{dq_{rev}}{T}$$

where $q_{rev}$ is that associated with a reversible process i.e. to calculate $\Delta S$ between two states, the system must be changed in a reversible manner.

The second law can be restated then as:

Along any reversible path, there is an integrating factor $T$ such that

$$dS = \frac{dq_{rev}}{T}$$

is an exact differential, i.e. $S$ is a state function (this defines the temperature scale) and

$$\Delta S = \int_{A}^{B} \frac{dq_{rev}}{T}$$

for a reversible process

and

$$\Delta S > \int_{A}^{B} \frac{dq}{T}$$

for all other processes

where $T$ is the temperature of the surroundings.
The third law

The third law of thermodynamics states:

If the entropy of each element in a crystalline state is assumed zero at absolute zero, every substance has a finite positive entropy but at absolute zero, the entropy may become zero and does become so for a perfect crystal.

This is often described by Boltzmann’s equation for entropy:

$$S = k_B \ln N$$

where $k_B$ is Boltzmann’s constant and $N_\Omega$ is the number of microstates of the system. A microstate is a specific configuration of the components of the system, which in a perfect crystal is 1, giving an entropy of zero. This ties the idea of entropy directly to the probability of a given microstate (a material/system value), which in turn is related to the number of degrees of freedom of the individual components (atoms/molecules) of the system.

Energy

The third law allows for the calculation of the absolute entropy as

$$S - S_a = \int_{S_a}^{S} \frac{dQ}{T}$$

where the first law for a simple system can then be written as:

$$dE = TdS - pdV$$

which is an alternative form of the internal energy calculation in the absence of kinetic work.

Summary

The thermodynamic behaviour of a system can be described by state functions.

<table>
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<tr>
<th>function</th>
<th>Potential form</th>
<th>Differential form</th>
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<tbody>
<tr>
<td>Internal energy</td>
<td>$U$</td>
<td>$dU = TdS - pV$</td>
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<tr>
<td>Enthalpy</td>
<td>$H = U + pV$</td>
<td>$dH = TdS + Vdp$</td>
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<tr>
<td>Helmholtz function a.k.a.</td>
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<tr>
<td>Helmholtz free energy</td>
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<td>Work function</td>
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<td>Free energy</td>
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<td>Thermodynamic potential</td>
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</tbody>
</table>

The exact justification of these expressions is an exercise in abstract functional reasoning and not relevant for study. As for internal energy versus enthalpy described before, the choice of which state function is used, depends on which state variables are varied and which are held constant.