THE SECOND LAW OF THERMODYNAMICS

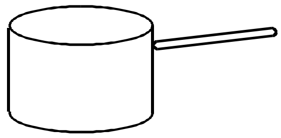
The FIRST LAW is a statement of the fact that ENERGY (a useful concept) is conserved. It says nothing about the WAY, or even WHETHER one form of energy can be converted to another.

For example:-
The ocean temperature is typically between ~ 280 - 290K.
It therefore contains a vast quantity of energy (relative to 0K).
Why can't we build a ship, and, by converting some of the ocean's thermal energy to mechanical energy propel it through the water?

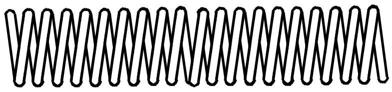
The SECOND LAW is concerned with the usefulness of energy or, more specifically, with the DIRECTION in which energy transfers may occur.

QUESTION: If you had a lifting job to do, which of the following energy sources would you choose?
They all contain (relative to SSL conditions) approximately the same amount of energy (~ 356 kJ).

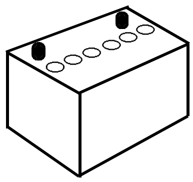
1 kg of water at 100°C.



A spring (of rate 2848 N/mm) compressed 0.5m.

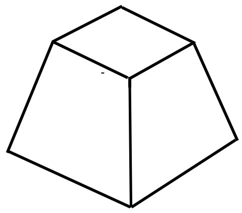


A 12V 8.25 amp-hour battery.

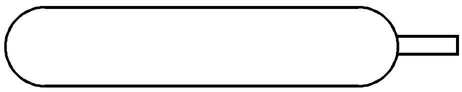


36.3 m of water held at a mean height of 1m.

363 kg of steel held at a height of 100m.



8 litres of compressed air at 100 bar gauge pressure.



Which energy source would you be **least** likely to choose? Why?

We know from experience that hot water is pretty useless as a source of mechanical energy.
We cannot use it directly (as with some of the other sources) - we would need an energy converter to convert the thermal energy to mechanical energy.
(in fact we would need a Heat Engine)-

Even with a suitable converter, we would find that we could not fully convert all of the heat energy to mechanical energy.
(neither could we fully convert the energy of the other systems, but, in most cases, very little potential is lost)

Work (Mechanical Energy) is very much more 'useful' than Heat (Thermal Energy).

In converting Heat to Work the First Law states that:-

Net Work = ΣHeat 'in' + ΣHeat 'out' [$W_{net} = Q_{net} = \Sigma Q$]
[NB: Heat 'out' is negative]

The Second Law states that the Net Work is always **less** that the Heat SUPPLIED.

There are many statements of the SECOND LAW.

It is impossible to construct a device, operating in a cycle, producing as its sole effect net positive work while exchanging heat with only one reservoir.

No heat engine can have a thermal efficiency higher than that of a Reversible Carnot Engine.
(The Heat Engine Rule - HER!)

The latter statement raises a number of questions:-

What is a Heat Engine?

What do we mean by Thermal Efficiency?

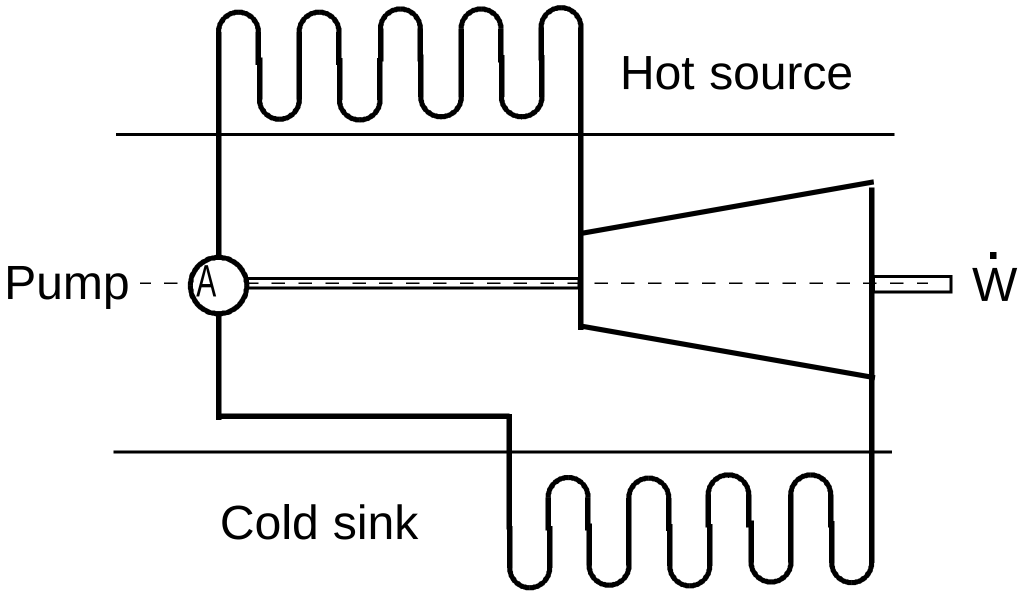
What is a Reversible Carnot Engine?

HEAT ENGINES

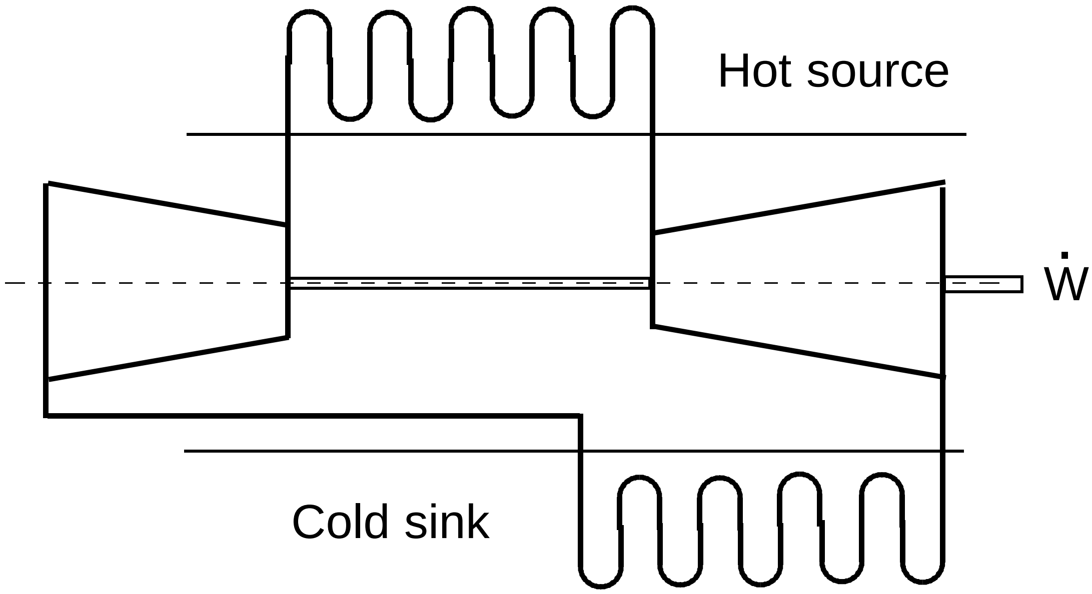
A Heat Engine is a device designed to operate **continuously** (cyclically) in which heat is supplied and work is done.
It follows from the first statement of the Second Law that heat must be supplied at one temperature and rejected at a different (lower) temperature.

Examples:-

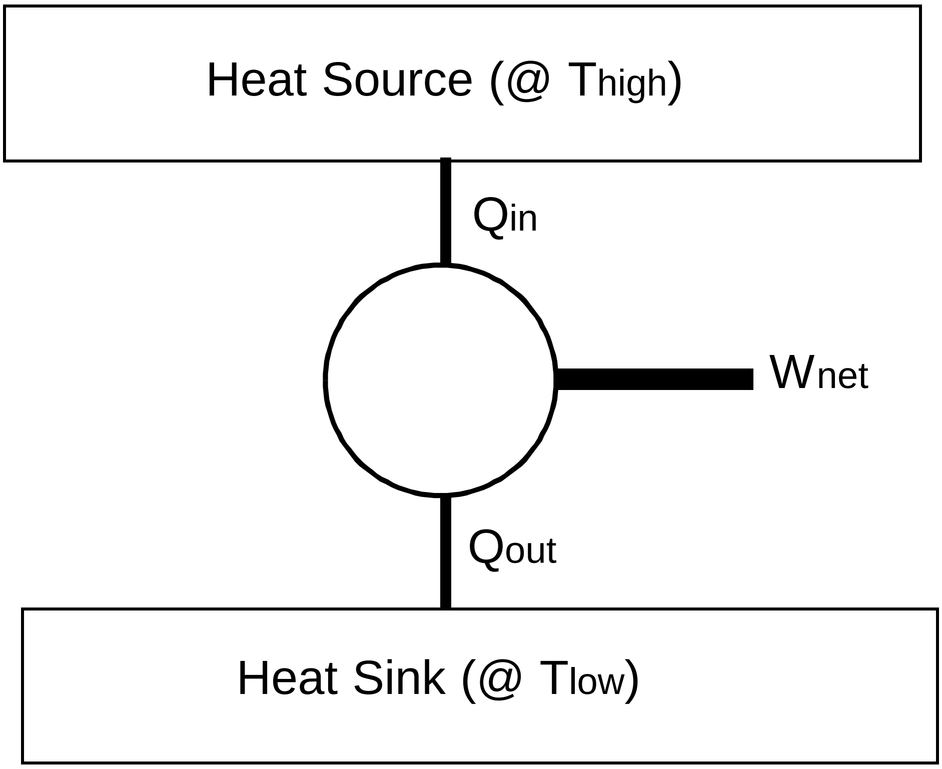
Steam turbine:



Closed cycle gas turbine:



Whatever the type of Heat Engine, we can represent it as:-



THERMAL EFFICIENCY (η_{th})

Thermal efficiency is defined as the proportion of the Heat Supplied which is converted to Work.

$$W_{net} = \eta_{th} Q_{in}$$

or

$$\eta_{th} = \frac{W_{net}}{Q_{in}}$$

Again, from the second statement of the Second Law, η_{th} can never equal 100%.

NB: From the First Law $W_{net} = Q_{in} + Q_{out}$

Therefore $\eta_{th} = \frac{Q_{in} + Q_{out}}{Q_{in}} = 1 + \frac{Q_{out}}{Q_{in}}$

[NB: Q_{out} is negative !]

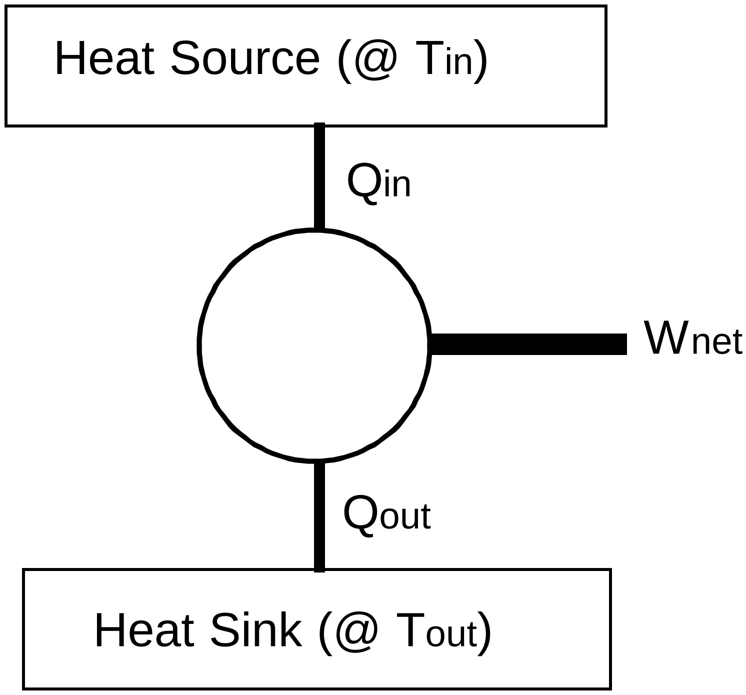
For an Engine that works by consecutive processes in a cycle:-

$$\eta_{th} = \frac{\text{Net Work per cycle}}{\text{Heat supplied per cycle}}$$

REVERSIBLE CARNOT ENGINE

A Reversible Carnot Engine is one which accepts heat at a single unique temperature by reversible heat transfer and rejects heat at a unique temperature by reversible heat transfer.
This assumes that in accepting and rejecting heat the temperature of the heat source and sink remains unaffected, ie an **infinite** heat source and sink.

ie we have :

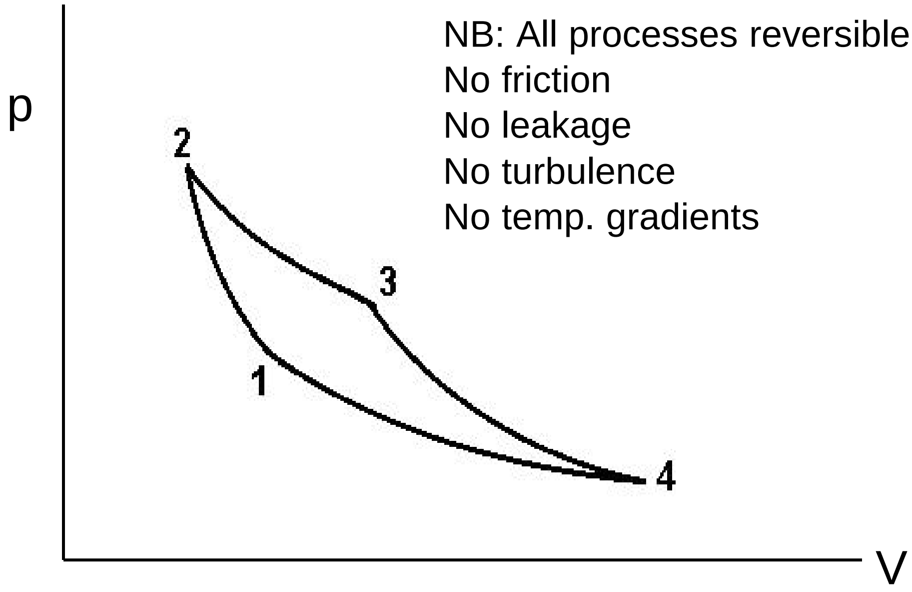


It is possible to devise such a cycle using a perfect gas as the working fluid.
It would consist of the following processes:-

1 > 2 Adiabatic compression
2 > 3 Isothermal heating of the gas
3 > 4 Adiabatic expansion
4 > 1 Isothermal cooling of the gas

Compare this with a petrol engine :
adiabatic compression;
isochoric heating;
adiabatic expansion;
isochoric cooling.

Cycle:-



NB: All processes reversible:-
No friction
No leakage
No turbulence
No temp. gradients

Analysis table:-

Q	W	ΔU
1 → 2 0 Adiabatic compression	$\dfrac{p_2V_2 - p_1V_1}{\gamma - 1}$	$m\,C_v\,(T_2 - T_1)$
2 → 3 equal & opposite to W Isothermal heating	$p_2V_2 \ln\left(\frac{V_2}{V_3}\right)$	0
3 → 4 0 Adiabatic expansion	$\dfrac{p_4V_4 - p_3V_3}{\gamma - 1}$	$m\,C_v\,(T_4 - T_3)$ [NB: $T_4 = T_1$ & $T_3 = T_2$]
4 → 1 equal & opposite to W Isothermal cooling	$p_4V_4 \ln\left(\frac{V_4}{V_1}\right)$	0
ΣQ	ΣW	0

$$\eta_{th} = \frac{W_{net}}{Q_{in}}$$

$$= \frac{Q_{23} + Q_{41}}{Q_{23}}$$

$$= 1 + \frac{Q_{41}}{Q_{23}}$$

$$= 1 + \frac{mRT_1 \ln \frac{V_4}{V_1}}{mRT_2 \ln \frac{V_2}{V_3}}$$

$$= 1 - \frac{T_{out} \ln \frac{V_4}{V_1}}{T_{in} \ \ln \frac{V_3}{V_2}}$$

But from process 1 → 2 $\quad p_1V_1^{\gamma} = p_2V_2^{\gamma} \quad$ (i)

and from process 3 → 4 $\quad p_4V_4^{\gamma} = p_3V_3^{\gamma} \quad$ (ii)

also from process 2 → 3 $\quad p_2V_2 = p_3V_3 \quad$ (iii)

and from process 4 → 1 $\quad p_1V_1 = p_4V_4 \quad$ (iv)

Dividing (ii) by (i) gives: $\quad \frac{p_4V_4^{\gamma}}{p_1V_1^{\gamma}} = \frac{p_3V_3^{\gamma}}{p_2V_2^{\gamma}}$

using (iii) on the RHS
and (iv) on the LHS : $\quad \frac{V_4}{V_1} = \frac{V_3}{V_2}$

therefore

$$\boxed{\eta_{th} = 1 - \frac{T_{out}}{T_{in}}}$$

Note:

1. All the Heat is supplied at T_{in}

2. All the Heat is rejected at T_{out}

3. The Thermal Efficiency is a function of temperature only. ie independent of the gas itself.

$$\eta_{carnot} = 1 - \frac{T_{out}}{T_{in}}$$

4. It implies that η_{carnot} could be 100% if T_{out} = 0K (absolute zero of temperature) or if T_{in} was infinite.

5. In practice it indicates that the highest thermal efficiency will be obtained when the Heat supply temperature is **high** and the Heat rejection temperature is **low.**

But first a slight diversion

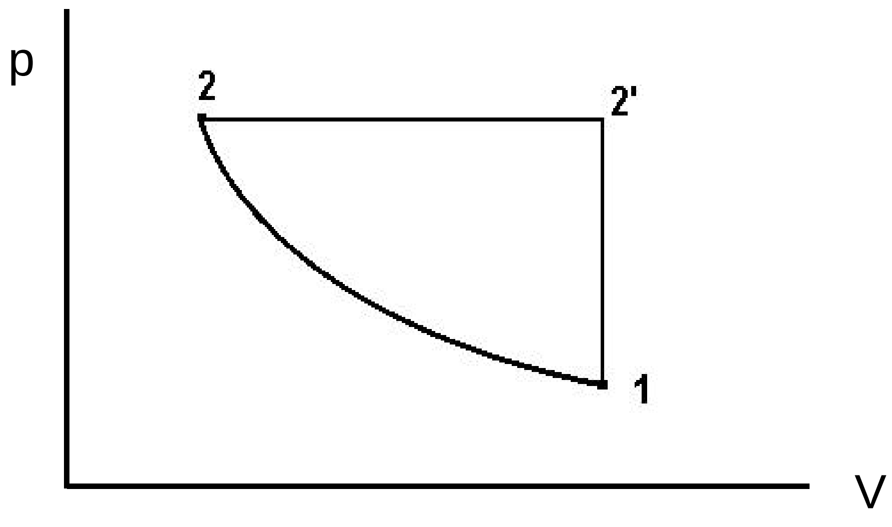
There is a system property the change in which can be found by integrating the REVERSIBLE Work Transfer divided by the Pressure when the system changes from one state (1) to another (2).

$$\text{ie This property} = \int_1^2 \frac{dW_{rev}}{p}$$

Reversible work means work done with no friction at all. It is always possible to make a system change from one state to another by allowing it to do (or have done on it) **reversible** work. It may also mean allowing heat to enter or leave it, but this is OK.

eg. If we have a gas at p_1 & V_1, changing to p_2 & V_2.

We may be able to connect these states on a p-V diagram by a **reversible** polytropic expansion: thus



If $pV^n = \text{constant}$

and $dW_{rev} = pdV$

then $\frac{dW_{rev}}{p} = dV$

and $\int_1^2 \frac{dW_{rev}}{p} = V_2 - V_1$

ie this property, which we so defined, turns out to be the familiar property of VOLUME.

Note that we can only use the expression {∫dW/p} to determine the change in volume if we use $dW_{\mathbf{rev}}$, which we did by usng a **theoretically reversible process** which we could integrate.

IN PRACTICE if we tried to use this expression - by measuring the work output from the system & dividing by the instantaneous pressure at any point - we would only get a true measure of the volume change IF the process was absolutely frictionless.

In real life this is impossible, therefore the actual accumulated work would be less than the ideal and evaluation of the expression {∫dW/p} would be LESS than the actual volume change.

However, that doesn't detract from the fact that VOLUME is a real property of the system (which can, of course, be measured by other means), and that it is quite OK to determine it from a theoretical reversible process connecting the two actual end states.

ie generally $\int \frac{dW}{p} \leq V_2 - V_1$

The equality is only true for the **ideal reversible** (frictionless) process.

Now to return to Entropy

The reason for all of the above is that **Entropy** is also a system property and it 'behaves' in the same way as volume.

If, in the above analysis, we had started out with:

There is a system property the change in which can be found by integrating the REVERSIBLE Heat Transfer divided by the Temperature when the system changes from one state (1) to another (2);

we could go through exactly the same argument, but the property whose change we could measure is known as ENTROPY.

ie $$\boxed{\int \frac{dQ}{T} \leq S_2 - S_1}$$

The equality only being true for the **ideal reversible** process.

However, while we all have a 'feel' for what VOLUME is, what is this new property ENTROPY?
Where does it come from, and what does it mean?

Let us revisit the Carnot Cycle.

Ref: Course text

Along the isothermals, the property **temperature** remains constant.
What property (if any) remains constant along the adiabatics?

We transferred from one adiabatic to the other by processes 4 $\rightarrow$ 1 and 2 $\rightarrow$ 3 ie. by adding or abstracting heat at constant temperature

$$Q_{41} = mRT_1 \ln\left(\frac{V_1}{V_4}\right)$$

$$Q_{23} = mRT_2 \ln\left(\frac{V_3}{V_2}\right)$$

but $$\ln\left(\frac{V_1}{V_4}\right) = -\ln\left(\frac{V_3}{V_2}\right)$$

$$\therefore \quad \frac{Q_{41}}{mRT_1} = -\frac{Q_{23}}{mRT_2} \quad \text{or} \quad \frac{Q_{41}}{T_1} = -\frac{Q_{23}}{T_2}$$

but $\left(\frac{Q_{rev}}{T}\right)$ is ***entropy***

It was this property that increased from 2 $\rightarrow$ 3 and decreased by the **same amount** from 4 $\rightarrow$ 1.
It therefore appears that the property that remains constant during a ***reversible*** adiabatic process is entropy. Because of this it is also known as an isentropic process.

THE NATURE OF ENTROPY

The property ***internal energy*** (which we deduced from the First Law) is relatively easy to comprehend, in terms of the 'energy level' or 'degree of activity' of the system substance.

Entropy, however, seems much less tangible in terms of our comprehension of it.

A working concept of entropy is therefore useful.
It can be thought of in terms of the **degree of molecular disorder** within a substance.

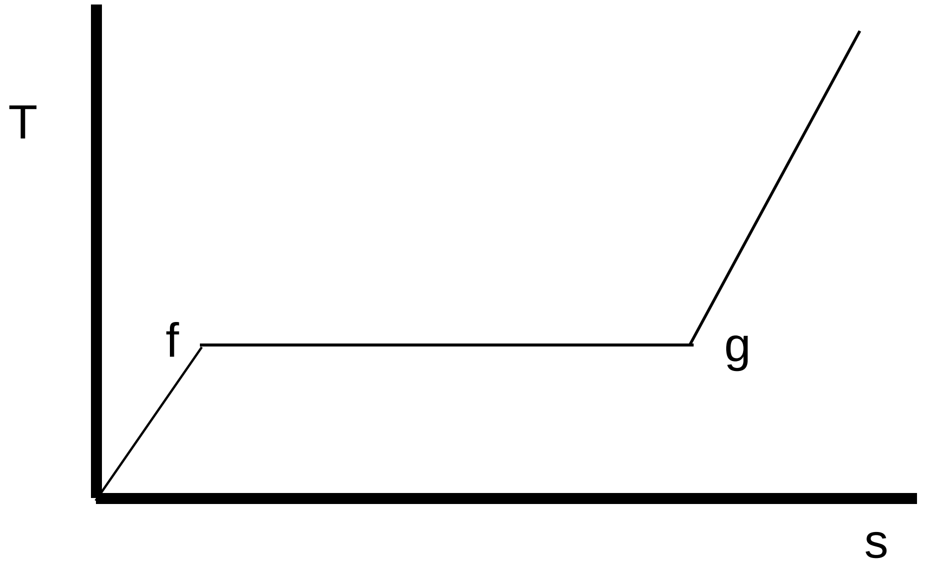
Examples:-

A solid substance (eg a metal) may be crystalline:
ie a highly ordered, regular, repeated pattern of molecular arrangement.

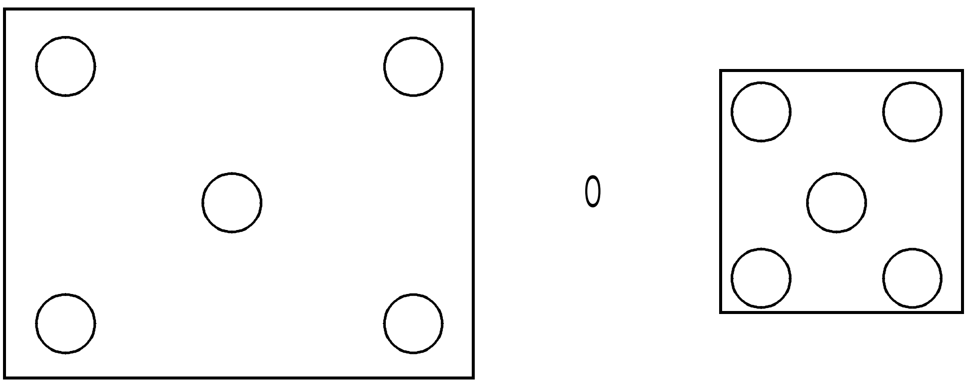
If this substance is heated, the molecular energy increases and the highly ordered structure begins to be shaken. ie become less well ordered.

If enough heat is supplied the structure begins to break down as it commences to melt. ie a very large increase in disorder occurs. With the addition of more heat more substance melts. All of the heat now goes in destroying the ordered nature of the solid and there is no change in temperature. In fact phase change can be better understood in entropy terms than in energy terms.

This process continues until all of the substance is a liquid.
A similar process occurs when the liquid vapourises.

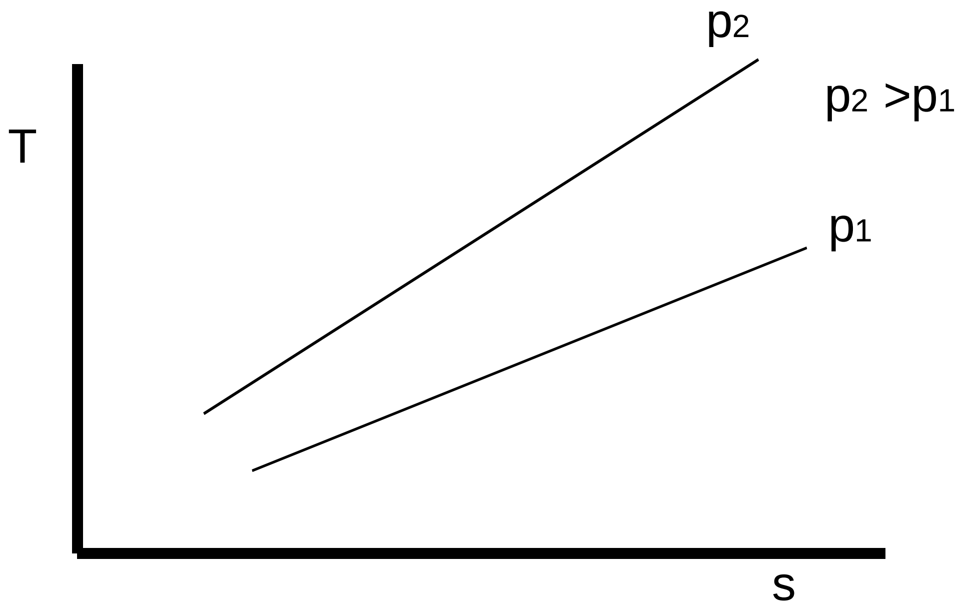


In a compression process, it is theoretically possible to maintain the molecular arrangement during the compression process.



In practice we distort the shape, we cannot avoid friction, leakage, turbulence etc, all of which at least partly destroys the molecular order.
This is particularly so of fluid dynamic compression processes. eg in a centrifugal or axial compressor

We can use this concept to predict how the entropy of a perfect gas will change with temperature and pressure:



at constant pressure $dq = c_p dT$

$$s_2 - s_1 = c_p \int dT/T$$

$$s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right)$$

at constant temperature $dq = dw = pdv$

$$s_2 - s_1 = \int R dv/v$$

$$s_2 - s_1 = R \ln\left(\frac{p_1}{p_2}\right)$$

Ref: Course text