Gas Processes in a Closed System

Many real processes are carried out in a piston-cylinder arrangement. Forecasting the behaviour of the working fluid is not simple due to the complex processes taking place.
However, by assuming that the working fluid behaves like a perfect gas and that the processes are reversible results can be obtained which are sufficiently accurate for many engineering purposes.

The Gas Laws

Boyle's law
This states that when a given mass of gas is kept at constant temperature its volume varies inversely as the absolute pressure.

$$V \propto \frac{1}{P} \quad \text{or} \quad pV = \text{constant}$$

Charles' Law
This states that when a given mass of gas is kept at constant pressure its volume varies directly as its absolute temperature.

$$V \propto T \quad \text{or} \quad \frac{V}{T} = \text{constant}$$

The Characteristic Equation of State
Consider a volume of gas V_1 at a pressure p_1 and temperature T_1 which undergoes the following process.

1) Expansion to some other volume V while the temperature remains constant at T_1.

From Boyle's law $\quad p_2 = \frac{p_1 V_1}{V} \quad$ call this equation 1

2) Heating at constant pressure from volume V to a new volume and temperature of V_2 and T_2

From Charles' law $\quad V = \frac{V_2 T_1}{T_2} \quad$ call this equation 2

If we substitute the value for Volume V from equation 2 into equation 1 we get

$$\frac{p_2 V_2}{T_2} = \frac{p_1 V_1}{T_1} = \text{Constant}$$

since the mass remains constant then we can say $\quad \frac{pV}{T} = \text{mass} \times \text{Constant}$

The constant in this equation is called the gas constant and is identified as **R** with units of Joules per kilogram Kelvin, note that each perfect gas has its own gas constant the equation is usually written as pV=mRT with the pressure temperature and volume all at the same state point.
pV=mRT is called the characteristic equation of state.

Universal Gas Constant R_o

The gas constant R defined above is unique to each gas, however a universal gas constant can be derived by modifying the form of the characteristic equation of state using Avogadro's hypothesis and a unit of molecular mass called the kilogram-mole in the following manner.

Molar mass

The word mole comes from a Latin word meaning heap or pile, so a mole is a pile of atoms or molecules, it has no units it is just an amount of matter.
Each element of substance has its own relative atomic mass, this is the average mass of its isotopes compared with the mass of a standard atom of carbon.
The molar mass of a substance is the mass of a mole of the substance and is its relative atomic or relative molecular mass.
For example, one molecule of Oxygen "O" contains 2 atoms written O_2, each atom has a relative atomic mass of 16 hence the relative molecular mass of Oxygen is 2 x 16 = 32 as this is a relative mass we can substitute whatever units we find convenient.
Most standard chemistry texts would consider 1 mole of substance having a mass measured in grams, this is too small for our purposes therefore we would consider a larger amount of substance the Kmole which has a mass measured in kilograms, so one Kmol of Oxygen has a mass of 32 kg.

The mass of a substance can therefore be defined as the number of molecules of substance times the mass of one molecule.
The molecular mass is given the symbol M with units of kg/Kmol

For n molecules of substance mass (kg) = n (Kmol) x M (kg/Kmol)

The characteristic equation $p \times V = m \times R \times T$ can be written as $p \times V = nM \times R \times T$

Avogadro's law

This states that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.

Consider two gases A and B occupying equal volumes at the same pressure and temperature

Gas A
n Kmol
M_A kg/Kmol
R_A kJ/kgK
Pressure p N/m^2
Volume V m^3
Temperature T K

Gas B
n Kmol
M_B kg/Kmol
R_B kJ/kgK
Pressure p N/m^2
Volume V m^3
Temperature T K

According to Avogadro if there are **n** molecules of gas A there will be **n** molecules of gas B.

For gas A $p \times V = nM_A \times R_A \times T$ and for gas B $p \times V = nM_B \times R_B \times T$

Therefore $\frac{pV}{nT} = M_A \times R_A$ and $\frac{pV}{nT} = M_B \times R_B$

From Avogadro, the quantity $\frac{pV}{nT}$ is a constant for all gases and is referred to as the universal gas constant and given the symbol R_o

Therefore $R_o = M \times R$

Experiments have shown that 1 mol of any perfect gas at 1 bar and 0°C is around 22.71 m^3, if we use this in the above equations a numerical value for R_o can be obtained;

$$R_o = \frac{pV}{nT} = \frac{1 \times 10^5 \times 22.71}{1 \times 273.15} = 8314.1 \frac{\text{J}}{\text{molK}}$$

The units for R_0 have been given as J/**mol** K, since the molecular mass is a relative mass the units of J/**kmol** K could also have been used in this case the molecular mass would be in kg/Kmol.
The characteristic constant for oxygen with a relative molecular mass of 32 is given by

$$R_o = M \times R \quad R = \frac{R_o}{M} = \frac{8314.1}{32} = 259.8 \frac{\text{J}}{\text{kgK}}$$

The volume of one mol of gas at standard temperatures and pressures (STP) will also be the same for all gasses at the same temperature and pressure, it is found to be 22.41 m^3.

$$V = \frac{n \times R_o \times T}{p} = \frac{1 \times 8314.1 \times 273.15}{1.01325 \times 10^5} = 22.41\,\text{m}^3$$

Specific Heats of Ideal Gasses

The basic definition of specific heat capacity is:

The amount of energy (Heat Transfer) that must be added to a particular mass to raise its temperature through one degree.

$$Q = m\ c\ T$$

Heat transfer describes a particular method or path of energy transfer and is not a property.
The amount of heat transfer required to change a property from one value to another depends on the path followed, so if the path is known then the heat required depends only on the working substance the specific heat is then a property of the fluid.

In the analysis of gas cycles two particular processes are of interest constant pressure and constant volume.

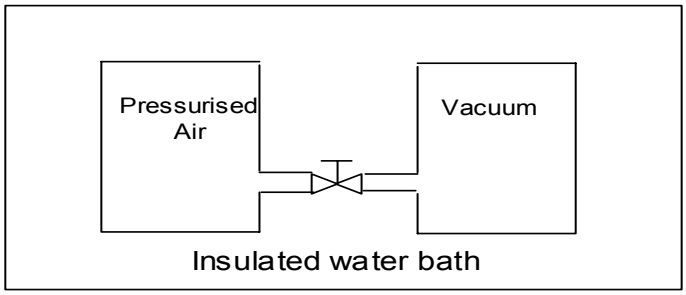
Specific heat at constant volume

To develop this further we must introduce Joules law which investigates the internal energy of a gas.

Joules Law

The internal of a fluid is due to the movement of molecules within the substance of a system and as such is a function of temperature, Joule used the apparatus below to investigate this.

When the system was in thermal equilibrium, the valve was opened and the pressurised air flowed into the vacuum, careful measurements showed that the temperature did not change. Since there had been no work transfer and the tank was insulated to prevent heat transfer then from the non flow energy equation the internal energy had not changed thus Joule reasoned that since the pressure and volume had changed and the temperature had not, the internal energy of a given mass of gas was only dependant on temperature.



From the first law and non flow energy equation Q = W + U

Therefore If Q=0 and W=0 then U =0

Consider a constant volume process in which m kg of gas is heated from temperature T_1 to T_2

In a constant volume process there is no work transfer therefore Q=U

$$Q = m \times c_v \times (T_2 - T_1) = U$$

The change of internal energy is always given by m x c_v x ($T_2 - T_1$) regardless of the process between the two points however only in a constant volume process does the heat transfer equal the change of internal energy.

Specific heat at constant pressure

From the definition of specific heat $Q = m \times c_p \times (T_2 - T_1)$

Where c_p is the specific heat capacity at constant pressure.

Relationship between the specific heats

Consider a closed system in which m kg of gas is receiving heat and expanding so the pressure remains constant.

Applying the NFEE $Q = W + (U_2 - U_1)$

Where $Q = m \times c_p \times (T_2 - T_1)$

$(U_2 - U_1) = m \times c_v \times (T_2 - T_1)$

$W = p(V_2 - V_1) = m \times R \times (T_2 - T_1)$

Substituting the above expressions gives

$$m \times c_p \times (T_2 - T_1) = m \times c_v \times (T_2 - T_1) + m \times R \times (T_2 - T_1)$$

$$c_p = c_v + R$$

Ratio of specific heats

The ratio of the two specific heats c_p / c_v is usually denoted by symbol γ,

Ratio of specific heats $\frac{c_p}{c_v} = \gamma$ therefore $c_p = \gamma c_v$ if we substitute this relationship in $c_p - c_V = R$

We can obtain the following relationships $c_v = \frac{R}{\gamma - 1}$ and $c_p = \frac{\gamma R}{\gamma - 1}$

These relationships are true for both real and perfect gases.

For perfect gases γ is a constant, since both c_p and c_v are constants.

For real gases γ is a property, and hence its value depends on the state point.

Since both c_p and c_v increase with temperature and the difference between them (R) remains constant, γ tends to decrease as the temperature increases.

Since the specific heats are positive and $c_p > c_v$, γ is positive, and greater than one.

For Monatomic gasses such as Argon (A) γ is about 1.6

For Diatomic gasses such as oxygen (O_2) and Nitrogen (N_2) γ is about 1.4

For Triatomic gasses such as Carbon Dioxide (CO_2) γ is about 1.3

Enthalpy of a gas

Enthalpy is defined as the sum of internal energy and flow energy H = U + pV

$$H = m \times c_v \times T + m \times R \times T$$

$$H = m \times T(c_v + R)$$

but $c_p = c_v + R$

Therefore $$H = m \times c_p \times T$$

REVERSIBILITY

When a system changes state in such a way that the state point at any instant can be located on a process diagram, then the process is considered to be reversible.
A reversible process between any two states can therefore be drawn as a solid line on a property diagram.
This can be summarised in the following statement.
If a fluid is subject to a reversible process, both the fluid and its surroundings can always be returned to their original state.

In real processes, the intermediate states of the fluid cannot be determined thus a continuous path cannot be traced on a property diagram.
These real processes are called irreversible and are drawn on a property diagram as a dotted line between the end states to indicate that the intermediate states cannot be determined.
To allow us to consider a reversible process several criteria must met.

(a) The process must be frictionless.
The fluid itself must have no internal friction and there must be no mechanical friction (e.g. between cylinder and piston).

(b) The difference in pressure between the fluid and its surroundings during the process must be infinitely small.
This means that the process must take place infinitely slowly, since the force to accelerate the boundaries of the system is infinitely small.

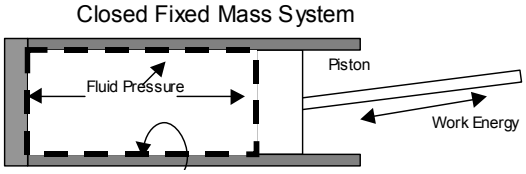
(c) The difference in temperature between the fluid and its surroundings during the process must be infinitely small.
This means that the heat supplied or rejected to or from the fluid must be transferred infinitely slowly.

The above criteria show that in practice no process is truly reversible.
However, they all consider the fluid and the surroundings so if we draw the system boundary inside the surroundings we can concentrate on the fluid itself and introduce the concept of internal reversibility.
In an internally reversible process, the surroundings are ignored and can never be restored to their original state, but the fluid itself is always in an equilibrium state and the process path can be retraced to the initial state.

In general,
Non flow processes such as those occurring in cylinders with a reciprocating piston are assumed to be internally reversible.
Flow processes such as those occurring in rotary machinery (e.g. turbines) are known to be irreversible due to the high degree of turbulence and scrubbing of the fluid

REVERSIBLE WORK

We should be able to recall from earlier studies that work is obtained when a force acts over a particular distance and that force is the product of pressure and area.

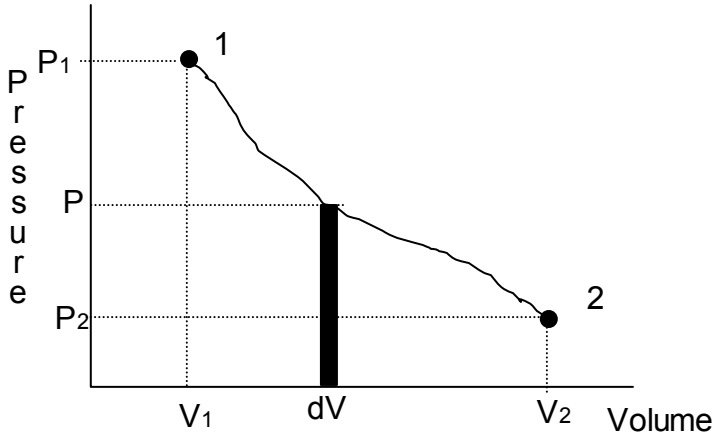


If we consider a piston in a cylinder as shown above then the work done by the fluid is
Force times distance.

$$\text{Work Done by Fluid} = \text{Fluid Pressure} \times \text{Piston area} \times \text{length of stroke}$$

Area times length is a volume therefore the work done can be written as pressure times volume, since the pressure and volume are continuously changing during the cycle and our equations only allow us to obtain particular points we must calculate the pressure for small changes in volume and determine the respective small change in work transfer we can then sum all these small changes.
These changes in pressure and volume can be plotted on a p-V diagram the area of which is given by the product of p and V.
Hence the area of a p-V diagram represents work transfer and is the summation of the element strips p x dV shown in the diagram below.

This is written mathematically as $\text{Work Done by Fluid} = \int_1^2 pdv$



This is only true if the available force has not been used to accelerate the boundary or to overcome friction.
In other words it is assumed that reversibility criteria “a” and “b” apply.

Reversible Non-Flow Processes

Constant Volume or Isochoric Process

In this process the working substance is held in a rigid container such as an air bottle. Since the shell or boundary of this bottle is fixed then the only work transfer that can take place is a work input due to the fluid being stirred such as running a centrifugal pump with the discharge valve shut, since this should be avoided and is of no real use in the context of thermodynamic cycles, it is usually assumed that constant volume means no work transfer.
This can be reinforced by the p/V diagram shown below which has no area.

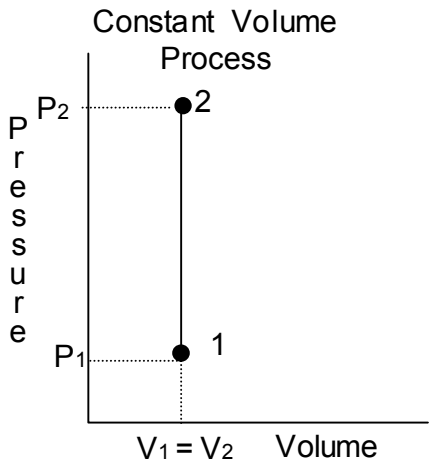
Applying the NFEE

$Q = W + (U_2 - U_1)$ W=0

$Q = (U_2 - U_1)$

$Q = m \times c_v \times (T_2 - T_1)$

Thus all the heat supplied in a constant volume process goes to increasing the internal energy of the fluid.



Constant Pressure or Isobaric Process

In the constant volume process when heat is applied the pressure rises, so to maintain the pressure constant the boundary must move against an external resistance.
From the previous definition of work

Work Done by Fluid $= \int_1^2 p\,dv$

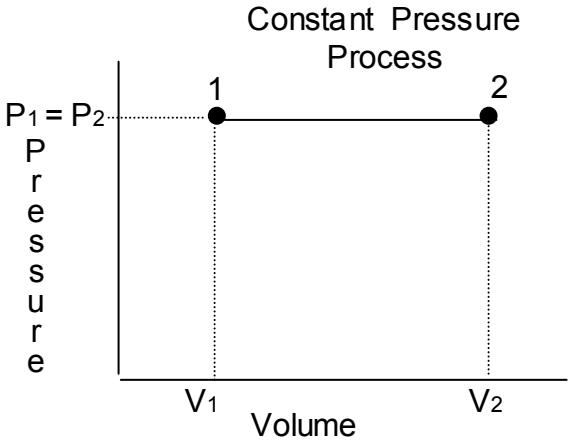
Work Done by Fluid $= p(V_2 - V_1)$

Apply the NFEE

$Q = W + (U_2 - U_1)$

$Q = p(V_2 - V_1) + (U_2 - U_1)$

$Q = (U_2 + pV_2) - (U_1 + pV_1)$



But $H = U + pV$

$$Q = H_2 - H_1 = m \times c_p \times [T_2 - T_1]$$

Constant Temperature or Isothermal Process

When a fluid expands from a high pressure to low pressure in a closed system there is a tendency for the temperature to fall, therefore to keep this constant, heat must be continuously added.

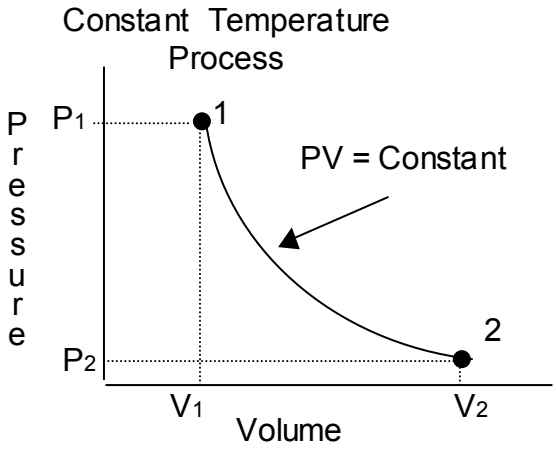
Similarly in an isothermal compression heat must be continuously removed

From the characteristic equation

$$p \times V = m \times R \times T$$

If the temperature is constant then

$$p_1 \times V_1 = p_2 \times V_2 = cons\tan t$$



$$\text{Work Done by Fluid} = \int_1^2 p\,dv$$

but $p = \dfrac{Cons\tan t}{V}$

substituting this value in the work equation gives

$$\text{Work Done by Fluid} = \text{constant}\int_1^2 \frac{dv}{v} = cons\tan t\left(Lnv\right)_{v_1}^{v_2} = cons\tan t \times Ln\frac{v_2}{v_1}$$

The constant is pV and can be at either state point 1 or state point 2 hence the work transfer is

$$\text{Work Done by Fluid} = p_1 V_1 \text{Ln}\frac{v_2}{v_1}$$

This can be modified by substituting pressure for volume and mRT for pV to give

$$W = p_1 V_1 \text{Ln}\frac{p_1}{p_2} \quad \text{or} \quad W = mRT_1 \text{Ln}\frac{p_1}{p_2} \quad \text{or} \quad W = mRT_1 \text{Ln}\frac{v_2}{v_1}$$

Since $U_2 - U_1 = m \times c_v \times \left(T_2 - T_1\right)$ and there is no change in temperature then there is no change in internal energy and the heat flow is the same as the work flow.

Q=W

It should be remembered that this only applies to a perfect gas

Reversible Adiabatic Process

In an adiabatic process no heat is transferred to or from the fluid, a sudden expansion or compression of a gas is initially adiabatic because there is no time for the heat to enter or leave the gas.

If $Q = 0$ then $W = (U_2 - U_1)$

while such a process can be reversible or irreversible, only the reversible process will be considered here.

When the property of Entropy is introduced later it will be shown that in a reversible adiabatic process the entropy remains constant, hence such a process is termed an Isentropic process.

For a perfect gas the law controlling the relationship between the pressure and volume for an adiabatic process can be derived from the NFEE as follows

For a reversible adiabatic process $Q = 0$ from the first law $Q = W + (U_2 - U_1)$

Therefore $\delta Q = \delta U + \delta W$ now $\delta W = p\delta V$ and $\delta U = c_v \delta T$

the equation becomes $0 = c_v \delta T + p\delta V$ to eliminate δT

Consider a unit mass of gas, the characteristic equation is $pV = RT$

Since both pressure and volume may change the characteristic equation

becomes $p\delta V + V\delta p = R\delta T$

Then $\delta T = \dfrac{p\delta V + V\delta p}{R}$ substitute in the NFEE

$$0 = c_v \frac{p\delta V + V\delta p}{R} + p\delta V$$

or $0 = c_v (p\delta V + V\delta p) + Rp\delta V$

now $R = c_p - c_v$

therefore $0 = c_v (p\delta V + V\delta p) + (c_p - c_v) p\delta V$

hence $0 = c_v V\delta p + c_p p\delta V$

or $0 = V\delta p + \dfrac{c_p}{c_v} p\delta V$

but $\gamma = \dfrac{c_p}{c_v}$

Therfore $0 = V\delta p + \gamma p\delta V$

so $$0 = \frac{\delta p}{p} + \gamma \frac{\delta V}{V}$$

integrating gives $$0 = \int \frac{dp}{p} + \gamma \int \frac{dV}{V}$$

Which gives $\log_e p + \gamma \log_e V = A$ where A is a constant

Therefore $pV^{\gamma} = e^{A}$ but e^{A} is a constant

Therefore $pV^{\gamma} = cons\tan t$

This then is the law of a reversible adiabatic process, do not worry about the maths as you would not be required to show this proof.

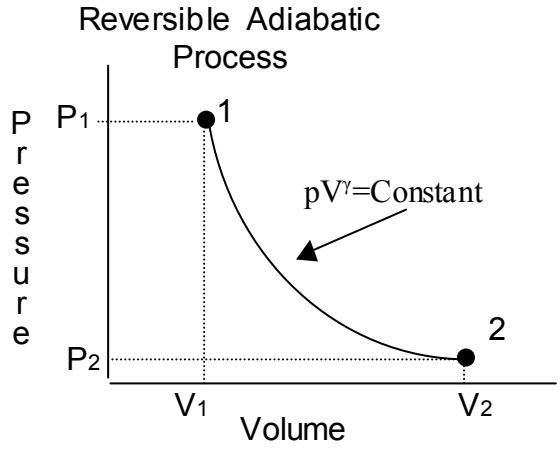
The heat flow for this process is obtained from the NFEE while the work is obtained from the area under the pV diagram.

$Q = W + (U_2 - U_1)$

Work Done by Fluid $= \int^{2} \mathrm{pdv}$

$\mathrm{p} = \dfrac{\text{constant}}{\mathrm{V}^{\gamma}}$

Work Done by Fluid $= \int^{2} cons\tan t \dfrac{\mathrm{dv}}{\mathrm{V}^{\gamma}}$



Work Done by Fluid $= \text{constant} \int_{V_1}^{V_2} \dfrac{\mathrm{dv}}{\mathrm{V}^{\gamma}} = c\left[\dfrac{V^{1-\gamma}}{1-\gamma}\right]_{V_1}^{V_2}$

Work Done by Fluid $= \dfrac{\mathrm{c}}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$ now $\mathrm{c} = \mathrm{p}_1 V_1^{\gamma} = p_2 V_2^{\gamma}$

and $\mathrm{p}_1 V_1^{\gamma} \times V_1^{1-\gamma} = p_1 V_1$ and $\mathrm{p}_2 V_2^{\gamma} \times V_2^{1-\gamma} = p_2 V_2$

therefore Work Done by Fluid $= \dfrac{1}{\gamma - 1}(\mathrm{p}_2 V_2 - p_1 V_1) = \dfrac{\mathrm{p}_1 V_1 - p_2 V_2}{\gamma - 1}$

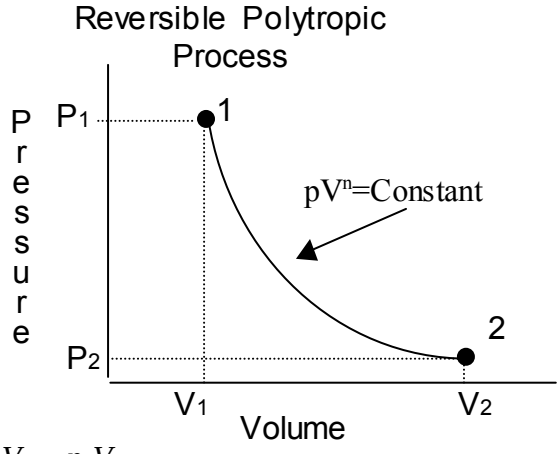
Polytropic Processes

It has been found that in practice many processes follow the law pV^n= constant, where "n" is a constant which describes the curve of the pv diagram.

In a polytropic process the index "n" depends only on the heat and work quantities during the process and consequently there could be an infinate number of values for this index.

The four processes already examined are considered special cases of the polytropic process for a perfect gas.

For the general case when the polytropic index is "n" the diagram is the same as for the adiabatic process and since the pV relationship is identical the equation for work is identical



$$\text{Work Done by Fluid} = \int_1^2 p\,dv$$

$$\text{Work Done by Fluid} = \int_1^2 cons\tan t\,\frac{dv}{V^n}$$

$$\text{Work Done by Fluid} = \frac{1}{n-1}\left(p_2V_2 - p_1V_1\right) = \frac{p_1V_1 - p_2V_2}{n-1}$$

The heat flow can be obtained from the NFEE,

$$Q = W + \left(U_2 - U_1\right)$$

$$W = \frac{p_1V_1 - p_2V_2}{n-1} = \frac{mR\left(T_1 - T_2\right)}{n-1} \qquad U_2 - U_1 = m \times c_v \times \left(T_2 - T_1\right)$$

$$Q = \frac{mR\left(T_1 - T_2\right)}{n-1} + mc_v\left(T_2 - T_1\right) \quad \text{Therefore} \quad Q = \frac{mR\left(T_1 - T_2\right)}{n-1} - mc_v\left(T_1 - T_2\right)$$

If we substitute $c_v = \frac{R}{\gamma - 1}$ we get $Q = \frac{mR\left(T_1 - T_2\right)}{n-1} - \frac{mR\left(T_1 - T_2\right)}{\gamma - 1}$

$$Q = mR\left(T_1 - T_2\right)\left(\frac{1}{n-1} - \frac{1}{\gamma - 1}\right) \quad \text{This gives}$$

$$Q = mR\left(T_1 - T_2\right)\left(\frac{(\gamma - 1) - (n-1)}{(\gamma - 1)(n-1)}\right)$$

$$Q = mR\left(T_1 - T_2\right)\left(\frac{\gamma - n}{(\gamma - 1)(n-1)}\right) \quad \text{This gives} \quad Q = \left(\frac{mR\left(T_1 - T_2\right)}{(n-1)}\right)\left(\frac{\gamma - n}{(\gamma - 1)}\right)$$

$$Q = \left(\frac{\gamma - n}{(\gamma - 1)}\right) \times \text{Work}$$

You should be aware that in most questions on non flow polytropic processes the adiabatic index γ will be unknown, therefore the heat can be calculated using the NFEE.

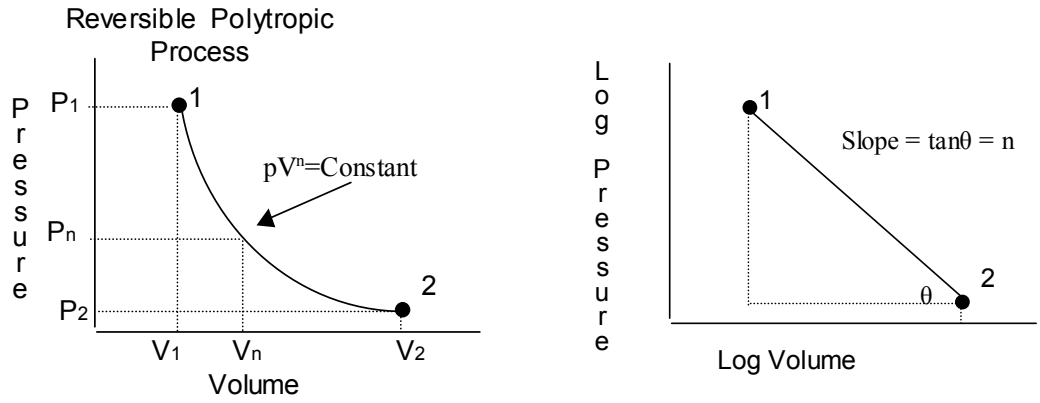
The Polytropic Index "n"

Since the index "n" describes the expansion or compression process, then it would be reasonable to assume that its value could be obtained from the pV diagram.
If the pV diagram is plotted on a log scale the result would be a straight line if the curve was of the form pV^n= constant.

$$pV^n = c \qquad \text{Take logs} \qquad \log p + n\log V = \log c$$

$$\log p = -n\log V + \log c$$

this is of the form $y = mx + c$ hence we have a straight line slope of -n



The index could also be derived in a similar manner if two values of pressure and volume were known.

$$p_1V_1^n = p_2V_2^n \qquad \frac{p_1}{p_2} = \left(\frac{V_2}{V_1}\right)^n \qquad \log\frac{p_1}{p_2} = n\log\frac{V_2}{V_1}\left(\frac{V_2}{V_1}\right)$$

$$\frac{\log\dfrac{p_1}{p_2}}{\log\dfrac{V_2}{V_1}} = n$$

Other useful relationships

We have seen that $p\,V^n = \text{constant}$ and that $\frac{p\,V}{T} = \text{Constant}$,we can now combine these relationships to form further relationships which you must be able to recall and use at will.

From $\frac{p_2V_2}{T_2} = \frac{p_1V_1}{T_1}$ $\qquad$ $\frac{T_2}{T_1} = \frac{p_2V_2}{p_1V_1}$

From $p_1V_1^{\gamma} = p_2V_2^{\gamma}$ we obtain $\qquad$ $\frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^n$ we can use this to eliminate pressures in the above equation to give $\qquad$ $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^n\left(\frac{V_2}{V_1}\right)$

rearranging gives $\qquad$ $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^n\left(\frac{V_1}{V_2}\right)^{-1}$

Hence $\qquad$ $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1}$

We can now do the same thing to eliminate volumes

$p_1V_1^{\gamma} = p_2V_2^{\gamma}$ gives $\frac{V_2}{V_1} = \left(\frac{p_1}{p_2}\right)^{\frac{1}{n}}$ $\qquad$ rearranging gives $\frac{V_2}{V_1} = \left(\frac{p_2}{p_1}\right)^{-\frac{1}{n}}$

substitute this into $\frac{T_2}{T_1} = \frac{p_2V_2}{p_1V_1}$ gives $\qquad$ $\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)\left(\frac{p_2}{p_1}\right)^{-\frac{1}{n}}$

multiplying out gives $\qquad$ $\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}$

these can be combined to give $\qquad$ $\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} = \left(\frac{V_1}{V_2}\right)^{n-1}$

This equation is very useful and should be remembered

Since "γ" is a particular value of "n" Then the equation becomes

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Process Summary

Constant pressure process

When n = 0 Pv^0 = constant, i.e. p = constant

Constant volume process

When n = ∞, $pv\infty$ = constant or $p^{1/}\infty\, v$ = constant, i.e. v = constant

Isothermal process

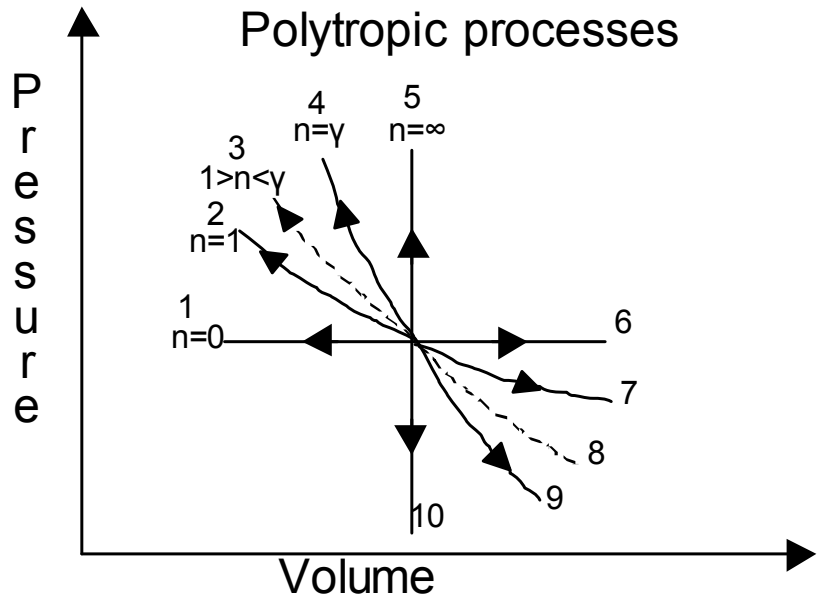
When n = 1 pv = constant, i.e. T = constant

Reversible Adiabatic process

When n = γ Pv^{γ} = constant, i.e. Reversible Adiabatic

Polytropic Process

This is any other process apart from the four special cases, a particular value when "n" is greater than one but less than γ is shown as curve 3 on the diagram below but the value could be anywhere within the compression and expansion quadrants of the diagram



Curve 1 is constant pressure cooling, Curve 6 is constant pressure heating both (n = 0)
Curve 2 is isothermal compression, Curve 7 is isothermal expansion both (n = 1)
Curve 3 is a reversible polytropic compression Curve 8 Expansion both (1<n>γ)
Curve 4 reversible adiabatic compression Curve 9 reversible adiabatic expansion (n=γ)
Curve 5 is constant volume heating, Curve 10 is constant volume cooling (n = :)
Note that, since γ, is always greater than one, then curve 4 must lie between curves 2 and 5; similarly, Curve 9 must lie between curves 7 and 10.
For a vapour a generalisation such as the above is not possible.
Tables must be used to find the properties at the end states.

Expansion and Compression of Gasses Summary of equations					
	Heating at Constant volume	Heating at Constant Pressure	Polytropic Process $pV^n=C$	Isothermal Process $pV=C$	Adiabatic process $pV^\gamma=C$
Change of Internal energy $U_2 - U_1$	**$mCv(T_2-T_1)$**	$mCv(T_2-T_1)$	$mCv(T_2-T_1)$	$U_2-U_1=0$ Since $T_2=T_1$	$mCv(T_2-T_1)$
Work Done W	Since no movement **$W=0$**	$P(V_2-V_1)$	$\frac{P_1V_1-P_2V_2}{n-1}$	$P_1V_1 \text{ Ln} \frac{V_2}{V_1}$	$\frac{P_1V_1-P_2V_2}{\gamma-1}$
Heat Exchange $Q=W+(U_2 - U_1)$	**$mCv(T_2-T_1)$**	$P(V_2-V_1) + mCv(T_2-T_1)$	$\frac{\gamma-n}{\gamma-1}$ **x** Work done	$P_1V_1 \text{ Ln} \frac{V_2}{V_1}$	0

Constant Volume process = Isochoric. Constant Pressure = Isobaric. Constant temperature = Isothermal

Polytropic Process = No property remains constant. The heat transfer is equal to the sum of the internal energy plus the work transfer. It cannot be evaluated directly

Adiabatic Process = The heat transfer to or from the surroundings is zero. During a reversible adiabatic process in a closed system, the heat transfer is zero and the work transfer is equal to the change of internal energy

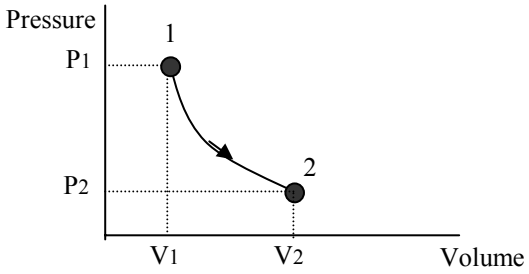
Non flow process examples

1 $0.03m^3$ of gas, initially at a pressure of 1.4 MN/m^2 and temperature 150°C, is expanded in a closed system to a volume of 0.2 m^3 according to the law $pV^{1.2} = C$.
For the gas R = 640 J/kgK and c_p= 2000 J/kgK
Calculate

a) The mass of the gas
b) The change of internal energy
c) The heat flow through the cylinder walls sating its direction.

As with all examples a diagram is essential to picture the process. In this case a p-V will be required a table to collate the values will also be usefull.

	P	V	T
1	14 bar	$0.03m^3$	423K
2		$0.2m^3$	



Since we have pV and T at point 1 the mass can be found using the equation

$$p_1V_1 = mRT_1$$

$$mass = \frac{p_1V_1}{RT_1} = \frac{14\times10^5\times0.03}{640\times423} = 0.155\,kg$$

For the internal energy we need the temperature and since we have the volume ratio we can
use the polytropic relationship

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{n-1} = 423\left(\frac{0.03}{0.2}\right)^{1.2-1} = 289\,K$$

The change of internal energy can now be found using the following

$$U_2 - U_1 = mc_v(T_2 - T_1)$$

We have been given c_p and R so c_v is found from

$$c_c = c_p - R = 2000 - 640 = 1360\ \frac{J}{kgK}$$

$$U_2 - U_1 = 0.155 \times 1360\left(289 - 423\right)$$

$$U_2 - U_1 = -28.24\,kJ$$

Since this is an expansion the temperature has fallen giving a drop in internal energy
The heat flow is obtained from the Non Flow Energy Equation

$$Q = W + \left(U_2 - U_1\right)$$

But we need the work transfer first

We can calculate the work transfer for the polytropic process using

$$W = \frac{p_1V_1 - p_2V_2}{n-1}$$

However since we have already have the temperatures so we can use the equation

$$p\,V = mRT$$

To modify the equation for work to give $W = \dfrac{mR\left(T_1 - T_2\right)}{n-1}$

$$W = \frac{0.155 \times 640\left(423 - 289\right)}{1.2 - 1} = 66.46\,kJ$$

This gives a work transfer of 66.46 kJ out of the system, but the internal energy has only fallen by 28.24 kJ so the extra energy must have come from somewhere and the only option left is a heat transfer, hence

$$Q = W + \left(U_2 - U_1\right)$$

$$Q = 66.46 + \left(-28.24\right) = 38.22\,kJ$$

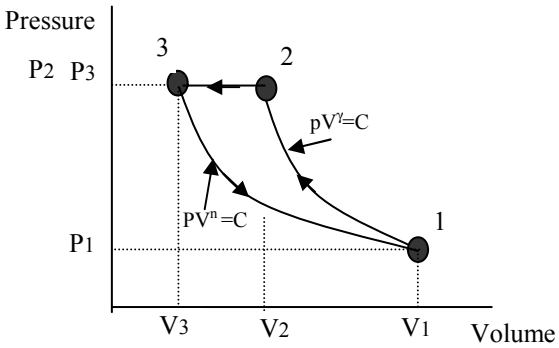
Since the process 1 to 2 is an expansion the work transfer is positive, the internal energy has fallen (negative) and this has provided some of the work energy, the remaining work transfer can only be the result of heat transfer into the system

2 $1m^3$ of air at 110 kN/m^2 and 15°C is compressed adiabatically in a close system to one quarter of its original volume.
The air is then cooled at constant pressure until its temperature is 15°C.
The air is then expanded back to its original condition.
For air $\gamma = 1.4$
Calculate

a) The temperature and pressure at the end of compression.
b) The volume at the end of heat rejection.
c) The work transfer during compression and constant pressure cooling.
d) The polytropic exponent of the expansion process.

We must first draw a p-V diagram to picture the process and again a table is useful to collate the data as it is calculated.

	P bar	V m^3	T K
1	1.1	1	288
2	*7.66*	0.25	*501*
3	*7.66*	*0.1437*	288



Using basic relationships we can find T_2, P_2 and V_3.

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 288\left(\frac{1}{0.25}\right)^{1.4-1} = 501\,K$$

$$p_1V_1^{\gamma} = p_2V_2^{\gamma} \qquad p_2 = p_1\left(\frac{V_1}{V_2}\right)^{\gamma} = 1.1\left(\frac{1}{0.25}\right)^{1.4} = 7.66\,bar$$

$$\frac{p_2V_2}{T_2} = \frac{p_3V_3}{T_3} \qquad V_3 = V_2\left(\frac{T_3}{T_2}\right) = 0.25\left(\frac{288}{501}\right) = 0.1437\,m^3$$

Work transfer 1 to 3 is given by the adiabatic process and the constant volume process.

$$W = \frac{p_1V_1 - p_2V_2}{\gamma - 1} + p_2(V_3 - V_2)$$

$$W = \frac{1.1\times10^5\times1 - 7.66\times10^5\times0.25}{1.4-1} + \left[7.66\times10^5(0.1437 - 0.25)\right]$$

$$W = -203.27 + [-81.425]$$

$$W = -285.175\,kJ$$

The work transfer is negative for the compression process as expected

Using the equation $p_3 V_3^{\,n} = p_1 V_1^{\,n}$ for the expansion process re-arranging and taking logs of both side gives

$$\log\left(\frac{p_3}{p_1}\right) = n\log\left(\frac{V_1}{V_3}\right) \qquad \log\left(\frac{7.66}{1.1}\right) = n\log\left(\frac{1}{0.11437}\right)$$

From this the index of expansion is found to be "1" which is expected since this was an isothermal process.

All examples on non flow processes follow the same pattern,

- Draw the process on a pV diagram,
- Identify the data that has been given,
- Calculate the required data,
- Answer the question using the relevant equation.

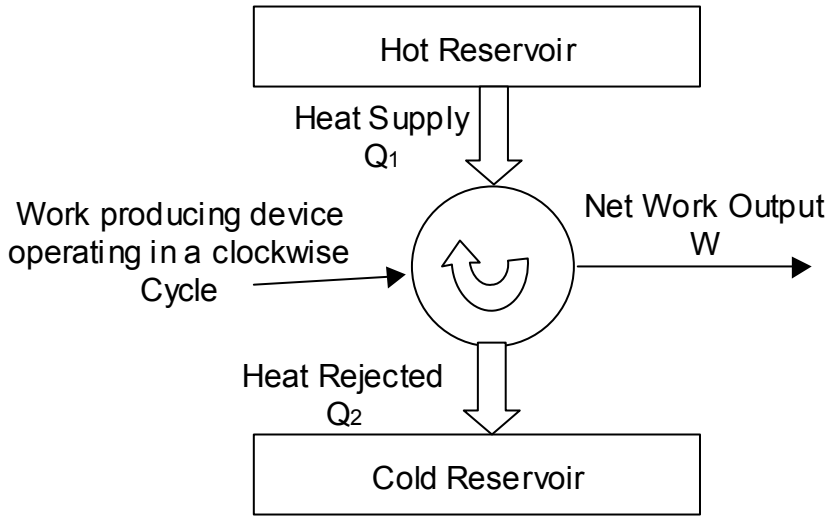
You may have to vary the equations depending what information is given but remember you can not make up your own.

THE SECOND LAW OF THERMODYNAMICS

The First Law based on the conservation of energy says that work cannot be produced during a cycle without some supply of heat.
It basically says that what goes into a system either stays there or comes out again, another way of saying this is that the net work output can never be greater than the heat supplied, there is no concept of how effective the energy transfer has been therfore the efficiency of the transfer could be 100%.

The Second Law is a statement of the fact that some heat must always be rejected during the cycle, and therefore the net work output must always be less than the heat supply so that the cycle efficiency is always less than 100%.

The second law can be shown on a diagram considered to be a schematic diagram of a heat engine cycle and is shown below

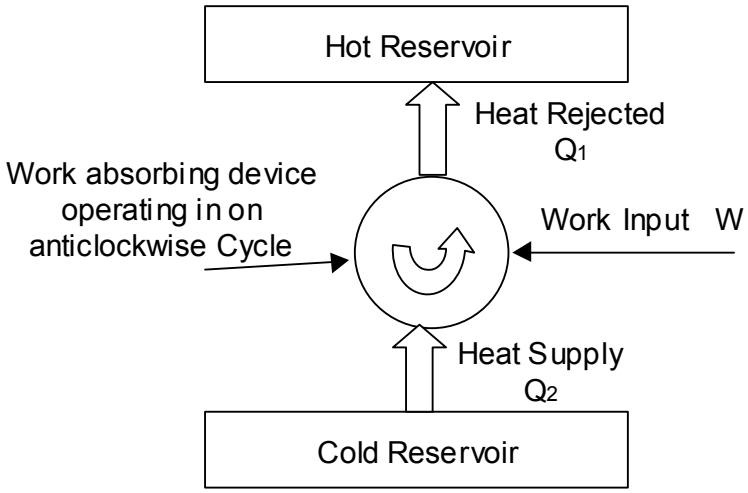


Thus the Second Law implies that if a system is to undergo a cycle and produce work, it must operate between at least two reservoirs of different temperature, however small this difference may be.
Thus the second law applied to a work producing heat engine is given by

Net Work = Heat Supplied - Heat rejected

$$W = Q_1 - Q_2$$

Other cycles can be devised during which the net work is done on the system while a net amount of heat is rejected. In this case the quantities are of opposite sign, i.e. Q_1, is the heat rejected, Q_2 is the heat supplied, and W is the net work done on the system. Such a cycle would be a vapour compression refrigeration plant.



$$Q_1 = W + Q_2$$

An important consequence of the Second Law is that, work is a more valuable form of energy transfer than heat:

Heat can never be transformed continuously and completely into work, whereas work can always be transformed continuously and completely into heat, and, if properly used, can even result in a supply of heat which is greater than the quantity of work expended such as the refrigeration cycle used as a heat pump.
These cycles are dealt with in detail in further sections

The Second Law cannot be deduced from the First but like the First Law, its validity rests upon the fact that neither the law, nor any of its consequences, have ever been disproved by experience.

SUMMARY
The implications of the second law of thermodynamics are as follows:

- Heat transfer will only occur and will always naturally occur when a temperature difference exists and always naturally down the temperature gradient
- If, due to temperature difference, there is heat transfer availability then work transfer is always possible. However, there is always some heat transfer loss.
- Temperature can be elevated but not without the expenditure of external energy. Elevation of temperature cannot occur unaided.
- There is no possibility of work transfer if only a single heat energy source or reservoir at a fixed temperature is available.
- If work transfer is supplied to a system, it can all be transformed in heat energy.
- No contradiction of the second law of thermodynamics has been demonstrated.

Entropy

The term and concept of entropy was introduced in the nineteenth century by Clausius.

It is a property of a system and is given the symbol "S" Uppercase referring to the entropy of a system in J/K, or lower case "s" referring to the specific entropy J/kg K.

It is used as a means of providing quick solutions to problems dealing with the adaiabatic expansion and compression of gasses and vapours, in these cases it is the change of entropy that we are interested in rather than a particular value.

Many text books have been written on this topic which is difficult to visualise, however a common explanation is to consider it as a measure of the randomness of a system or a measure of the disorder in the microstate.

The molecules of a system may be distributed more or less at random in a system, a liquid being more random than a crystal and consequently has a higher entropy, the randomness of distribution concerns the extent to which the properties of a very small portion, a microstate, of a large system deviate from the average for the whole system.

Thus a third law of thermodynamics has been developed:

"At the absolute zero of temperature the entropy of a perfect crystal of a substance is zero."

Entropy can also be considered as a measure of how efficiently energy can be converted into work.

In all real processes the entropy of the system increases and we are able to extract less work from the system than would have been the case if the same process had been made reversibly at constant entropy.

Thus associated with the increase of entropy is the "loss" of some energy which could have been used for work.

The energy does not vanish as this would violate the first law, it becomes degraded in that it is less useful for work.

The increase of entropy is an irreversible change and is thus a measure of the extent to which the energy becomes degraded in the change.

So in order to extract the maximum amount of useful energy from a system all changes must be performed in a reversible manner.

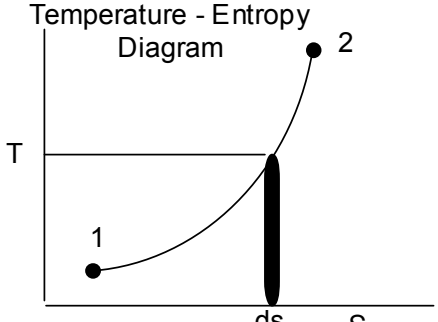
Determination of Entropy values

The change in entropy can be found from a knowledge of the quantity of heat transferred only during a reversible non flow process.

Since no real process is reversible, values of entropy cannot be found from measurements of heat and temperature in direct experiments, however it is a property and can thus be expressed in terms of other properties in real processes.

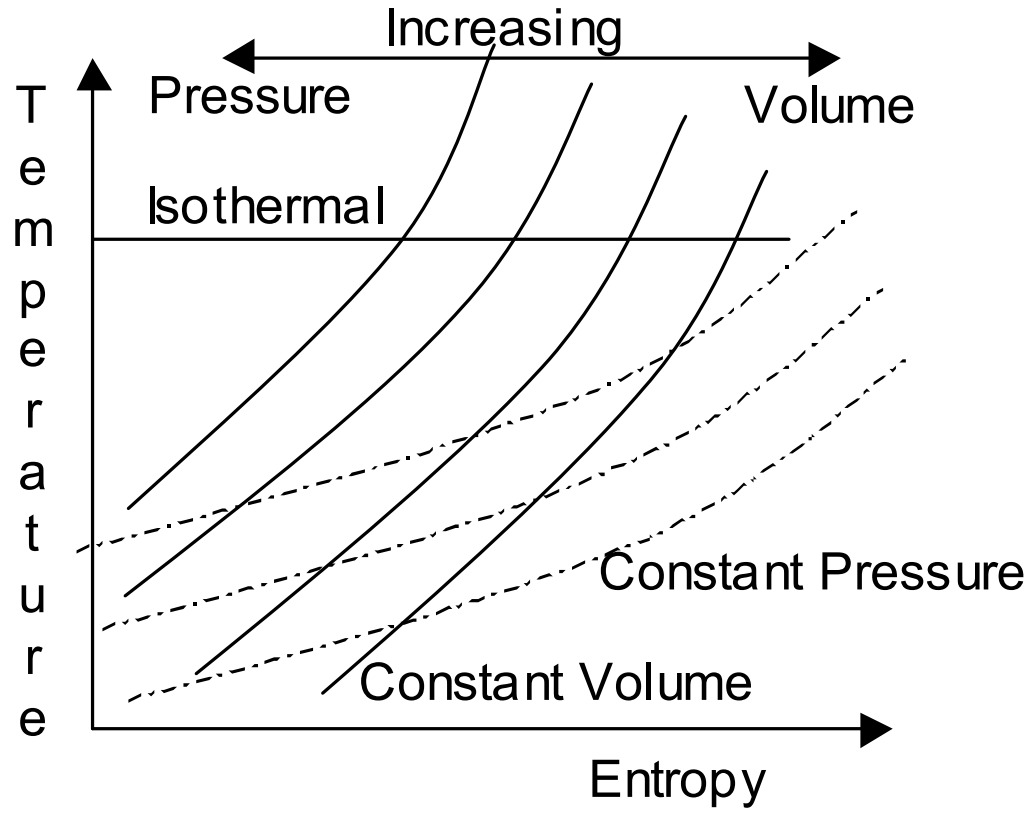
Temperature / Entropy Diagrams are a useful way of illustrating processes and cycles, the area under a T-s diagram represents heat so the area is given as

$$Q = \int_1^2 Tds \quad \text{from which} \quad ds = \frac{dQ}{T}$$



Since it is the change in entropy that we require, “real” fluid values of specific entropy can be obtained from tables.
However for a gas we must calculate them so we need some information regarding the process involved during the entropy change.

A temperature entropy diagram for a gas has lines of constant pressure and lines of constant volume, since we know the equations for heat flow during these processes we can evaluate the equation.



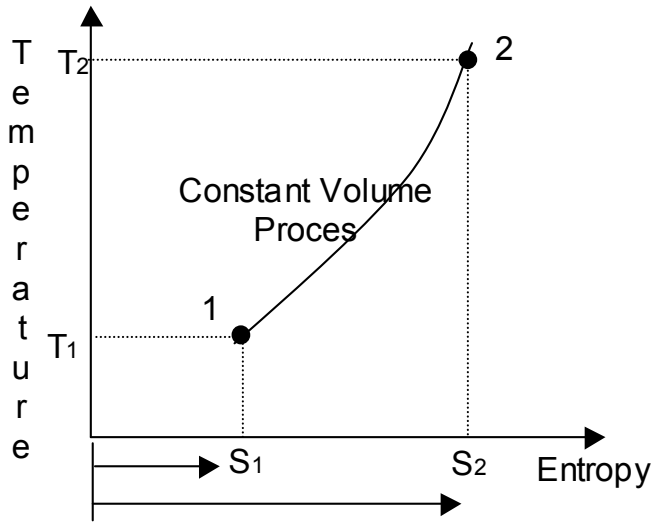
The temperature entropy diagram for a perfect gads consist of three main lines

Isothermal lines which are horizontal
Isobaric lines Constant pressure shown chain dotted above
Isochoric lines Constant volume shown solid above

Note that the volume lines are steeper than the pressure lines and that volumes increase towards the right and pressure increases towards the left.
Temperature is increasing upwards and entropy increases towards the right.

Since we have lines of constant volume, pressure and temperature on this diagram the integral can be evaluated for these processes and the change in entropy determined

Entropy Change Constant Volume



For a constant volume process $Q = m \times c_v \times (T_2 - T_1)$ therefore $dQ = m \times c_v \times dT$

Substituting this value in the equation $\mathrm{ds} = \frac{\mathrm{dQ}}{\mathrm{T}}$ or $S_2 - S_1 = \int_1^2 \frac{\mathrm{dQ}}{\mathrm{T}}$

gives $S_2 - S_1 = \int_1^2 \frac{\mathrm{m} \times \mathrm{c_v} \times dT}{\mathrm{T}}$ and hence $S_2 - S_1 = \mathrm{m} \times \mathrm{c_v} \int_1^2 \frac{dT}{\mathrm{T}}$

Note that the mass is included in this equation and is a constant, it could be left out and the specific entropy values would be obtained.
The symbol would then be lower case s.
Integrating 1/T gives a result similar to that for isothermal work and result in the following equation

$$S_2 - S_1 = \mathrm{m} \times \mathrm{c_v} \times Ln \frac{T_2}{T_1}$$

Entropy Change Constant Pressure
In this case the process line on the diagram is less steep but the procedure is identical with a similar result

$$Q = m \times c_p \times (T_2 - T_1) \qquad dQ = m \times c_p \times dT$$

$$S_2 - S_1 = \mathrm{m} \times \mathrm{c_p} \times Ln \frac{T_2}{T_1}$$

Since c_p is greater than c_v the entropy change between the same temperatures will be greater for a constant pressure process than a constant volume process.

Entropy Change Isothermal Process

This is determined in exactly the same way only in an isothermal process Q=W

Therefore $W = \int_1^2 \frac{dv}{v}$ substituting this in the relevant equation with T constant gives $S_2 - S_1 = \frac{pV}{T}\int_1^2 \frac{dv}{v}$ but $\frac{pV}{T} = m \times R$ and following the same integration as for isothermal work we have

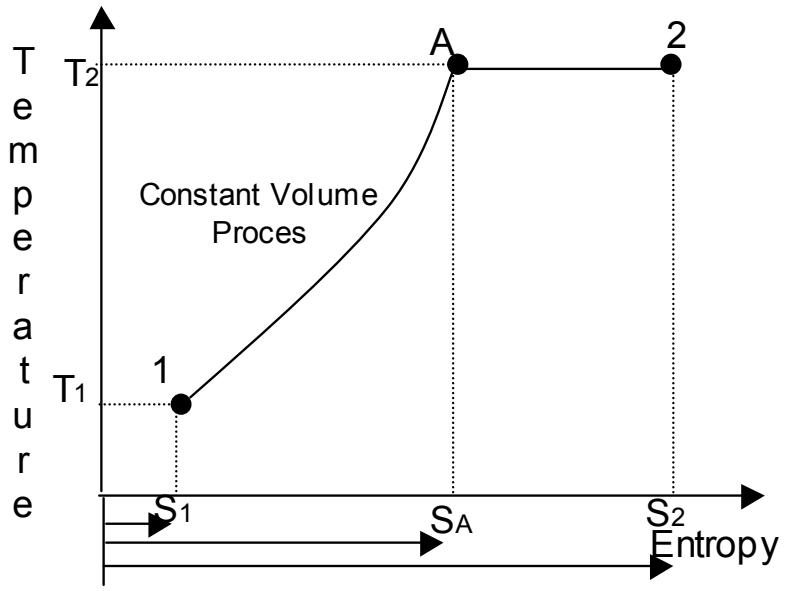
$$S_2 - S_1 = m \times R \times Ln\frac{V_2}{V_1} \quad \text{or} \quad S_2 - S_1 = m \times R \times Ln\frac{p_1}{p_2}$$

Entropy Change Polytropic Process

In this pressure, volume and temperature change throughout the process which makes it difficult to evaluate the integral.

However it is the end states that dictate the entropy change not the process so it does not matter how we get there.

So a polytropic process can be replaced by any two other processes providing we obey a couple of rules.



In this case we can calculate the change by a constant volume process between the Temperatures T_2 and T_1, followed by an isothermal process.

The isothermal process must be between the volumes V_1 and V_2 because the slope of this line is steeper than the pressure line hence the position of V_1 T_2 on the diagram will not be the same as p_1 T_2.

In actual practice which ever process that is used for the change between the temperature will dictate the Ln ratio for the isothermal process.

In solving these problems it is important to get the diagram correct and be guided by the direction of the process, because the numeric value of Ln for a particular ratio is

the same for the inverse apart from the sign change, hence you could become confused with addition and subtraction of negative quantities

Reversible Flow Processes

Although this section deals with non flow process we must consider flow processes which in practice are usually highly irreversible but it is sometimes convenient to assume that a flow process is reversible in order to provide an ideal comparison. Imagine you were acting as an observer and travelled with the flowing fluid you would appear to see a change in thermodynamic properties as in a non-flow process. Such would be the case in a reversible adiabatic process for a perfect gas, you would appear to see a process pv^{γ} = constant taking place, but the work input would not be given by $\int_1^2 pdv$, or by the change in internal energy $W = (U_2 - U_1)$

Some work is done by virtue of the forces acting between the moving gas and its surroundings.

For example, for a reversible adiabatic flow process for a perfect gas, from the flow equation

$$\frac{c_1^2}{2} + h_{11} + Q = \frac{c_2^2}{2} + h_2 + W$$

Then since Q = 0

$$-W = \frac{c_2^2 - c_1^2}{2} + h_2 - h_1$$

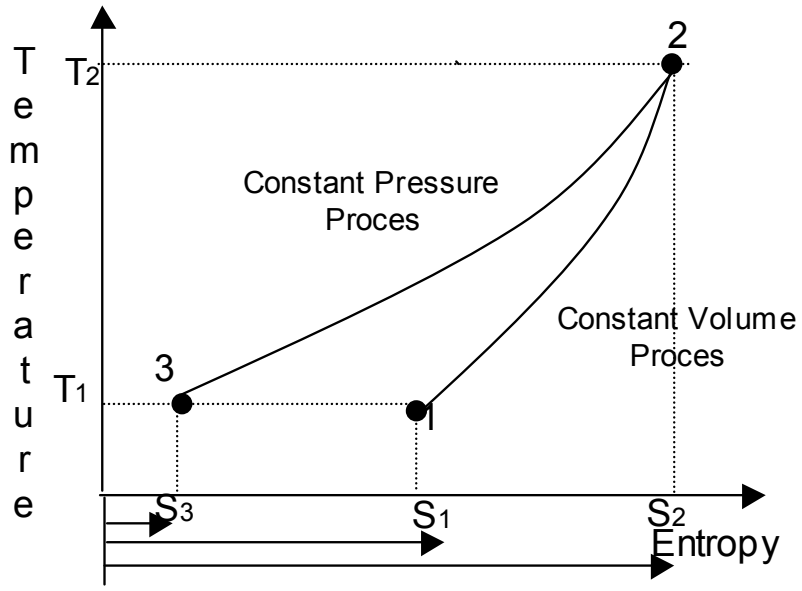
Also, since the process is assumed to be reversible, then for a perfect gas, pv^{γ} = constant. This equation can be used to fix the end states. Note that even if the kinetic energy terms are negligibly small the work input in a reversible adiabatic flow process between two states is not equal to the work input in a reversible adiabatic non-flow process between the same states as given by equation

This concept will be used later when we look at gas turbine cycles.

Entropy Example 1
In a reversible process 0.3m^3 of Nitrogen at a pressure of 1.2 bar and temperature of 25°C is heated at constant volume to a pressure of 4.8.bar.
It is then cooled at constant pressure back to the original temperature.
For Nitrogen; R=297 J/kgK, c_p=1040 J/kgK

a) Sketch the process on a Temperature- Entropy diagram.
b) Calculate
   i) The net flow of heat during the process
   ii) The net change of entropy.

Remember this is a perfect gas and on the T-s diagram the volume lines would be steeper than the pressure lines.



We could start by calculating the mass since we need heat and entropy rather than values based on unit mass.
Using the equation of state gives

$$\mathbf{m} = \frac{\mathbf{p_1 V_1}}{\mathbf{R T_1}} = \frac{1.2\times10^5 \times 0.3}{297 \times 298} = 0.407kg$$

$$\mathbf{p_1} \times \mathbf{V_1} = \mathbf{m} \times \mathbf{R} \times \mathbf{T_1}$$

We also need the temperature at the end of the heating process, for this we can use the equation of state again since it is a constant volume process we know the final pressure.

$$\mathbf{p_2 \times V_2 = m \times R \times T_2}$$

$$\mathbf{T_2 = \frac{p_2 V_2}{mR}} = \frac{4.8 \times 10^5 \times 0.3}{297 \times 0.407} = 1192K$$

Heat supply at constant volume is given by

$$\mathbf{Heat\ supply = m \times c_v (T_2 - T_1)}$$

$\mathbf{R = c_p - c_v}$ $\qquad$ $\mathbf{c_v = c_p - R = 1040 - 297 = 743\ J/kgK}$

$$\mathbf{Heat\ supply = 0.4067 \times 743 \times (1192 - 298)}$$

$$\mathbf{Heat\ supply = 270.147\ kJ}$$

Heat removed at constant pressure is given by

$$\mathbf{Heat\ removed = m \times c_p (T_3 - T_2)}$$

$$\mathbf{Heat\ removed = 0.4067 \times 1040 \times (298 - 1192)}$$

$$\mathbf{Heat\ removed = -378.13\ kJ}$$

Net heat flow = 270.14 – 378 13 = 107.98 kJ out of the system

The T-s diagram shows that the entropy increases during the heating process at constant volume and then decreases during the constant pressure heat removal.

For the constant volume process

$$\mathbf{S_2 - S_1 = m \times c_v \times Ln \frac{T_2}{T_1}}$$

$$\mathbf{S_2 - S_1 = 0.4067 \times 743 \times Ln \frac{1192}{298}}$$

$$\mathbf{S_2 - S_1 = 418.9\ J/K}$$

For the constant pressure process

$$\mathbf{S_3 - S_2 = m \times c_p \times Ln \frac{T_3}{T_2}}$$

$$\mathbf{S_3 - S_2 = 0.4067 \times 1040 \times Ln \frac{298}{1192}}$$

$$\mathbf{S_3 - S_2 = -586.3\ J/K}$$

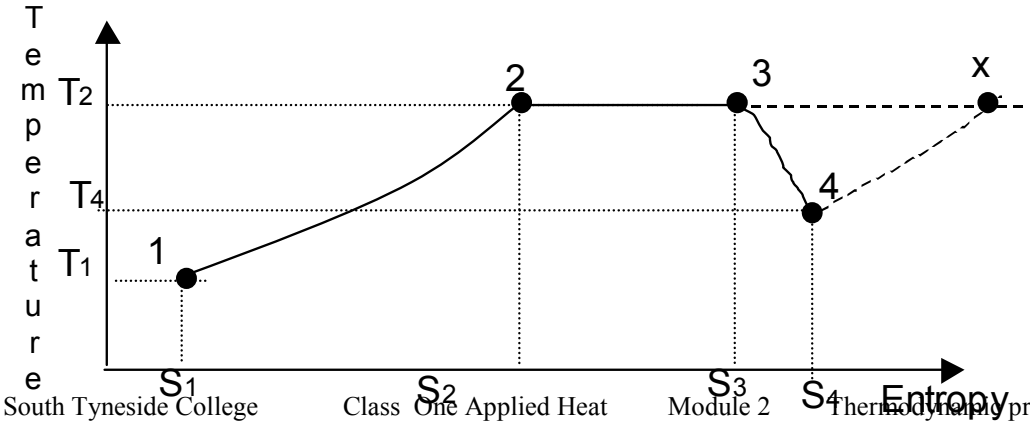
The net change in entropy is therefore the difference between these values which is –167.5 J/K

Entropy Example 2

In a series of reversible processes, 2 kg of air is heated at constant pressure from 10 bar 50°C to 250°C. It is then expanded isothermally until its pressure is 5 bar, the air is then expanded in a polytropic process to a pressure and temperature of 2 bar 140°C. For Air; γ=1.4, c_v= 718 J/kgK

c) Sketch the processes on a Temperature- Entropy diagram.
d) Calculate the change of entropy for each process

Remember this is a perfect gas and on the T-s diagram the volume lines would be steeper than the pressure lines and pressure, volume and temperature change in a polytropic process.



$$\gamma = \frac{c_p}{c_v} \qquad \gamma \times c_v = c_p$$

$$c_p = 1.4 \times 718 = 1005 \text{ J/kgK}$$

$$\mathbf{R = c_p - c_v} \qquad \mathbf{R = 1005 - 718 = 287 \text{ J/kgK}}$$

The T-s diagram shows that the entropy increases during the constant pressure heating process and also during the isothermal expansion, there is a further increase during the polytropic process.

For the constant pressure process

$$\mathbf{S_2 - S_1 = m \times c_p \times Ln \frac{T_2}{T_1}}$$

$$\mathbf{S_2 - S_1 = 2 \times 1005 \times Ln \frac{523}{323}}$$

$$\mathbf{S_2 - S_1 = 968.7 \text{ J/K}}$$

For the Isothermal process between the pressures of 10 bar and 5 bar

$$\mathbf{S_3 - S_2 = m \times R \times Ln \frac{p_2}{p_3}}$$

$$\mathbf{S_3 - S_2 = 2 \times 287 \times Ln \frac{10}{5}}$$

$$\mathbf{S_3 - S_2 = 398 \text{ J/K}}$$

The poplytropic process can be replaced with an isothermal process between the pressures of 5 bar and 2 bar, this will have the effect of increasing the entropy, this will be followed by a constant pressure process to the lower temperature which will have the effect of reducing the entropy.

For the isothermal operation

$$\mathbf{S_x - S_3 = m \times R \times Ln \frac{p_3}{p_4}}$$

$$S_x - S_3 = 2 \times 287 \times \mathrm{Ln} \frac{5}{2}$$

$$S_x - S_3 = 526.95 \text{ J/K}$$

For the constant pressure operation

$$\mathbf{S_4 - S_x = m \times c_p \times Ln \frac{T_4}{T_3}}$$

$$\mathbf{S_4 - S_x = 2 \times 1005 \times Ln \frac{413}{523}}$$

$$\mathbf{S_4 - S_x = -474.63 \text{ J/K}}$$

The change in entropy for this process is the addition of theses two values

$$\mathbf{S_4 - S_3 = 526.95 - 474.63 \text{ J/K}}$$

$$S_4 - S_3 = 52.32 \text{ J/K}$$