First Law – Processes in Closed Systems

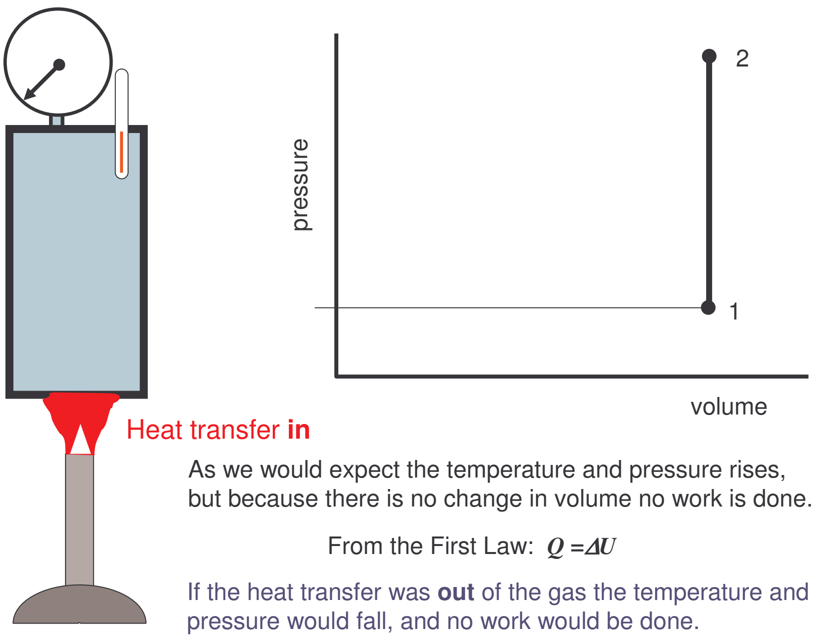
A process occurs when a system's state (as measured by its properties) changes for any reason. Processes may be **reversible**, or actual (irreversible). In this context the word 'reversible' has a special meaning.
A reversible process is one which is *wholly theoretical*, but can be imagined as one which occurs without incurring friction, turbulence, leakage or anything which causes unrecoverable energy losses.

All of the processes we are going to study at this stage will be considered to be **reversible**.
We will deal with actual (real or practical) processes later (THER205).

Processes may occur in particular ways:
This may be because we deliberately 'arrange' it to be so,
or as a 'natural consequence' of the way it is carried out.

at constant temperature : **isothermal**
at constant pressure : **isobaric**
at constant volume : **isochoric**
at constant enthalpy : **isenthalpic**
at constant entropy : **isentropic**
with no heat transfer to the surroundings : **adiabatic**

Heat transfer to/from a perfect gas (closed system) keeping the volume constant



As we would expect the temperature and pressure rises, but because there is no change in volume no work is done.

From the First Law: $Q = \Delta U$

If the heat transfer was **out** of the gas the temperature and pressure would fall, and no work would be done.

Heat transfer at constant volume (closed system)
Heat can be transferred to (often called a heating process) or from (called a cooling process) a gas at **constant volume** (isochorically).

The process is described by: $V = const$ and the properties are related by:

$$pV = mRT$$

Since the volume remains constant there is no work transfer:

$$W_{12} = 0$$

therefore the only effect of the heat transfer is to raise the internal energy level.

$$Q_{12} = \Delta U$$

From calorimetry the heat transfer required to change the temperature by a given amount is given by:

$$\boxed{Q_{12} = m\, c_v\, \Delta T}$$

where c_v is the specific heat capacity of the gas at constant volume.

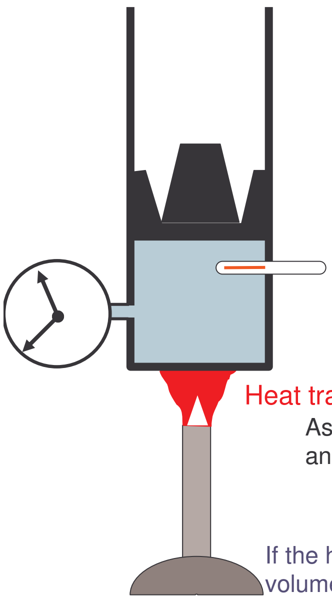
For a perfect gas the internal energy is dependent ONLY on temperature*, so we can write:

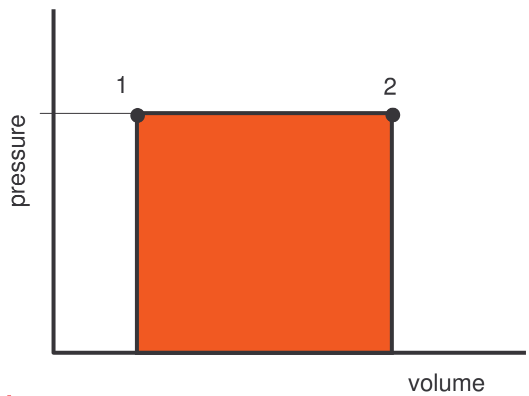
$$\boxed{\Delta U = m\, c_v\, \Delta T}$$

Irrespective of how a temperature change may occur, this will always be true.

*Joule's Law

Heat transfer to/from a perfect gas (closed system) keeping the pressure constant





Heat transfer **in**

As we would expect the temperature and volume increases and work is done by the system. $W_{12} = -p\,(V_2 - V_1)$

From the First Law: $Q + W = \Delta U$

If the heat transfer was **out** of the system the temperature and volume would decrease, and the work transfer would be positive.

Heat transfer at constant pressure (closed system)
Heat can be transferred to (often called a heating process) or from (called a cooling process) a gas at **constant pressure** (isobarically).

The process is described by: $p = const$ and the properties are related by:

$$pV = mRT$$

Since the <u>volume changes</u> there is work transfer:

$$W_{12} = -p(V_2 - V_1)$$

From the First Law:

$$Q_{12} = \Delta U - W_{12} = \Delta U + p(V_2 - V_1)$$

since $pV = mRT$

$$p(V_2 - V_1) = mR(T_2 - T_1)$$

and $\Delta U = m c_v \, \Delta T$

$$\therefore \underline{Q_{12}} = m c_v \, \Delta T + m R \, \Delta T = \underline{m(c_v + R)\Delta T}$$

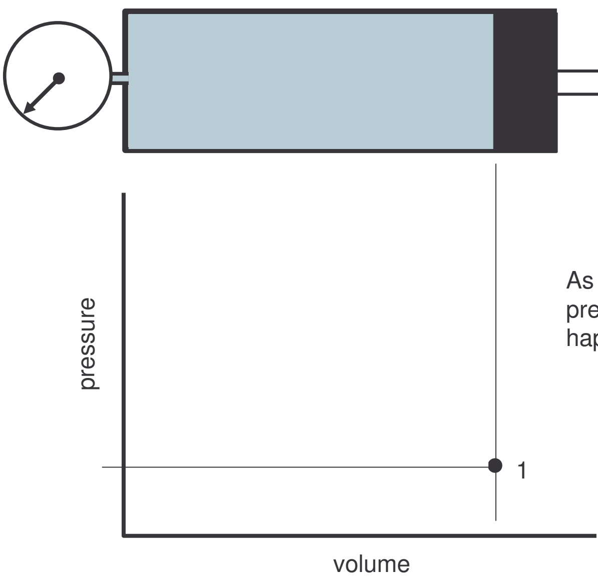
Since c_v and R are characteristics of the gas and remain approximately constant for moderate temperature ranges we combine them to obtain the specific heat capacity of the gas at constant pressure c_p.

$$c_p = c_v + R$$

The heat transfer at constant pressure is given by:

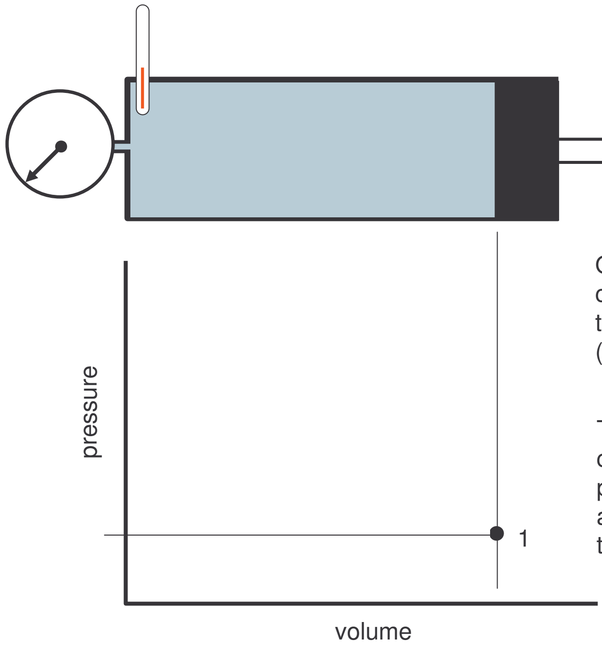
$$\boxed{Q_{12} = m c_p \Delta T}$$

Work transfer <u>in</u> to a perfect gas (closed system)



As we would expect the pressure rises, but what happens to the **temperature**?

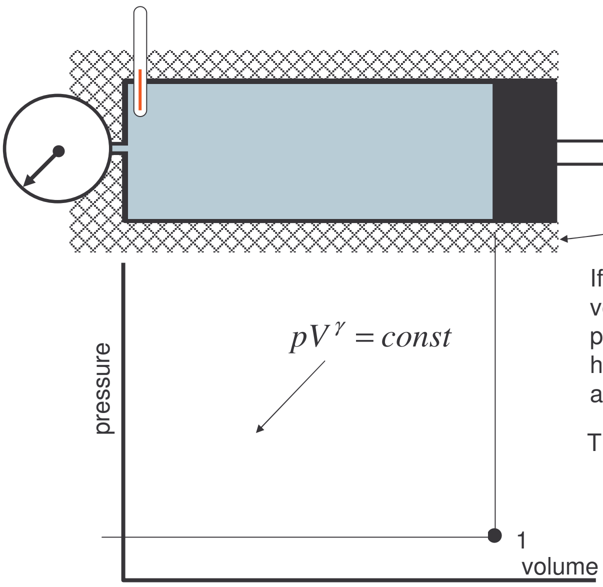
Work transfer in to a perfect gas (closed system)



Our normal experience of compressing a gas is that its temperature rises. (e.g. a bicycle pump).

This is because we normally carry out the compression process relatively quickly and the 'heat' does not have time to escape.

Adiabatic Work transfer in to a perfect gas (closed system)



If we carry out the process very quickly or ensure that it is perfectly insulated then **no** heat will escape at all……… an **ADIABATIC** process.

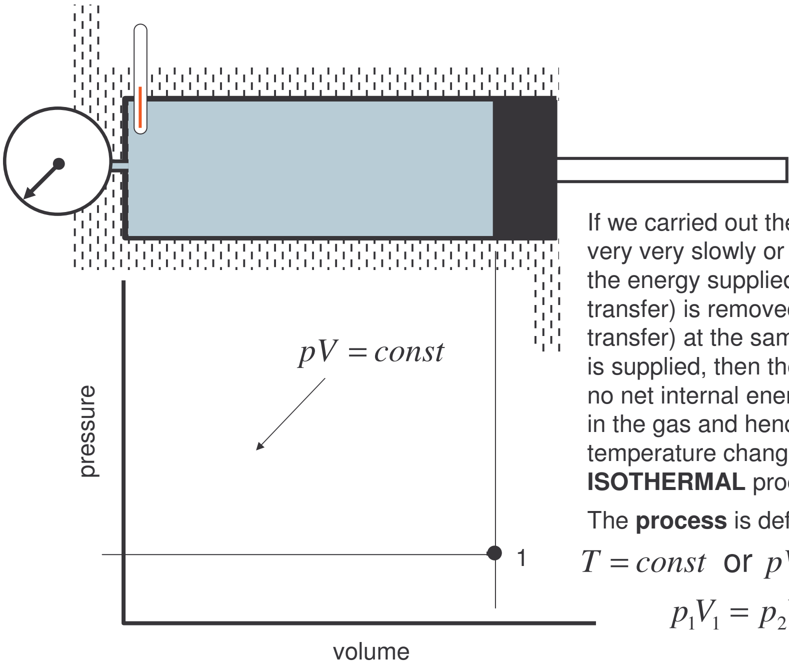
The **process** is defined by:

$$pV^{\gamma} = const$$

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$$

γ is known as the adiabatic index of a gas. It can be shown that $\gamma = \frac{c_p}{c_v}$

Isothermal work transfer in to a perfect gas (closed system)



If we carried out the process very very slowly or ensured that the energy supplied (by work transfer) is removed (by heat transfer) at the same rate that it is supplied, then there will be no net internal energy change in the gas and hence no temperature change…an **ISOTHERMAL** process

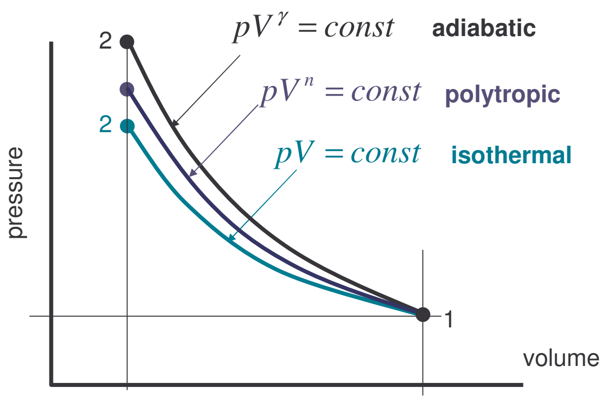
The **process** is defined by:

$$T = const \text{ or } pV = const$$

$$p_1V_1 = p_2V_2$$

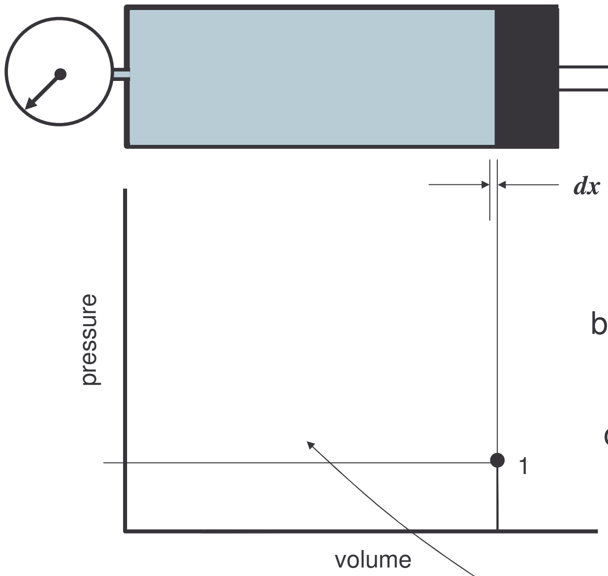
When work is transferred to a gas (often referred to as a compression process) its volume decreases and its pressure increases. Its temperature may increase or remain the same depending on whether we allow heat transfer or not.

We often illustrate such processes on a pressure/volume graph.



If the heat transfer (out) exactly equals the work transfer (in) there is no net energy change and the compression occurs without the temperature rising (an isothermal process). In practice, the actual process tend to lie between the two – called **polytropic.**

Calculation of Work transfer in to a perfect gas (closed system)



The work done dW by force F moving an infinitesimal distance dx is given by: $dW = Fdx$

but $F = pA$

$$\therefore \quad dW = pAdx$$

but $Adx = -dV$

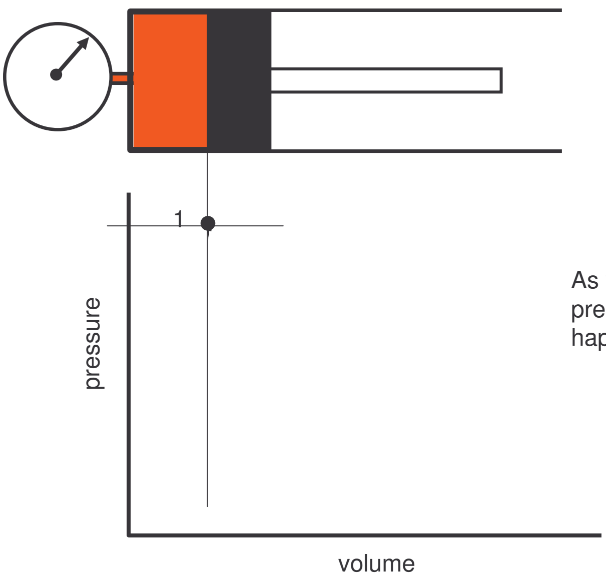
$$\therefore \quad dW = -pdV$$

or $$W_{12} = -\int_{V_1}^{V_2} pdV$$

$$W_{12} = -\int_{1}^{2} pdV$$

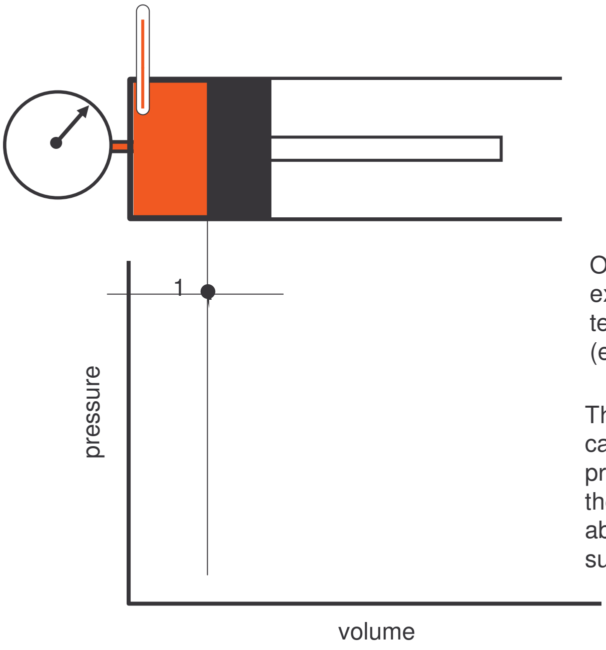
the area under the p-V graph

Work transfer out of a perfect gas (closed system)



As we would expect the pressure falls, but what happens to the **temperature**?

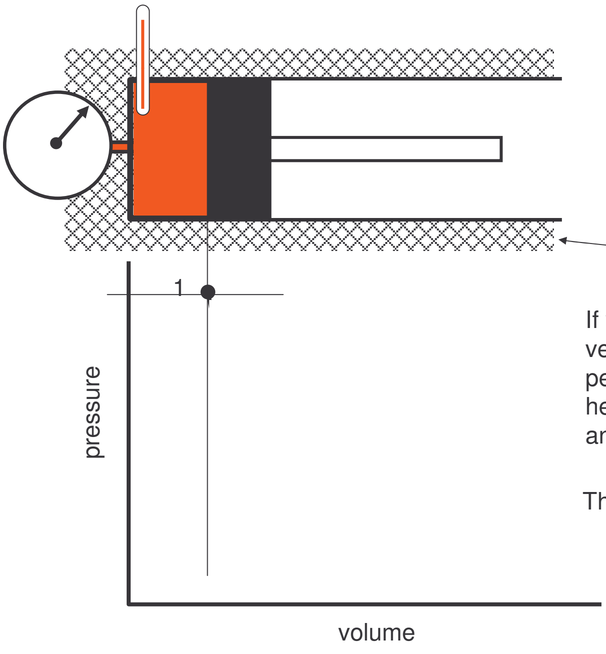
Work transfer out of a perfect gas (closed system)



Our normal experience of expanding a gas is that its temperature falls.
(e.g. letting the air out of a tire).

This is because we normally carry out the expansion process relatively quickly and the gas does not have time to absorb 'heat' from the surroundings.

Adiabatic work transfer out of a perfect gas (closed system)



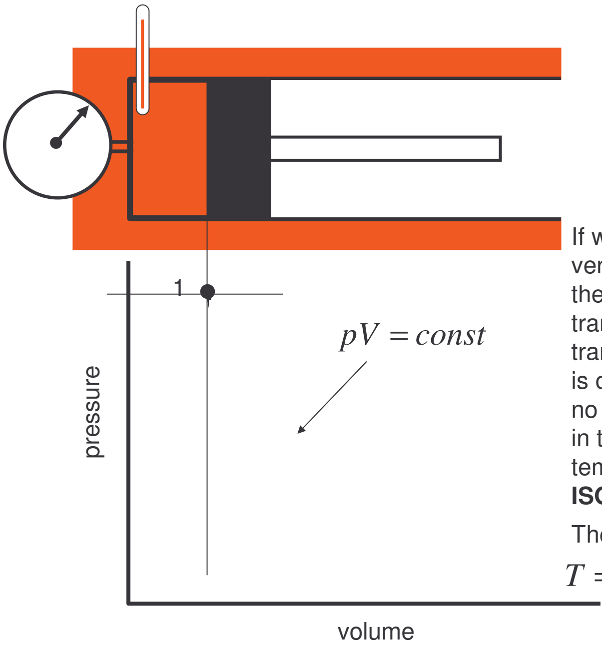
If we carry out the process very quickly or ensure that it is perfectly insulated then **no** heat will enter at all………
an **ADIABATIC** process.

The **process** is defined by:

$$pV^{\gamma} = const$$

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$$

Isothermal work transfer out of a perfect gas (closed system)



If we carried out the process very very slowly or ensured that the energy obtained (by work transfer) is replaced (by heat transfer) at the same rate that it is obtained, then there will be no net internal energy change in the gas and hence no temperature change…an **ISOTHERMAL** process

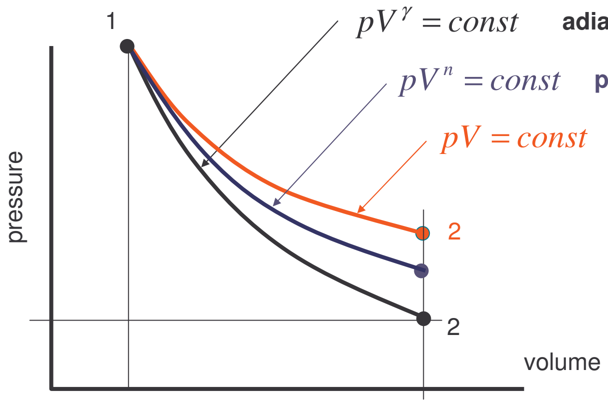
The **process** is defined by:

$T = const$ or $pV = const$

$p_1 V_1 = p_2 V_2$

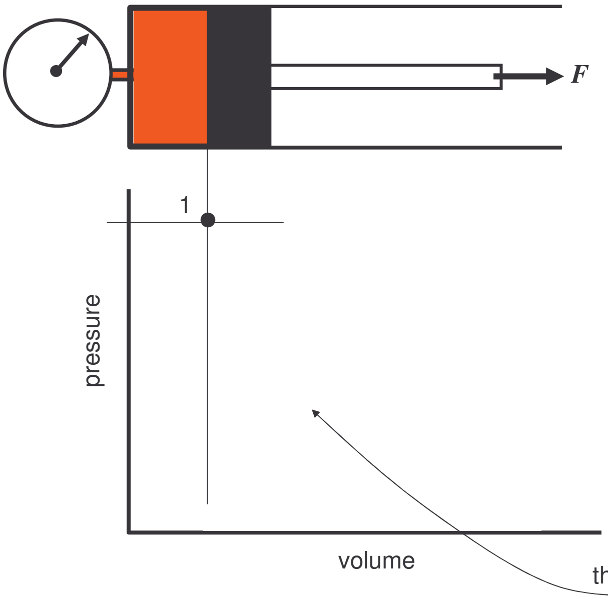
When work is transferred from a gas (often referred to as a expansion process) its volume increases and its pressure decreases. Its temperature may decrease or remain the same depending on whether we allow heat transfer or not.

We often illustrate such processes on a pressure/volume graph.



If the heat transfer (in) exactly equals the work transfer (out) there is no net energy change and the expansion occurs without the temperature falling (an isothermal process). In practice, the actual process tend to lie between the two – called **polytropic.**

Calculation of Work transfer <u>out</u> of a perfect gas (closed system)



The work done $\boldsymbol{dW}$ by force $\boldsymbol{F}$ moving an infinitesimal distance $\boldsymbol{dx}$ is given by: $dW = Fdx$

and using exactly the same procedure as for compression we can show that:

$$W_{12} = -\int_1^2 pdV$$

the area under the p-V graph

Summary – Adiabatic Processes (closed system)

If there is <u>no</u> heat transfer (an **adiabatic** process) the temperature changes because the work transfer increases or decreases the internal energy.

In practice, this may be closely achieved by carrying out the process very rapidly - giving no time for heat transfer to occur, or by ensuring the system is very well insulated.

During a reversible adiabatic work transfer process the pressure and volume are related by:

$pV^{\gamma} = const$ and the properties are related by: $pV = mRT$

γ is a characteristic of the gas known as the adiabatic index - it may be looked up in tables.

$$W_{12} = -\int_1^2 pdV = -\int_1^2 const \times V^{-\gamma} dV = -\frac{1}{1-\gamma}[constV_2^{1-\gamma} - constV_1^{1-\gamma}]$$

$$= -\frac{1}{1-\gamma}[p_2 V_2^{\gamma} V_2^{1-\gamma} - p_1 V_1^{\gamma} V_1^{1-\gamma}] = \frac{p_2 V_2 - p_1 V_1}{\gamma - 1}$$

The work transfer during an adiabatic compression or expansion process is given by:	$W_{12} = \frac{p_2 V_2 - p_1 V_1}{\gamma - 1}$

Summary – Isothermal Processes (closed system)
If there is no temperature change (an **isothermal** process) the temperature remains constant because the work transfer in to or out of the system is exactly offset by the heat transfer out of or in to the system and therefore there is no change in internal energy of the system. In practice, this may be closely achieved either by carrying out the process very very slowly - giving time for heat transfer to occur, and/or ensuring the system can easily transfer heat to/from the surroundings.
During a reversible isothermal work transfer process the temperature remains constant:

$T = const$ and the properties are related by: $pV = mRT$

$$W_{12} = -\int_1^2 pdV = -\int_1^2 \frac{mRT}{V} dV = -mRT \int_1^2 \frac{dV}{V} = -mRT[\ln V_2 - \ln V_1]$$

$$= -mRT \ln \frac{V_2}{V_1} = p_1 V_1 \ln \frac{V_1}{V_2}$$

The work transfer during an isothermal compression or expansion process is given by:	$W_{12} = p_1 V_1 \ln \frac{V_1}{V_2}$

Summary – Polytropic Processes (closed system)
In practice because many compression and expansion processes are carried out very rapidly they can be reasonably approximated by an adiabatic process. When compressing a gas there is an advantage in trying to cool the process. However, it is difficult to obtain an actual isothermal process – so the process ends up somewhere between an isothermal process and an adiabatic process. The process is called a **polytropic** process. During a reversible polytropic work transfer process the pressure and volume are related by:

$pV^n = const$ and the properties are related by: $pV = mRT$

n is a known as the polytropic index – and depends on how exactly the process is carried out – it typically has to be found by experiment.

$$W_{12} = -\int_1^2 pdV = -\int_1^2 const \times V^{-n} dV = -\frac{1}{1-\gamma}[constV_2^{1-n} - constV_1^{1-n}]$$

$$= -\frac{1}{1-\gamma}[p_2 V_2^n V_2^{1-n} - p_1 V_1^n V_1^{1-n}] = \frac{p_2 V_2 - p_1 V_1}{n-1}$$

The work transfer during a polytropic compression or expansion process is given by:	$W_{12} = \frac{p_2 V_2 - p_1 V_1}{n-1}$