

## Ideal Gases and Heat Engines

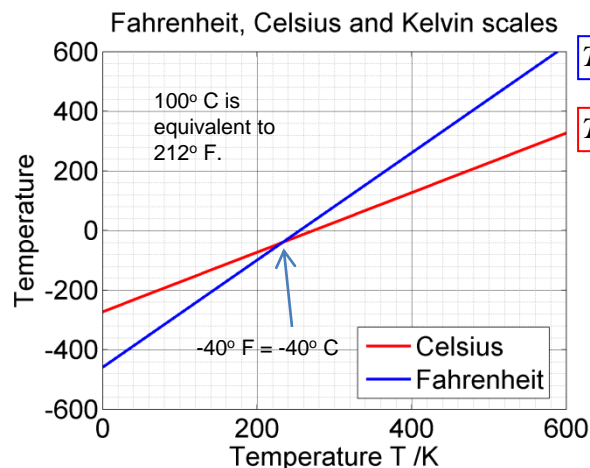
The operation, and theoretical *efficiency*, of combustion driven piston engines (e.g. diesel or petrol fuelled) can be analysed by considering changes to pressure, temperature and volume of the gaseous components. This proceeds by accounting for the energy changes in the gas as a result of *heat* applied and *work done* combined with the *ideal gas equation*, which relates the physical properties of the gas.

### Ideal Gas Equation

$$pV = nRT$$

$p$	Pressure in Pascals (Pa)	$R$	Molar gas constant 8.314 Jmol <sup>-1</sup> K <sup>-1</sup>
$V$	Volume / cubic metres		
$n$	Number of moles of gas	$T$	Temperature / Kelvin

### Temperature scales



$$T_F = \frac{9}{5} T_C + 32$$

$$T_C = T - 273$$

The **Kelvin** temperature scale (or “absolute” scale) is proportional to the **mean kinetic energy of molecules**.

$$U = \frac{1}{2} \alpha nRT$$

Internal energy of  $n$  moles of gas

Number of degrees of freedom of molecular motion (e.g.  $\alpha = 3$  for x,y,z translation)

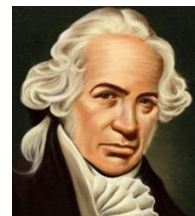
1 mol =  $6.02 \times 10^{23}$  molecules. So energy of a *molecule* is  $u = \frac{1}{2} \alpha n k_B T$   
Boltzmann's constant  $k_B = R / 6.02 \times 10^{23} = 1.38 \times 10^{-23} \text{ J K}^{-1}$

**Fahrenheit** is a **temperature scale**, where 32° F is the freezing point of water and 212° F is the boiling point of water, defined at sea level at **standard atmospheric pressure** (101,325Pa). It was proposed in 1724 by Daniel Gabriel Fahrenheit. 0° F corresponded to the lowest temperature he could cool brine (salt water) and 100° F was the average human body temperature (37°C).

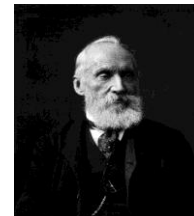
A more popular scale is the **Celsius** scale, with 0° C and 100° C representing the freezing and boiling points of water at standard atmospheric pressure.



Anders Celsius  
1701-1744



Daniel Fahrenheit  
1686-1736



William Thompson  
(Lord Kelvin)  
1824-1907



Robert Boyle  
1627-1691



Jacques Charles  
1746-1823

### Ideal Gas Equation in practical units

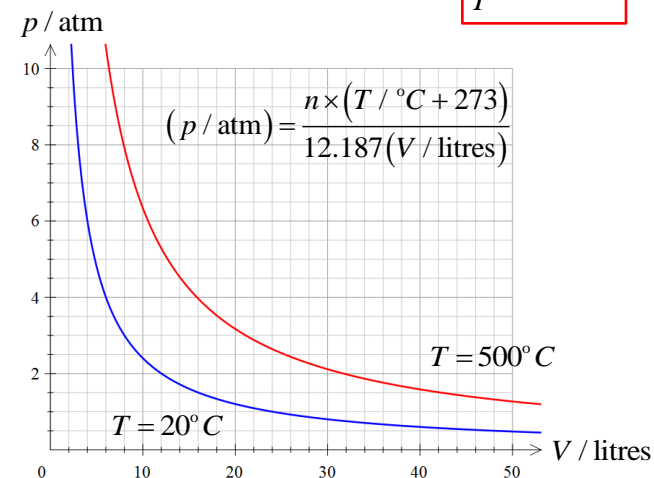
$$\left( \frac{p}{\text{atm}} \times 101325 \right) \left( \frac{V}{\text{litres}} \times \frac{1}{1000} \right) = 8.314 \times \left( \frac{T}{\text{K}} \right) \times n$$

$$\left( p / \text{atm} \right) = \frac{n \times (T / ^\circ\text{C} + 273)}{12.187 (V / \text{litres})}$$

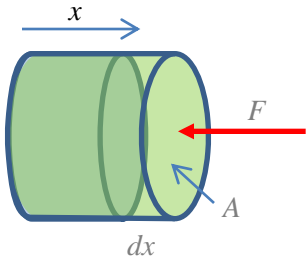
Special cases of the ideal gas equation:

**Boyles' Law.** At constant temperature, gas pressure is inversely proportional to volume.  $p \propto \frac{1}{V}$   
 $\therefore pV = \text{constant}$

**Charles' Law.** At constant pressure, gas volume is proportional to temperature.  $V \propto T$   
 $\therefore \frac{V}{T} = \text{constant}$



## Heat, work and internal energy of an ideal gas



Consider a cylinder of gas being compressed by a force  $F$ . The work done *on the gas* by the force is:

$$dW = Fdx$$

The pressure acting upon the gas is:

$$p = \frac{F}{A}$$

and the volume change is:

$$dV = -Adx$$

$$\therefore dW = pA \times -\frac{dV}{A}$$

$$dW = -pdV$$

If heat  $dQ$  is supplied to the gas then the **First Law of Thermodynamics** (that Energy in a closed system is conserved) means the internal energy change is

$$dU = dQ - pdV$$

$$\therefore dQ = dU + pdV \quad \text{First Law}$$

The internal energy for  $n$  moles of an ideal gas is

$$U = \frac{1}{2} \alpha nRT$$

The Ideal Gas Equation is

$$pV = nRT$$

$$\therefore U = \frac{1}{2} \alpha pV$$

### Constant volume process (isochoric)

Constant volume heat capacity for  $n$  moles

$$C_v = \frac{dQ}{dT}$$

$$\therefore dQ = C_v dT$$

$$U = \frac{1}{2} \alpha nRT$$

$$\therefore dU = \frac{1}{2} \alpha nR dT$$

$$dV = 0 \quad \text{i.e. no work done on gas}$$

$$\therefore dQ = dU \quad \text{First Law}$$

$$\Rightarrow C_v dT = \frac{1}{2} \alpha nR dT$$

$$\therefore C_v = \frac{1}{2} \alpha nR$$

So for a constant volume change, the heat capacity is a *constant* for an ideal gas.

$$c_v = \frac{1}{2} \frac{\alpha R}{M}$$

Constant volume specific heat capacity.  $M$  is the molar volume /kg

Total amount of heat supplied to  $m$  kg of gas is therefore:

$$Q = mc_v \Delta T$$

Gas	$M/\text{g mol}^{-1}$
Acetylene	26.04
Air	28.966
Ammonia	17.02
Argon	39.948
Benzene	78.11
Butane	58.12
Carbon dioxide	44.01
Carbon Monoxide	28.011
Chlorine	70.906
Ethyl Alcohol	46.07
Fluorine	37.996
Helium	4.003
Hydrogen Chloride	36.461
Hydrogen Sulphide	34.076
Krypton	83.80
Methane	16.044
Natural Gas	19.00
Nitrogen	28.0134
Neon	20.179
Oxygen	31.9988
Ozone	47.998
Propane	44.097
Sulphur dioxide	64.06
Toluene	92.13
Xenon	131.30
Water vapour	18.02

### Constant pressure process (isobaric)

$$C_p = \frac{dQ}{dT} \quad \text{Constant pressure heat capacity for } n \text{ moles of ideal gas}$$

$$\therefore dQ = C_p dT$$

$$U = \frac{1}{2} \alpha nRT$$

$$\therefore dU = \frac{1}{2} \alpha nR dT$$

Since  $p = \text{constant}$

$$pV = nRT \quad \text{Ideal Gas Equation}$$

$$\therefore pdV = nR dT$$

$$dQ = dU + pdV \quad \text{First Law}$$

$$\therefore C_p dT = \frac{1}{2} \alpha nR dT + nR dT$$

$$\Rightarrow C_p = \frac{1}{2} \alpha nR + nR$$

$$C_v = \frac{1}{2} \alpha nR$$

$$\therefore C_p = C_v + nR \quad \text{Mayer Relationship}$$

Experimentally it is very hard to maintain a constant volume as heat is added, so constant volume heat capacity is difficult to measure directly.

However, constant pressure heat capacity is much easier to measure, as one can allow volumes to change in order to maintain equilibrium with the ambient pressure.

The Mayer relationship is therefore very useful in working out the constant volume heat capacity *from* the constant pressure heat capacity.

## Heat supplied and work done for an isobaric process

$$dQ = C_p dT$$

$$\therefore Q = mc_p \Delta T$$

$$c_p = \frac{C_p}{nM} = \frac{C_v + nR}{nM} = \frac{\frac{1}{2}\alpha nR + nR}{nM}$$

$$c_p = \frac{R(\frac{1}{2}\alpha + 1)}{M}$$

$$W = \int_{V_0}^V -pdV$$

$$W = p(V_0 - V) \quad \text{Since } p \text{ is constant}$$

## The Mayer Relationship and $\gamma$

$$C_p = C_v + nR$$

$$\frac{C_p}{C_v} = 1 + \frac{nR}{C_v}$$

$$C_v = \frac{1}{2}\alpha nR$$

$$\frac{C_p}{C_v} = 1 + \frac{nR}{\frac{1}{2}\alpha nR}$$

$$\gamma = \frac{C_p}{C_v} = \frac{c_p}{c_v} = 1 + \frac{2}{\alpha}$$

$$\gamma c_v = c_v + \frac{R}{M}$$

$$c_v(\gamma - 1) = \frac{R}{M}$$

$$c_v = \frac{R}{M} \frac{1}{\gamma - 1}$$

$$c_p = \frac{R}{M} \frac{\gamma}{\gamma - 1}$$

$$C_p = C_v + nR$$

$$\frac{C_p}{Mn} = \frac{C_v}{Mn} + \frac{nR}{Mn}$$

$$c_p = c_v + \frac{R}{M}$$

## Adiabatic (or isentropic) process

i.e. no heat added. *Work done is the sole cause of changes in internal energy*

$$U = \frac{1}{2}\alpha nRT$$

$$pV = nRT$$

$$\therefore U = \frac{1}{2}\alpha pV$$

$$\therefore dU = \frac{1}{2}\alpha d(pV)$$

$$dU = \frac{1}{2}\alpha V dp + \frac{1}{2}\alpha p dV$$

$$dQ = 0 \quad \text{This defines an adiabatic change}$$

$$\therefore dU = -pdV$$

$$dU = -pdV$$

$$\therefore \frac{1}{2}\alpha V dp + \frac{1}{2}\alpha p dV = -pdV$$

$$(\frac{1}{2}\alpha + 1)pdV = -\frac{1}{2}\alpha V dp$$

$$(1 + \frac{2}{\alpha})pdV = -V dp$$

$$(1 + \frac{2}{\alpha})\frac{dV}{V} = -\frac{dp}{p}$$

$$(1 + \frac{2}{\alpha})\ln V = -\ln p + k$$

$$\ln(pV^{1+\frac{2}{\alpha}}) = k$$

$$pV^{1+\frac{2}{\alpha}} = \text{constant}$$

$$pV^\gamma = \text{constant}$$

$$pV^\gamma = p_0V_0^\gamma$$

## Work done on gas for an adiabatic change

$$dW = -pdV$$

$$W = -\int p dV$$

$$W = -p_0V_0^\gamma \int_{V_0}^V V^{-\gamma} dV$$

$$W = \frac{-p_0V_0^\gamma}{1-\gamma} (V^{-\gamma+1} - V_0^{-\gamma+1})$$

$$W = \frac{-p_0V_0}{1-\gamma} \left( \left( \frac{V}{V_0} \right)^{-\gamma+1} - 1 \right)$$

$$W = \frac{1}{2}\alpha p_0V_0 \left( \left( \frac{V}{V_0} \right)^{\frac{2}{\alpha}} - 1 \right)$$

$$W = \frac{1}{2}\alpha p_0V_0 \left( \left( \frac{V_0}{V} \right)^{\frac{2}{\alpha}} - 1 \right)$$

$$pV^\gamma = p_0V_0^\gamma$$

$$\therefore p = p_0V_0^\gamma V^{-\gamma}$$

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{\alpha} \therefore \gamma - 1 = \frac{2}{\alpha}$$

So work done *by* gas on the surroundings is:

$$W = \frac{p_0V_0}{\gamma - 1} \left( 1 - \left( \frac{V_0}{V} \right)^{\gamma-1} \right)$$

## Constant temperature (isothermal) process

$$dU = 0$$

$$T = \text{constant}$$

$$dQ = pdV \quad \text{First Law}$$

$$dQ = \frac{nRT}{V} dV \quad \text{Using the Ideal Gas Equation}$$

$$Q = nRT \int_{V_0}^V \frac{1}{V} dV$$

$$Q = nRT \ln \left( \frac{V}{V_0} \right) \quad \text{Heat supplied to gas}$$

## Work done on gas

$$dW = -pdV$$

$$W = -\int p dV$$

$$W = -\int dQ$$

$$W = -Q$$

$$W = nRT \ln \left( \frac{V_0}{V} \right)$$

## Heat Engines

### Carnot Cycle

#### Positions 1 to 2

*Isothermal expansion* of an ideal gas at the hot reservoir temperature. Since gas temperature, and therefore internal energy is constant, the work done by the gas on the surroundings must exactly equate to the heat absorbed by the gas.

#### Positions 2 to 3

*Isentropic* (i.e. adiabatic or 'no heat added or lost') *expansion* of the gas. The work done by the gas on the surroundings is powered by the loss of internal energy of the gas as it cools from the temperature of the hot reservoir to the temperature of the cold reservoir.

#### Positions 3 to 4

*Isothermal compression* of the gas. In order for the temperature, and hence the internal energy, to remain constant, the heat lost by the gas to the cold reservoir must equate to the work done on it by the surroundings.

#### Positions 4 to 1

*Isentropic compression* of the gas, heating it from the temperature of the cold reservoir to the temperature of the cold reservoir.

Assume we have  $n$  moles of ideal gas, none of which are lost in the process. **Input parameters** are:

$T_H$  Hot reservoir temperature (Kelvin)

$T_C$  Cold reservoir temperature (Kelvin)

$V = V_1$  Volume of gas at position 1 in the cycle

$V = V_2$  Volume of gas at position 2 in the cycle

These two volumes are *derived* from the other inputs:

$V = V_3$  Volume of gas at position 3 in the cycle

$V = V_4$  Volume of gas at position 4 in the cycle

Ideal gas equation

$$pV = nRT$$

$$U = \frac{1}{2} \alpha nRT$$

Mayer relation

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

$$pV = \text{constant}$$

$$Q = nRT \ln \left( \frac{V}{V_0} \right)$$

$$pV^\gamma = \text{constant}$$

$$W = \frac{p_0 V_0}{\gamma - 1} \left( 1 - \left( \frac{V_0}{V} \right)^{\gamma-1} \right)$$

Work done by the ideal gas on the surroundings

#### Between positions 1 and 2

$$p_1 V_1 = nRT_H$$

$$Q_{\text{in}} = nRT_H \ln \left( \frac{V_2}{V_1} \right)$$

$$W_{1,2} = nRT_H \ln \left( \frac{V_2}{V_1} \right)$$

$$pV = p_1 V_1 = nRT_H$$

$$\therefore p = \frac{nRT_H}{V}$$

#### Between positions 3 and 4

$$p_3 V_3 = nRT_C$$

$$Q_{\text{out}} = nRT_C \ln \left( \frac{V_3}{V_4} \right)$$

$$W_{3,4} = -nRT_C \ln \left( \frac{V_3}{V_4} \right)$$

$$pV = p_3 V_3 = nRT_C$$

$$\therefore p = \frac{nRT_C}{V}$$

#### Between positions 4 and 1

$$p_4 V_4 = nRT_C$$

$$pV^\gamma = p_4 V_4^\gamma \therefore p = p_4 \left( \frac{V_4}{V} \right)^\gamma$$

$$W_{4,1} = \frac{p_4 V_4}{\gamma - 1} \left( 1 - \left( \frac{V_4}{V_1} \right)^{\gamma-1} \right)$$

$$p_1 = p_4 \left( \frac{V_4}{V_1} \right)^\gamma \Rightarrow \frac{nRT_H}{V_1} = \frac{nRT_C}{V_4} \left( \frac{V_4}{V_1} \right)^\gamma$$

$$V_4^{\gamma-1} = \frac{T_H}{T_C} V_1^{\gamma-1} \Rightarrow V_4 = \left( \frac{T_H}{T_C} \right)^{\frac{1}{\gamma-1}} V_1$$

To complete the cycle

#### Between positions 2 and 3

$$p_2 V_2 = nRT_H$$

$$pV^\gamma = p_2 V_2^\gamma \therefore p = p_2 \left( \frac{V_2}{V} \right)^\gamma$$

$$W_{2,3} = \frac{p_2 V_2}{\gamma - 1} \left( 1 - \left( \frac{V_2}{V_3} \right)^{\gamma-1} \right)$$

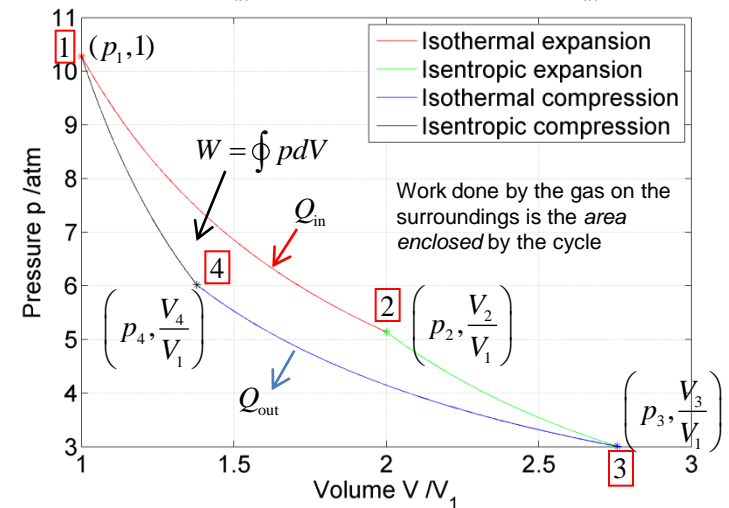
$$p_2 = \frac{nRT_H}{V_2}, \quad p_3 = \frac{nRT_C}{V_3}$$

$$p_3 = p_2 \left( \frac{V_2}{V_3} \right)^\gamma$$

$$\frac{nRT_C}{V_3} = \frac{nRT_H}{V_2} \left( \frac{V_2}{V_3} \right)^\gamma$$

$$V_3^{\gamma-1} = \frac{T_H}{T_C} V_2^{\gamma-1} \Rightarrow V_3 = \left( \frac{T_H}{T_C} \right)^{\frac{1}{\gamma-1}} V_2$$

Carnot cycle:  $T_H = 90^\circ\text{C}$ ,  $T_C = 20^\circ\text{C}$ ,  $V_1 = 0.1\text{m}^3$   
 $W = 13.9266\text{kJ}$ ,  $Q_{\text{in}} = 72.2194\text{kJ}$ , Efficiency =  $W/Q_{\text{in}} = 19.2837\%$



Nicolas Léonard  
Sadi Carnot  
(1796-1832)

Carnot engine cont....

Total work done is:

$$W = \oint p dV = W_{1,2} + W_{2,3} + W_{3,4} + W_{4,1}$$

$$W = nRT_H \ln\left(\frac{V_2}{V_1}\right) + \frac{p_2 V_2}{\gamma - 1} \left(1 - \left(\frac{V_2}{V_3}\right)^{\gamma-1}\right) - nRT_C \ln\left(\frac{V_3}{V_4}\right) - \frac{p_4 V_4}{\gamma - 1} \left(\left(\frac{V_4}{V_1}\right)^{\gamma-1} - 1\right)$$

$$W = nRT_H \ln\left(\frac{V_2}{V_1}\right) + \frac{nRT_H}{\gamma - 1} \left(1 - \left(\frac{T_C}{T_H}\right)^{\frac{1}{\gamma-1}}\right) - nRT_C \ln\left(\frac{V_2}{V_1}\right) - \frac{nRT_C}{\gamma - 1} \left(\left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}} - 1\right)$$

$$W = nRT_H \ln\left(\frac{V_2}{V_1}\right) + \frac{nRT_H}{\gamma - 1} \left(1 - \frac{T_C}{T_H}\right) - nRT_C \ln\left(\frac{V_2}{V_1}\right) - \frac{nRT_C}{\gamma - 1} \left(\frac{T_H}{T_C} - 1\right)$$

$$W = nR(T_H - T_C) \ln\left(\frac{V_2}{V_1}\right) + \frac{nRT_H}{\gamma - 1} - \frac{nRT_C}{\gamma - 1} - \frac{nRT_H}{\gamma - 1} + \frac{nRT_C}{\gamma - 1}$$

$$W = nR(T_H - T_C) \ln\left(\frac{V_2}{V_1}\right)$$

Define heat **engine efficiency** as the ratio of Work done by the gas to the heat input

$$\eta = \frac{W}{Q_{in}}$$

$$\eta = \frac{nR(T_H - T_C) \ln\left(\frac{V_2}{V_1}\right)}{nRT_H \ln\left(\frac{V_2}{V_1}\right)}$$

$$\eta = \frac{T_H - T_C}{T_H}$$

$$\eta = 1 - \frac{T_C}{T_H}$$

The Carnot Engine efficiency depends *only on the reservoir temperatures*.

Since the temperature range cannot go beyond the range of reservoir temperatures, the Carnot cycle represents the **most efficient** way of extracting work given an amount of heat input.\* Any other process would occupy *less area* in the  $S, T$  diagram.

$$V_3 = \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}} V_2 \quad V_4 = \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}} V_1 \quad p_1 V_1 = nRT_H \quad p_2 V_2 = nRT_H \quad p_3 V_3 = nRT_C \quad p_4 V_4 = nRT_C \quad Q_{in} = nRT_H \ln\left(\frac{V_2}{V_1}\right)$$

$$\frac{V_2}{V_3} = \left(\frac{T_C}{T_H}\right)^{\frac{1}{\gamma-1}} \quad \frac{V_4}{V_1} = \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}} \quad \therefore \frac{V_3}{V_4} = \frac{V_2}{V_1}$$

The efficiency of a Carnot heat engine can be more simply derived by consideration of **Entropy**  $S$ . This is a measure of *disorder* in a substance.

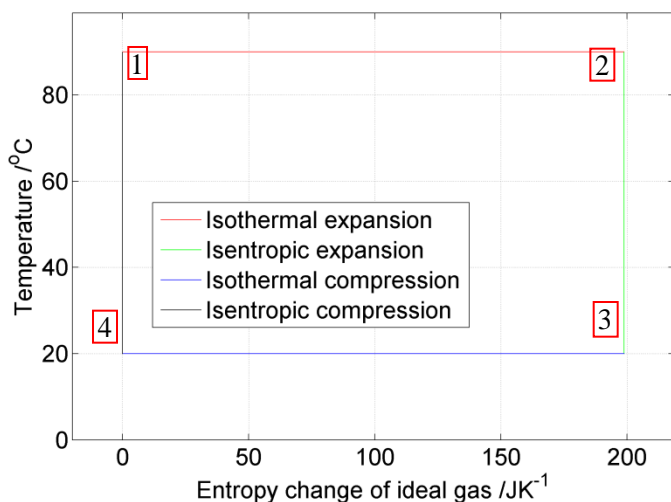
The **Second Law of Thermodynamics** states *for any change, the total amount of Entropy in the Universe must increase*.

If heat is added in a *reversible* process:  $dS = \frac{dQ}{T}$

For the Carnot cycle, the *isentropic stages have no heat change* hence they are at constant **Entropy**. (Note this applies to the ideal gas, the *surroundings* will change in entropy due to the exchange of work with the ideal gas). We cannot create entropy in the cycle for the gas, as the cycle returns to the original state ( $p, V, T$ ), and **Entropy is a scalar function of state** (i.e. like potential energy – the path does not matter). The  $(S, T)$  curve for the cycle is therefore a *rectangle*.

In the isothermal stages, temperature is a constant, so in both cases  $\Delta S = \frac{Q_{in}}{T_H} = \frac{Q_{out}}{T_C} = nR \ln\left(\frac{V_2}{V_1}\right)$

Carnot cycle:  $T_H = 90^\circ\text{C}$ ,  $T_C = 20^\circ\text{C}$ ,  $V_1 = 0.1\text{m}^3$   
 $W = 13.9266\text{kJ}$ ,  $Q_{in} = 72.2194\text{kJ}$ , Efficiency =  $W/Q_{in} = 19.2837\%$



From the **First Law of Thermodynamics**

$$dU = dQ - p dV \quad \therefore dU = T dS - p dV$$

Over the whole cycle the *internal energy doesn't change*, so the work done by the gas is:

$$W = \oint p dV = \oint T dS$$

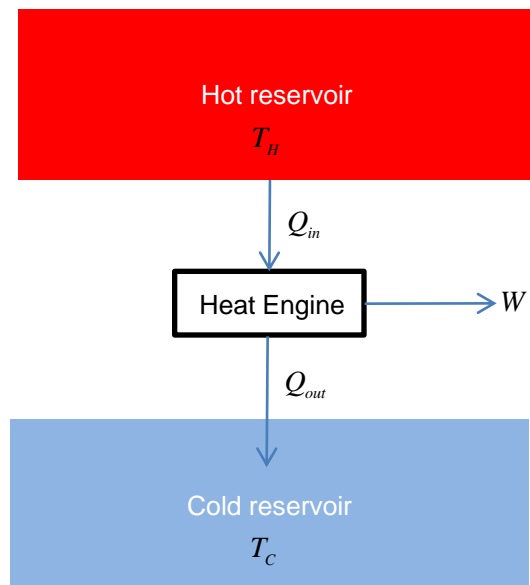
$$W = (T_H - T_C) \Delta S = (T_H - T_C) nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\therefore \eta = \frac{W}{Q_{in}} = \frac{(T_H - T_C) nR \ln\left(\frac{V_2}{V_1}\right)}{nRT_H \ln\left(\frac{V_2}{V_1}\right)} = 1 - \frac{T_C}{T_H}$$

## General notes regarding the Second Law of Thermodynamics, and the maximum possible efficiency of heat engines

It is possible to bound the efficiency of *any* heat engine using (i) the law of conservation of energy and (ii) the Second Law of Thermodynamics. That the upper bound of efficiency equates with the efficiency of the Carnot engine is perhaps an even stronger justification of the statement that *a Carnot engine is the most efficient scheme possible*, if indeed it could be practically realized.

*Any* heat engine is essentially flow of heat from a hot reservoir to a colder one. By a *reservoir* we mean a thermal mass that is so large that it will not change temperature when the heat we associate with our engine is taken from or added to it. The difference in heat taken from the hot reservoir, and the heat transferred to the cold reservoir, is the maximum possible work  $W$  done by the engine. This must be true to satisfy the *law of energy conservation*, or the **First Law of Thermodynamics**.



First Law:  $Q_{in} = Q_{out} + W$

The **Second Law of Thermodynamics** states that for every change there can *never be an overall decrease in Entropy*. For our idealized system, this means the loss of entropy of the hot reservoir must *at least* be compensated for by the gain in entropy of the cold reservoir.

$$\Delta S_H = -\frac{Q_{in}}{T_H} \quad \text{Entropy changes of hot and cold reservoirs}$$

$$\Delta S_C = \frac{Q_{out}}{T_C}$$

$$\Delta S_{total} = \Delta S_H + \Delta S_C = -\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_C}$$

$\Delta S_{total} \geq 0$  Second Law:

$$\therefore -\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_C} \geq 0$$

Combining with the First Law expression:

$$-\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_C} \geq 0$$

$$Q_{out} = Q_{in} - W$$

$$\therefore -\frac{Q_{in}}{T_H} + \frac{Q_{in} - W}{T_C} \geq 0$$

$$\therefore -\frac{1}{T_H} + \frac{1 - \frac{W}{Q_{in}}}{T_C} \geq 0$$

$$-\frac{T_C}{T_H} + 1 - \frac{W}{Q_{in}} \geq 0$$

Define engine efficiency:

$$\eta = \frac{W}{Q_{in}}$$

$$\therefore -\frac{T_C}{T_H} + 1 - \eta \geq 0$$

$$\therefore \eta \leq 1 - \frac{T_C}{T_H}$$

So since the Carnot engine has efficiency

$$\eta = 1 - \frac{T_C}{T_H}$$

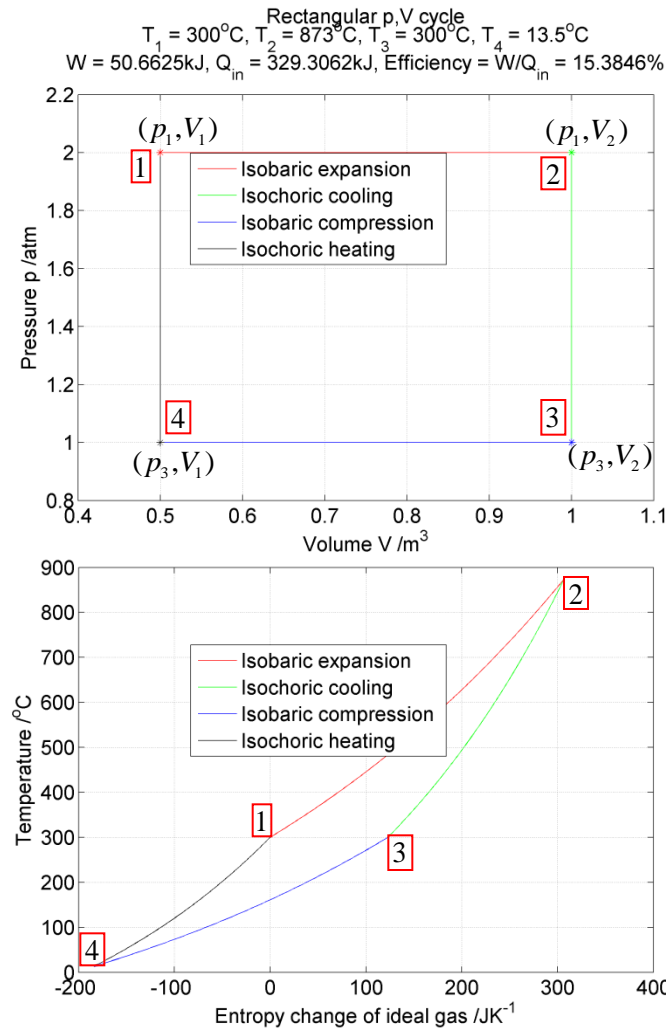
*this is as efficient as thermodynamics allows, so the Carnot cycle is (one example\*) of the most efficient heat engine possible.*

### Notes on reversibility

A reversible heat engine is one which is assumed to operate at *thermodynamic equilibrium* at all times. The ideal gas equations, and associated relationships, hold and there are *no losses* due to friction etc. In other words, the differential form of the First Law holds at all times; i.e. where changes  $dU$  in internal energy are fully accounted for by heat change  $dQ$  and work done  $dW = -pdV$ . This means that there is *no net internal energy and indeed entropy change over the complete cycle*. This means the 'ideal' cycle could be run in reverse without breaking the Second Law, since a *zero net entropy change is permitted*.



## Heat Engines - Rectangular $p, V$ cycle



Assume we have  $n$  moles of ideal gas, none of which are lost in the process. **Input parameters** are:

$T_1$  Gas temperature at position 1 in the cycle

$p_1$  Pressure at position 1 in the cycle

$p_3$  Pressure at position 3 in the cycle

$V = V_1$  Volume of gas at position 1,4 in the cycle

$V = V_2$  Volume of gas at position 2,3 in the cycle

Note Carnot efficiency for this heat engine would be

$$\eta = 1 - \frac{13.5 + 273}{873 + 273} = 75\%$$

### Between positions 1 and 2

$$p = p_1$$

$$p_1 V_1 = nRT_1 \Rightarrow n = \frac{p_1 V_1}{RT_1}$$

$$Q_{1,2} = nMc_p (T_2 - T_1) \quad \text{Heat input to gas}$$

$$W_{1,2} = p_1 (V_2 - V_1) \quad \text{Work done by gas}$$

$$\Delta S_{1,2} = \int_{T_1}^{T_2} nMc_p \frac{dT}{T} = nMc_p \ln \left( \frac{T_2}{T_1} \right)$$

### Between positions 2 and 3

$$V = V_2$$

$$p_1 V_2 = nRT_2 \Rightarrow T_2 = \frac{p_1 V_2}{nR}$$

$$Q_{2,3} = nMc_v (T_2 - T_3) \quad \text{Heat output from gas}$$

$$W_{2,3} = 0 \quad \text{Work done by gas}$$

$$\Delta S_{2,3} = \int_{T_2}^{T_3} nMc_v \frac{dT}{T} = nMc_v \ln \left( \frac{T_3}{T_2} \right)$$

### Net heat input

$$Q_{\text{in}} = Q_{1,2} + Q_{4,1}$$

$$Q_{\text{in}} = nMc_p (T_2 - T_1) + nMc_v (T_1 - T_4)$$

$$Q_{\text{in}} = \frac{nM}{nR} c_p (p_1 V_2 - p_1 V_1) + \frac{nM}{nR} c_v (p_1 V_1 - p_3 V_1)$$

$$Q_{\text{in}} = \frac{M}{R} \left\{ p_1 c_p (V_2 - V_1) + V_1 c_v (p_1 - p_3) \right\}$$

$$Q_{\text{in}} = \frac{\gamma}{\gamma - 1} p_1 (V_2 - V_1) + \frac{V_1}{\gamma - 1} (p_1 - p_3)$$

### Between positions 3 and 4

$$p = p_3$$

$$p_3 V_2 = nRT_3 \Rightarrow T_3 = \frac{p_3 V_2}{nR}$$

$$Q_{3,4} = nMc_p (T_3 - T_4) \quad \text{Heat output from gas}$$

$$W_{3,4} = -p_3 (V_2 - V_1) \quad \text{Work done by gas}$$

$$\Delta S_{3,4} = \int_{T_3}^{T_4} nMc_p \frac{dT}{T} = nMc_p \ln \left( \frac{T_4}{T_3} \right)$$

### Between positions 4 and 1

$$V = V_1$$

$$p_3 V_1 = nRT_4 \Rightarrow T_4 = \frac{p_3 V_1}{nR}$$

$$Q_{4,1} = nMc_v (T_1 - T_4) \quad \text{Heat input to gas}$$

$$W_{4,1} = 0 \quad \text{Work done by gas}$$

$$\Delta S_{4,1} = \int_{T_4}^{T_1} nMc_v \frac{dT}{T} = nMc_v \ln \left( \frac{T_1}{T_4} \right)$$

### Net work done by gas

$$W = W_{1,2} + W_{2,3} + W_{3,4} + W_{4,1}$$

$$W = p_1 (V_2 - V_1) - p_3 (V_2 - V_1)$$

$$W = (p_1 - p_3)(V_2 - V_1)$$

### Engine efficiency

$$\eta = \frac{W}{Q_{\text{in}}} = \frac{(p_1 - p_3)(V_2 - V_1)}{\frac{\gamma}{\gamma - 1} p_1 (V_2 - V_1) + \frac{V_1}{\gamma - 1} (p_1 - p_3)}$$

$$\eta = \left[ \frac{1}{\gamma - 1} \left\{ \frac{\gamma p_1}{p_1 - p_3} + \frac{V_1}{(V_2 - V_1)} \right\} \right]^{-1}$$

$$\frac{T_2}{T_1} = \frac{V_2}{V_1}$$

$$\frac{T_3}{T_2} = \frac{p_3}{p_1}$$

$$\frac{T_4}{T_3} = \frac{V_1}{V_2}$$

$$\frac{T_1}{T_4} = \frac{p_1}{p_3}$$

$$\gamma = \frac{c_p}{c_v} = 1 + \frac{2}{\alpha}$$

$$c_v = \frac{1}{2} \frac{\alpha R}{M}$$

$$c_v = \frac{R}{M} \frac{1}{\gamma - 1}$$

$$c_p = \frac{R}{M} \frac{\gamma}{\gamma - 1}$$

## Heat Engines – The Otto cycle

The **Otto Cycle** is the basis of spark-ignition piston engine, which is essentially how a typical petrol driven engine operates.

### Positions 0-1:

Air is drawn into piston/cylinder arrangement at constant pressure.

### Process 1-2

Adiabatic (isentropic) compression of the air via a piston.

### Process 2-3

Constant-volume heat transfer to the working gas from an external source while the piston is at maximum compression. This process is intended to represent the ignition of the fuel-air mixture and the subsequent rapid burning.

### Process 3-4

Adiabatic (isentropic) expansion (power stroke).

### Process 4-1

Constant-volume process in which heat is rejected from the air while the piston is at maximum expansion.

### Process 1-0

Air is released to the atmosphere at constant pressure.

Assume we have  $n$  moles of ideal gas, none of which are lost in the process. **Input parameters** are:

$p_1$  Pressure of gas at position 1 in the cycle

$p_3$  Pressure of gas at position 3 in the cycle

$V_1$  Volume of gas at position 1 in the cycle

$V_2$  Volume of gas at position 2 in the cycle

$T_1$  Temperature of gas at position 1 in the cycle

$$\gamma = \frac{c_p}{c_v} = 1 + \frac{2}{\alpha}$$

$$c_v = \frac{1}{2} \frac{\alpha R}{M}$$

$$c_v = \frac{R}{M} \frac{1}{\gamma - 1}$$

$$c_p = \frac{R}{M} \frac{\gamma}{\gamma - 1}$$

### Between positions 1 and 2

$$p_1 V_1 = nRT_1 \quad \therefore n = \frac{p_1 V_1}{RT_1}$$

$$pV^\gamma = p_1 V_1^\gamma \quad \therefore p = p_1 \left( \frac{V_1}{V} \right)^\gamma$$

$$W_{1,2} = \frac{p_1 V_1}{\gamma - 1} \left( 1 - \left( \frac{V_1}{V_2} \right)^{\gamma-1} \right)$$

$$Q_{1,2} = 0, \quad \Delta S_{1,2} = 0$$

-ve since work is being done on the gas

### Between positions 2 and 3

$$V = V_2$$

$$p_2 V_2 = nRT_2 \Rightarrow T_2 = \frac{p_2 V_2}{nR}$$

$$p_3 V_2 = nRT_3 \Rightarrow T_3 = \frac{p_3 V_2}{nR}$$

$$Q_{2,3} = nMc_v (T_3 - T_2) \quad \text{Heat input to gas via spark ignition}$$

$$W_{2,3} = 0$$

$$\Delta S_{2,3} = \int_{T_2}^{T_3} nMc_v \frac{dT}{T} = nMc_v \ln \left( \frac{T_3}{T_2} \right)$$

### Between positions 3 and 4

$$p_4 V_1 = nRT_4 \quad \therefore T_4 = \frac{p_4 V_1}{nR}$$

$$pV^\gamma = p_3 V_2^\gamma \quad \therefore p = p_3 \left( \frac{V_2}{V} \right)^\gamma$$

$$W_{3,4} = \frac{p_3 V_2}{\gamma - 1} \left( 1 - \left( \frac{V_2}{V_1} \right)^{\gamma-1} \right)$$

$$Q_{3,4} = 0, \quad \Delta S_{3,4} = 0$$

Work done by gas

### Between positions 4 and 1

$$V = V_1$$

$$Q_{4,1} = nMc_v (T_4 - T_1) \quad \text{Heat output via exhaust}$$

$$W_{4,1} = 0$$

$$\Delta S_{4,1} = \int_{T_4}^{T_1} nMc_v \frac{dT}{T} = nMc_v \ln \left( \frac{T_1}{T_4} \right)$$

To complete the cycle

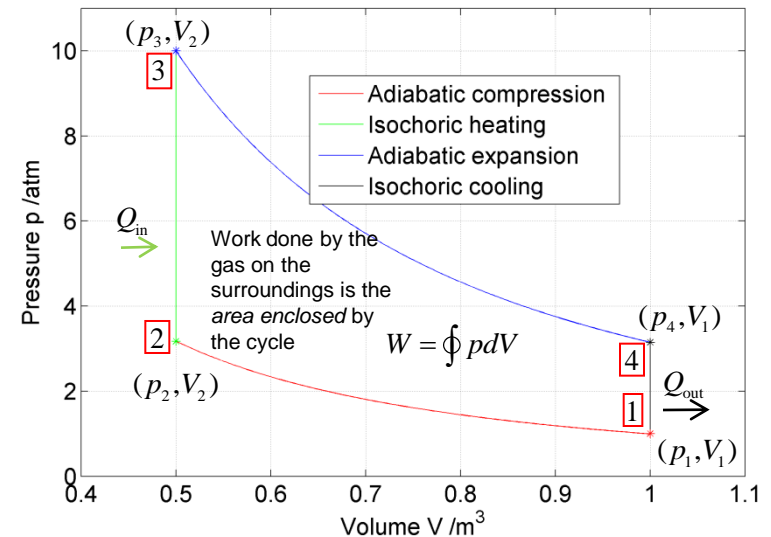
$$p_2 V_2^\gamma = p_1 V_1^\gamma$$

$$\therefore p_2 = p_1 \left( \frac{V_1}{V_2} \right)^\gamma$$

$$p_3 V_2^\gamma = p_4 V_1^\gamma$$

$$\therefore p_4 = p_3 \left( \frac{V_2}{V_1} \right)^\gamma$$

Otto cycle  
 $T_1 = 20^\circ\text{C}$ ,  $T_2 = 192.1085^\circ\text{C}$ ,  $T_3 = 1192^\circ\text{C}$ ,  $T_4 = 649.8922^\circ\text{C}$   
 $W = 191.9293\text{kJ}$ ,  $Q_{in} = 518.6724\text{kJ}$ , Efficiency =  $W/Q_{in} = 37.0039\%$



$$Q_{in} = Q_{2,3} = nMc_v (T_3 - T_2)$$

$$Q_{out} = Q_{4,1} = nMc_v (T_4 - T_1)$$

Nikolaus Otto  
(1832-1891)





Otto engine cont....

Define the  
compression ratio

$$r = \frac{V_1}{V_2}$$

Total work done is:

$$W = \oint p dV$$

$$W = W_{1,2} + W_{3,4}$$

$$W = \frac{p_1 V_1}{\gamma - 1} \left( 1 - \left( \frac{V_1}{V_2} \right)^{\gamma-1} \right) + \frac{p_3 V_2}{\gamma - 1} \left( 1 - \left( \frac{V_2}{V_1} \right)^{\gamma-1} \right)$$

$$W = \frac{V_2}{\gamma - 1} \left\{ p_1 r (1 - r^{\gamma-1}) + p_3 \left( 1 - \frac{1}{r^{\gamma-1}} \right) \right\}$$

$$W = \frac{V_2}{\gamma - 1} \left( 1 - \frac{1}{r^{\gamma-1}} \right) \left\{ p_1 r (1 - r^{\gamma-1}) \left( \frac{r^{\gamma-1}}{r^{\gamma-1} - 1} \right) + p_3 \right\}$$

$$W = \frac{V_2}{\gamma - 1} \left( 1 - \frac{1}{r^{\gamma-1}} \right) \{ p_3 - p_1 r^{\gamma} \}$$

From the previous page:

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right)^{\gamma} \quad T_2 = \frac{p_2 V_2}{nR} \quad T_3 = \frac{p_3 V_2}{nR}$$

$$Q_{in} = nMc_v (T_3 - T_2)$$

$$Q_{in} = \frac{nMc_v}{nR} \left( p_3 V_2 - p_1 \left( \frac{V_1}{V_2} \right)^{\gamma} V_2 \right)$$

$$c_v = \frac{R}{M} \frac{1}{\gamma - 1}$$

$$\therefore \frac{Mc_v}{R} = \frac{1}{\gamma - 1}$$

$$\therefore Q_{in} = \frac{V_2 (p_3 - p_1 r^{\gamma})}{\gamma - 1}$$

Define heat **engine efficiency** as the ratio of Work done by the gas to the heat input

$$\eta = \frac{W}{Q_{in}}$$

$$\eta = \frac{\frac{V_2}{\gamma - 1} \left( 1 - \frac{1}{r^{\gamma-1}} \right) \{ p_3 - p_1 r^{\gamma} \}}{\frac{V_2 (p_3 - p_1 r^{\gamma})}{\gamma - 1}}$$

$$\eta = 1 - \frac{1}{r^{\gamma-1}}$$

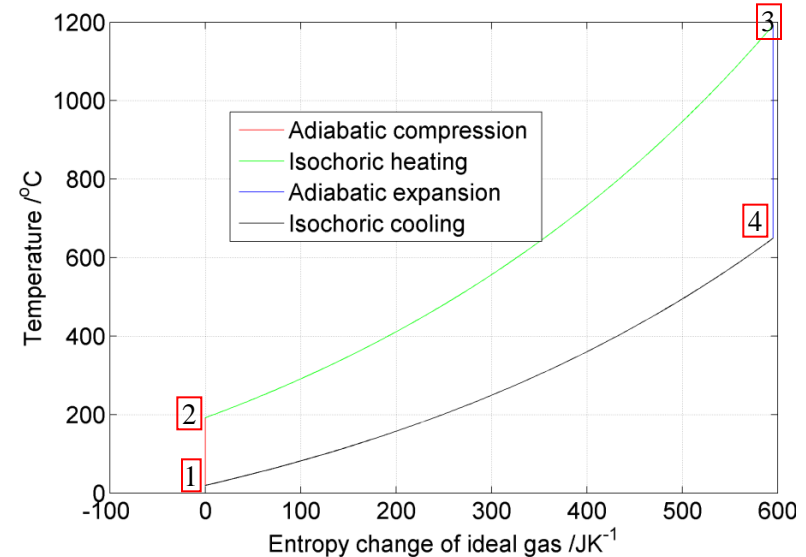
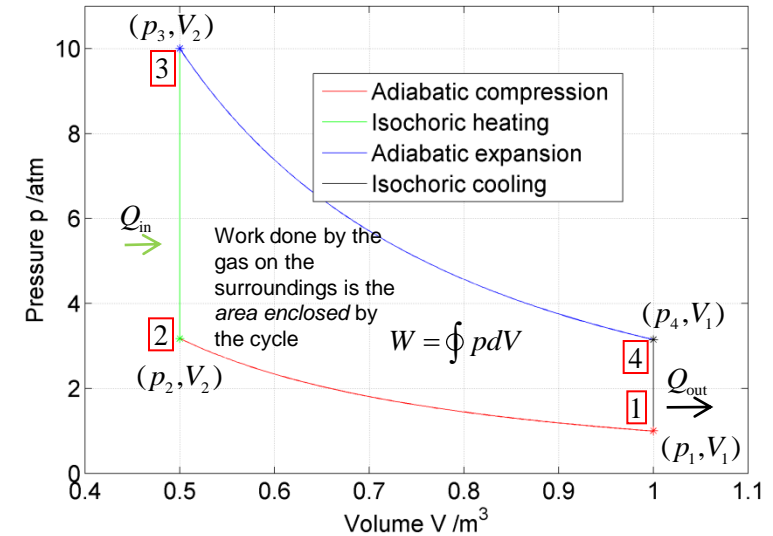
So the Otto Engine efficiency depends *only on the compression ratio, and the ratio of specific heats*

$$\gamma = \frac{c_p}{c_v} = 1 + \frac{2}{\alpha} \quad c_v = \frac{1}{2} \frac{\alpha R}{M}$$

$$c_v = \frac{R}{M} \frac{1}{\gamma - 1}$$

$$c_p = \frac{R}{M} \frac{\gamma}{\gamma - 1}$$

Otto cycle  
 $T_1 = 20^\circ\text{C}$ ,  $T_2 = 192.1085^\circ\text{C}$ ,  $T_3 = 1192^\circ\text{C}$ ,  $T_4 = 649.8922^\circ\text{C}$   
 $W = 191.9293\text{kJ}$ ,  $Q_{in} = 518.6724\text{kJ}$ , Efficiency =  $W/Q_{in} = 37.0039\%$



## Heat Engines – The Diesel cycle

The **Diesel Cycle** is the basis of a diesel engine, which is ubiquitous in transport applications. Unlike petrol-driven engines, diesel variants are more suited to heavy machinery. They can be found powering most ships as well as trucks, buses and cars.

### Positions 0-1:

Air is drawn into piston/cylinder arrangement at constant pressure.

### Process 1-2

Adiabatic (isentropic) compression of the air via a piston.

### Process 2-3

Constant-pressure (isobaric) heat transfer to the working gas from an external source while the piston is at maximum compression. This process is intended to represent the ignition of the fuel-air mixture and the subsequent rapid burning. *This is different from the Otto cycle, which is constant volume (isochoric) heating during this stage.* In the Diesel cycle, the heat generated from air compression is sufficient to ignite introduced fuel vapours. In the Otto cycle a spark plug is used instead to ignite the fuel.

### Process 3-4

Adiabatic (isentropic) expansion (power stroke).

### Process 4-1

Constant-volume process in which heat is rejected from the air while the piston is at maximum expansion.

### Process 1-0

Air is released to the atmosphere at constant pressure.

Assume we have  $n$  moles of ideal gas, none of which are lost in the process. **Input parameters** are:

$p_1$  Pressure of gas at position 1 in the cycle

$V_1$  Volume of gas at position 1 in the cycle

$V_2$  Volume of gas at position 2 in the cycle

$V_3$  Volume of gas at position 3 in the cycle

$T_1$  Temperature of gas at position 1 in the cycle

$$\gamma = \frac{c_p}{c_v} = 1 + \frac{2}{\alpha}$$

$$c_v = \frac{1}{2} \frac{\alpha R}{M}$$

$$c_v = \frac{R}{M} \frac{1}{\gamma - 1}$$

$$c_p = \frac{R}{M} \frac{\gamma}{\gamma - 1}$$

### Between positions 1 and 2

$$p_1 V_1 = nRT_1 \quad \therefore n = \frac{p_1 V_1}{RT_1}$$

$$pV^\gamma = p_1 V_1^\gamma \quad \therefore p = p_1 \left( \frac{V_1}{V} \right)^\gamma$$

$$W_{1,2} = \frac{p_1 V_1}{\gamma - 1} \left( 1 - \left( \frac{V_1}{V_2} \right)^{\gamma-1} \right)$$

$$Q_{1,2} = 0, \quad \Delta S_{1,2} = 0$$

-ve since work is being done on the gas

### Between positions 2 and 3

$$p = p_2$$

$$p_2 V_2 = nRT_2 \Rightarrow T_2 = \frac{p_2 V_2}{nR}$$

$$p_2 V_3 = nRT_3 \Rightarrow T_3 = \frac{p_2 V_3}{nR}$$

$$Q_{2,3} = nMc_p (T_3 - T_2) \quad \text{Heat input to gas during combustion}$$

$$W_{2,3} = p_2 (V_3 - V_2)$$

### Between positions 3 and 4

$$p_4 V_1 = nRT_4 \quad \therefore T_4 = \frac{p_4 V_1}{nR}$$

$$pV^\gamma = p_2 V_3^\gamma \quad \therefore p = p_2 \left( \frac{V_3}{V} \right)^\gamma$$

$$W_{3,4} = \frac{p_2 V_3}{\gamma - 1} \left( 1 - \left( \frac{V_3}{V_1} \right)^{\gamma-1} \right)$$

$$Q_{3,4} = 0, \quad \Delta S_{3,4} = 0$$

Work done by gas

### Between positions 4 and 1

$$V = V_1$$

$$Q_{4,1} = nMc_v (T_4 - T_1) \quad \text{Heat output via exhaust}$$

$$W_{4,1} = 0$$

$$\Delta S_{4,1} = \int_{T_4}^{T_1} nMc_v \frac{dT}{T} = nMc_v \ln \left( \frac{T_1}{T_4} \right)$$

To complete the cycle

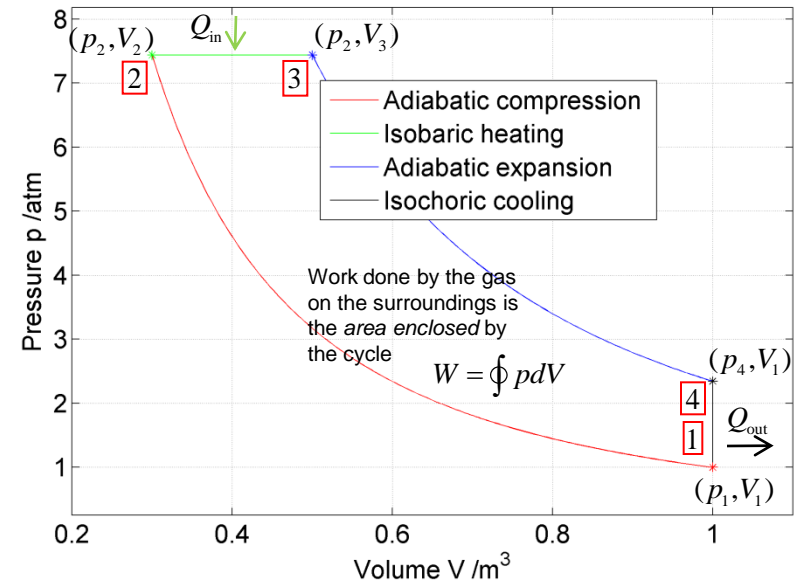
$$p_2 V_2^\gamma = p_1 V_1^\gamma$$

$$\therefore p_2 = p_1 \left( \frac{V_1}{V_2} \right)^\gamma$$

$$p_2 V_3^\gamma = p_4 V_1^\gamma$$

$$\therefore p_4 = p_2 \left( \frac{V_3}{V_1} \right)^\gamma$$

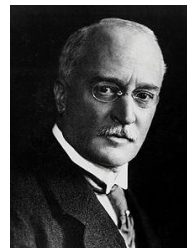
**Diesel cycle**  
 $T_1 = 20^\circ\text{C}$ ,  $T_2 = 380.8128^\circ\text{C}$ ,  $T_3 = 816.6881^\circ\text{C}$ ,  $T_4 = 413.4605^\circ\text{C}$   
 $W = 172.7357\text{kJ}$ ,  $Q_{\text{in}} = 376.835\text{kJ}$ , Efficiency =  $W/Q_{\text{in}} = 45.8386\%$



$$Q_{\text{in}} = Q_{2,3} = nMc_p (T_3 - T_2)$$

$$Q_{\text{out}} = Q_{4,1} = nMc_v (T_4 - T_1)$$

Rudolf Diesel  
(1858-1913)



Diesel engine cont....

Define the compression ratios

$$r = \frac{V_1}{V_2} \quad s = \frac{V_3}{V_2} \quad V_1 > V_3 > V_2 \quad \therefore r > s$$

Total work done is:

$$W = \oint p dV$$

$$W = W_{1,2} + W_{2,3} + W_{3,4}$$

$$W = \frac{p_1 V_1}{\gamma - 1} \left( 1 - \left( \frac{V_1}{V_2} \right)^{\gamma-1} \right) + p_2 (V_3 - V_2) + \frac{p_2 V_3}{\gamma - 1} \left( 1 - \left( \frac{V_3}{V_1} \right)^{\gamma-1} \right)$$

$$W = \frac{p_1 V_2}{\gamma - 1} r (1 - r^{\gamma-1}) + p_1 r^\gamma V_2 (s - 1) + \frac{p_1 r^\gamma V_2}{\gamma - 1} s \left( 1 - \left( \frac{s}{r} \right)^{\gamma-1} \right)$$

$$W = \frac{p_1 V_2}{\gamma - 1} \left\{ r (1 - r^{\gamma-1}) + r^\gamma (s - 1) (\gamma - 1) + r^\gamma s \left( 1 - \left( \frac{s}{r} \right)^{\gamma-1} \right) \right\}$$

$$W = \frac{p_1 V_2}{\gamma - 1} \{ r - r^\gamma + r^\gamma (s - 1) (\gamma - 1) + r^\gamma s - s^\gamma r \}$$

$$W = \frac{p_1 V_2}{\gamma - 1} \{ r (1 - s^\gamma) + r^\gamma (s - 1) (\gamma - 1) + r^\gamma (s - 1) \}$$

$$W = \frac{p_1 V_2}{\gamma - 1} \{ r (1 - s^\gamma) + r^\gamma (s - 1) \gamma \}$$

$$Q_{in} = n M c_p (T_3 - T_2)$$

$$Q_{in} = \frac{n M c_p}{n R} p_1 \left( \frac{V_1}{V_2} \right)^\gamma (V_3 - V_2)$$

$$\gamma = \frac{c_p}{c_v} = 1 + \frac{2}{\alpha} \quad c_v = \frac{1}{2} \frac{\alpha R}{M} \quad \therefore c_p = \gamma c_v = \frac{1}{2} \gamma \frac{\alpha R}{M}$$

$$\therefore \frac{M c_p}{R} = \frac{1}{2} \gamma \alpha = \frac{\gamma}{\gamma - 1}$$

$$\therefore Q_{in} = \frac{\gamma}{\gamma - 1} r^\gamma (s - 1) p_1 V_2$$

From the previous page:

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right)^\gamma = p_1 r^\gamma$$

$$T_3 = \frac{p_2 V_3}{n R} \quad T_2 = \frac{p_2 V_2}{n R}$$

Define heat engine efficiency as the ratio of Work done by the gas to the heat input

$$\eta = \frac{W}{Q_{in}}$$

$$\eta = \frac{\frac{p_1 V_2}{\gamma - 1} \{ r (1 - s^\gamma) + r^\gamma (s - 1) \gamma \}}{\frac{\gamma}{\gamma - 1} r^\gamma (s - 1) p_1 V_2}$$

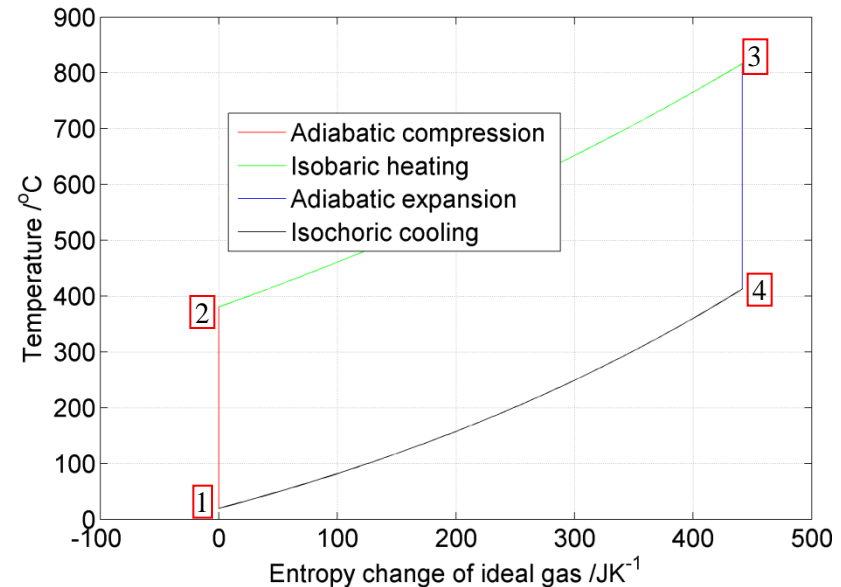
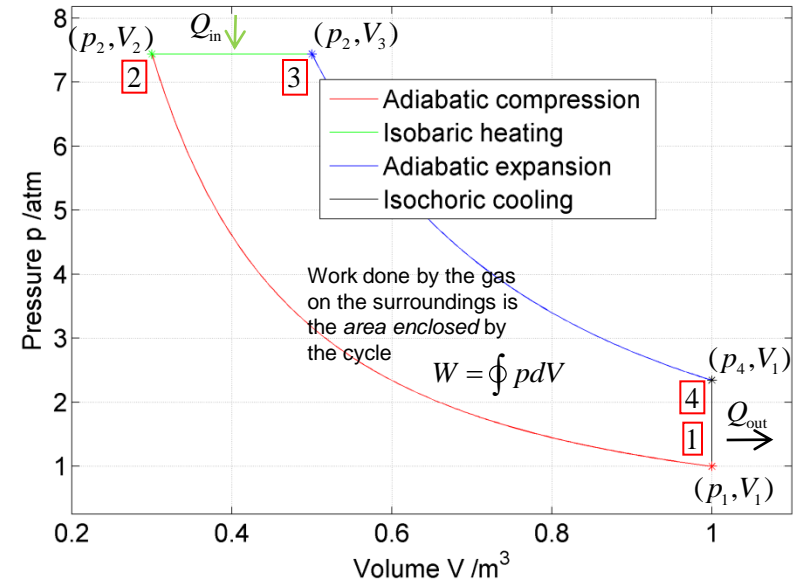
$$\eta = \frac{\{ r (1 - s^\gamma) + r^\gamma (s - 1) \gamma \}}{\gamma r^\gamma (s - 1)}$$

$$\eta = 1 - \frac{r (s^\gamma - 1)}{\gamma r^\gamma (s - 1)}$$

$$\eta = 1 - \frac{1}{r^{\gamma-1}} \left( \frac{s^\gamma - 1}{\gamma (s - 1)} \right)$$

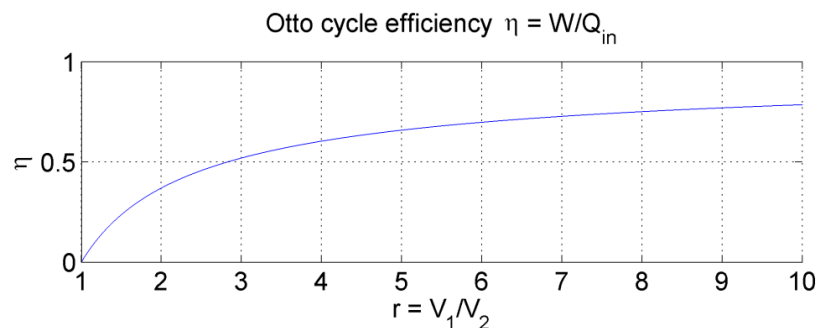
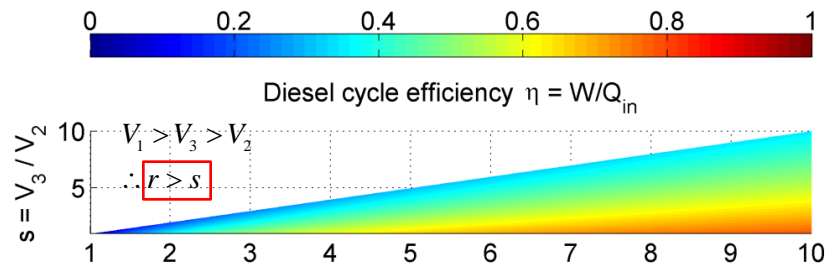
The Diesel engine is typically more efficient than a petrol (Otto) engine since the former works on the basis of self ignition due to high compression. This 'knocking' is undesirable for petrol engines, so a lower  $r$  value is required.

Diesel cycle  
 $T_1 = 20^\circ\text{C}$ ,  $T_2 = 380.8128^\circ\text{C}$ ,  $T_3 = 816.6881^\circ\text{C}$ ,  $T_4 = 413.4605^\circ\text{C}$   
 $W = 172.7357\text{kJ}$ ,  $Q_{in} = 376.835\text{kJ}$ , Efficiency =  $W/Q_{in} = 45.8386\%$



## Comparing Otto and Diesel heat engines

$$r = \frac{V_1}{V_2} \quad s = \frac{V_3}{V_2}$$



$$\eta = \frac{W}{Q_{in}}$$

$$\eta_{diesel} = 1 - \frac{1}{r^{\gamma-1}} \left( \frac{s^\gamma - 1}{\gamma(s-1)} \right)$$

$$\eta_{otto} = 1 - \frac{1}{r^{\gamma-1}}$$

### Diesel

$$W = \frac{p_1 V_2}{\gamma - 1} \left\{ r(1 - s^\gamma) + r^\gamma (s - 1) \gamma \right\}$$

$$Q_{in} = \frac{\gamma}{\gamma - 1} r^\gamma (s - 1) p_1 V_2$$

### Otto

$$W = \frac{V_2}{\gamma - 1} \left( 1 - \frac{1}{r^{\gamma-1}} \right) (p_3 - p_1 r^\gamma)$$

$$Q_{in} = \frac{V_2 (p_3 - p_1 r^\gamma)}{\gamma - 1}$$

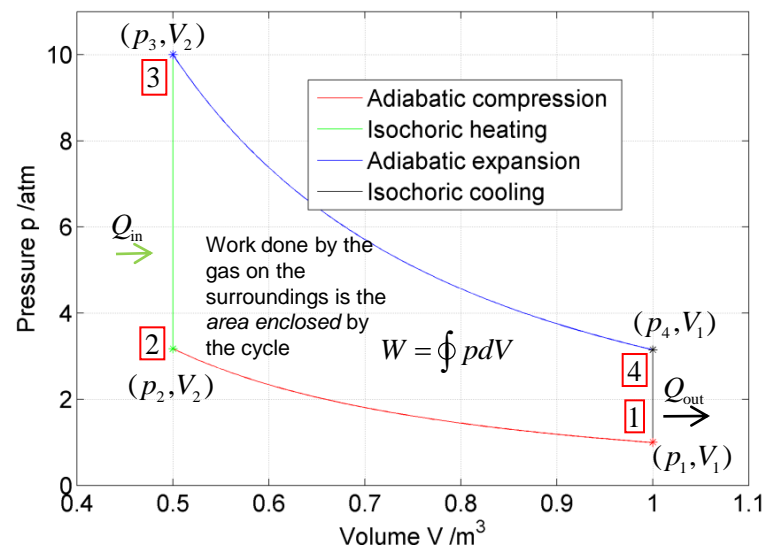
$$\gamma = \frac{c_p}{c_v} = 1 + \frac{2}{\alpha}$$

$$c_v = \frac{1}{2} \frac{\alpha R}{M}$$

$$c_v = \frac{R}{M} \frac{1}{\gamma - 1}$$

$$c_p = \frac{R}{M} \frac{\gamma}{\gamma - 1}$$

Otto cycle  
 $T_1 = 20^\circ\text{C}$ ,  $T_2 = 192.1085^\circ\text{C}$ ,  $T_3 = 1192^\circ\text{C}$ ,  $T_4 = 649.8922^\circ\text{C}$   
 $W = 191.9293\text{kJ}$ ,  $Q_{in} = 518.6724\text{kJ}$ , Efficiency =  $W/Q_{in} = 37.0039\%$



Diesel cycle  
 $T_1 = 20^\circ\text{C}$ ,  $T_2 = 380.8128^\circ\text{C}$ ,  $T_3 = 816.6881^\circ\text{C}$ ,  $T_4 = 413.4605^\circ\text{C}$   
 $W = 172.7357\text{kJ}$ ,  $Q_{in} = 376.835\text{kJ}$ , Efficiency =  $W/Q_{in} = 45.8386\%$

