The operation, and theoretical *efficiency*, of combustion driven piston engines (e.g. diesel or petrol fuelled) can be analysed by considering charges 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.

An *ideal gas* assumes a large[1] number of point particles *colliding elastically*. It *neglects any short-range intermolecular forces resulting from repulsion or attraction due to molecular charges*, and the fact that *molecules have a finite volume* i.e. are not infinitely small. This means a *real gas is not infinitely compressible* whereas an ideal gas has no such limits.

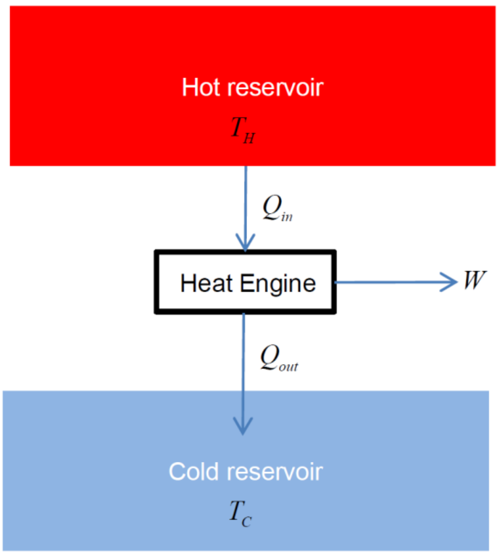
Ideal gas equation: $pV = nRT$. p is gas pressure in Pa (i.e. $\mathrm{Nm^{-2}}$), V is gas volume in $\mathrm{m^3}$, n is the number of moles of gas, T is the absolute temperature in K (Kelvin), and R is the molar gas constant $R = 8.314\mathrm{Jmol^{-1}K^{-1}}$. **273.15K = 0°C.**

The *Kelvin temperature scale* (or "absolute") temperature scale is proportional to the mean kinetic energy of molecules: $U = \frac{1}{2}\alpha nRT$ where α is the number of degrees of freedom of molecular motion. For just x, y, z translation (i.e. no rotation or stretching), $\alpha = 3$. If we neglect intermolecular forces, U is the **internal energy** of a gas.

Special cases of the ideal gas equation: (Note number of moles n is assumed to be constant).
Boyles's Law. At constant temperature, gas pressure is inversely proportional to volume. $p \propto 1/V$ or $pV = \text{constant}$.
Charles' Law. At constant pressure, gas volume is proportional to temperature. $V \propto T$ or $V/T = \text{constant}$.
Pressure law. At constant volume, pressure is proportional to temperature. $p \propto T$ or $p/T = \text{constant}$.

The First and Second Laws of Thermodynamics applied to Heat Engines

Any heat engine is essentially a *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:** $Q_{in} = Q_{out} + W$



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.

Entropy changes ΔS are defined as being the **heat change divided by the absolute temperature**. Hence:

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

The **Second Law** means: $\Delta S_{total} \geq 0 \quad \therefore -\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_C} \geq 0$. Hence by using the First Law: $Q_{out} = Q_{in} - W$, hence:

$$-\frac{Q_{in}}{T_H} + \frac{Q_{in} - W}{T_C} \geq 0 \quad \therefore -\frac{1}{T_H} + \frac{1 - \frac{W}{Q_{in}}}{T_C} \geq 0 \quad \therefore -\frac{T_C}{T_H} + 1 - \frac{W}{Q_{in}} \geq 0 \quad \therefore -\frac{T_C}{T_H} + 1 - \eta \geq 0$$ where **efficiency** $\eta = \frac{W}{Q_{\text{in}}}$.

Hence the efficiency of any heat engine is limited by:

$\eta \leq 1 - \frac{T_C}{T_H}$. A *Carnot* and *Brayton* heat engine has this maximum efficiency.

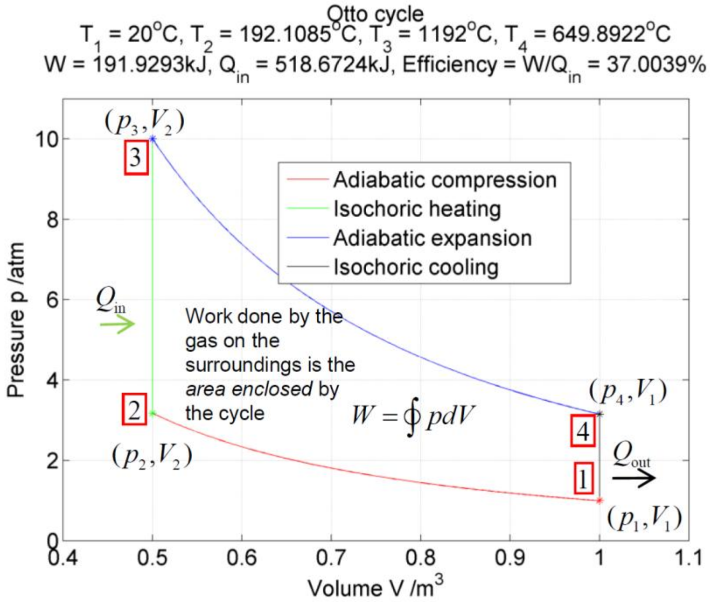
Stefan's law states the power per unit area Φ *radiated* by a body of uniform absolute temperature T is $\Phi = \sigma T^4$ where the *Stefan-Bolzmann constant* $\sigma = 5.67 \times 10^{-8}\mathrm{Wm^{-2}K^{-1}}$. *Wien's law* states the wavelength $\lambda_{\max}$ corresponding to the peak of the Planck 'Black Body' radiation spectrum (i.e. energy per unit frequency, vs frequency) is related to the absolute temperature T of the radiation source by the equation: $\lambda_{\max} T = 2.90 \times 10^{-3}\mathrm{m} \times \mathrm{K}$.

[1] A *mole* of gas contains *Avogadro's number* of particles: $N_A = 6.02 \times 10^{23}$. This is indeed a large number.

Work done compressing an ideal gas: $dW = -pdV$. Hence in differential form, the **First Law** is: $dU = dQ - pdV$. i.e. the change in internal energy equals the heat change of the gas + the work done on the gas. If the gas is compressed, $dV < 0$ which means the work done on the gas is positive. Note the work done *by* the gas (i.e. in a heat engine concept such as a petrol engine) is $-dW = pdV$.

This means the work done by a gas during a heat cycle is the sum of all the pdV work contributions within a *closed loop* of p,V space. i.e. the total work is:

$W = \oint pdV$. This is the *area* enclosed by the loop, as illustrated by the Otto cycle (an ideal petrol engine) on the right.



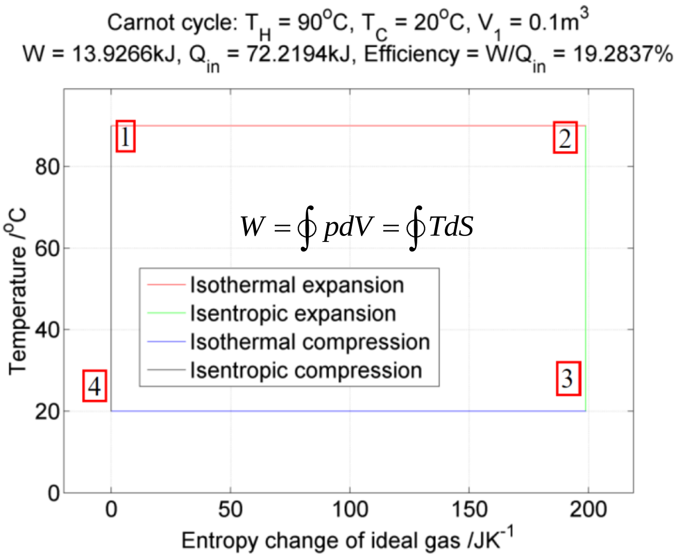
Entropy change $dS = \dfrac{dQ}{T}$, so can also write the

First Law as: $dU = TdS - pdV$

For a complete cycle: $\oint dU = 0$, hence:

$$W = \oint pdV = \oint TdS \text{ .}$$

So the area enclosed by a heat cycle plotted in temperature, entropy space, is also the work done.



Internal energy of an ideal gas:

$U = \frac{1}{2}\alpha nRT$, or using the ideal gas equation:

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

Hence if n is constant:

$dU = \frac{1}{2}\alpha nRdT$ or $dU = \frac{1}{2}\alpha\left(pdV + Vdp\right)$.

Heat engines can be analyzed by considering processes with:

- **constant volume (*isochoric*)**
- **constant pressure (*isobaric*),**
- **constant temperature (*isothermal*)**
- **constant entropy (*adiabatic* or *isentropic* i.e. when no heat is added i.e. $dQ = 0$).**

Constant volume (isochoric). i.e. $dV = 0$. Constant volume heat capacity is: $C_V = \dfrac{dQ}{dT}$.

First law: $\underbrace{\frac{1}{2}\alpha nRdT}_{dU} = \underbrace{C_V dT}_{dQ} - \underbrace{0}_{pdV}$. Hence: $C_V = \frac{1}{2}\alpha nR$. The total amount of heat supplied to m kg of gas is therefore:

$Q = c_V m\Delta T$ for a temperature change ΔT in an isochoric process. The specific heat capacity $c_V = \frac{1}{2}\alpha R/M$ where M is the molar mass of the gas. The molar mass of air is 28.97gmol^{-1}.

Constant pressure (isobaric). i.e. $dp = 0$. Constant pressure heat capacity is: $C_p = \frac{dQ}{dT}$. Since $dp = 0$, the ideal gas equation means $pdV = nRdT$.

First law: $\underbrace{\tfrac{1}{2}\alpha nRdT}_{dU} = \underbrace{C_p dT}_{dQ} - \underbrace{nRdT}_{pdV}$. Hence: $C_p = \left(\tfrac{1}{2}\alpha + 1\right)nR$ or $C_p = C_V + nR$, which the **Mayer Relationship.**

The total amount of heat supplied to m kg of gas is therefore: $Q = c_p m \Delta T$ for a temperature change ΔT in an isobaric process. The specific heat capacity $c_p = \tfrac{1}{2}\alpha R/M$ where M is the molar mass of the gas.

The ratio of specific heats: $\gamma = \frac{c_p}{c_v} = 1 + \frac{2}{\alpha}$.

Constant temperature (isothermal). i.e. $dT = 0$, which means the internal energy is constant and hence: $dU = 0$.

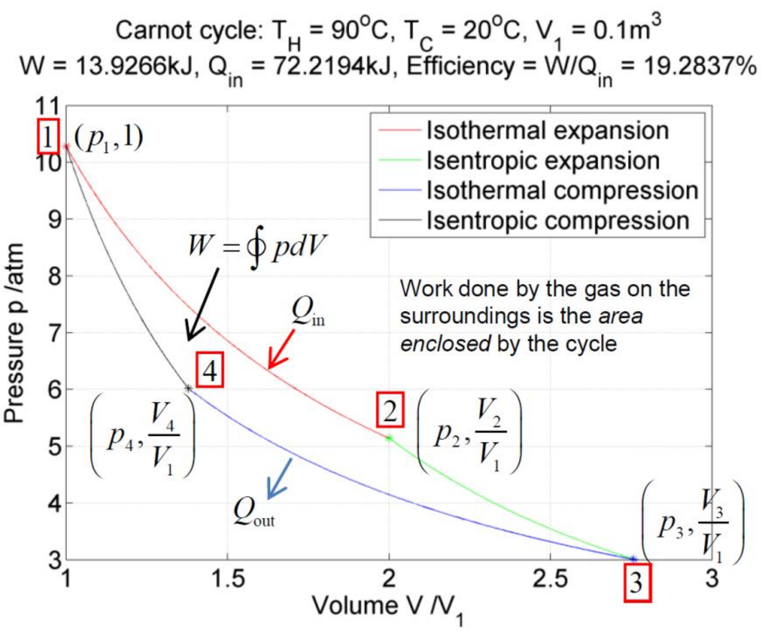
So work done *by* the gas is balanced by heat added: i.e. $dQ = pdV$. Using the ideal gas equation: $p = \frac{nRT}{V}$, the total heat added (and hence the work done) is: $W = Q = nRT\int_{V_1}^{V_2} \frac{1}{V} dV = nRT \ln\left(\frac{V_2}{V_1}\right)$. So if a gas doubles in size, isothermally, the heat added to the gas is $Q = nRT\ln 2$ and $W = nRT\ln 2$ joules of work is done by the gas during its expansion.

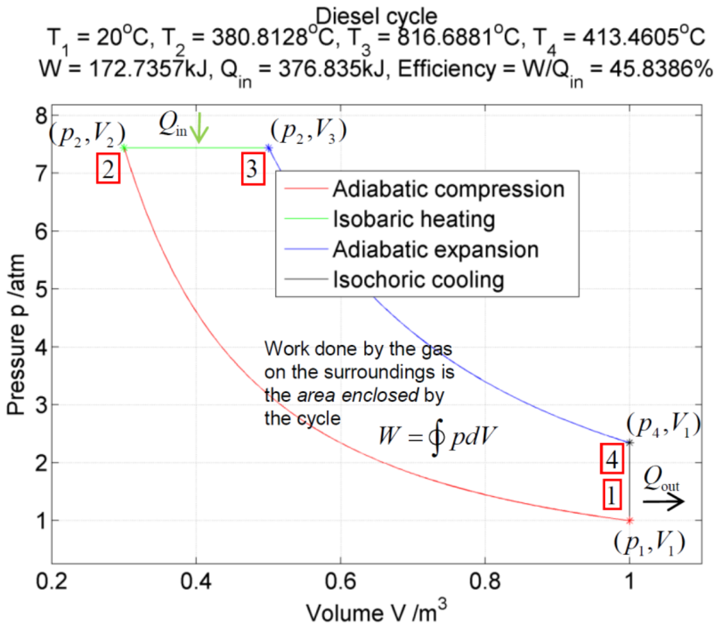
Constant entropy (adiabatic or isentropic). i.e. $dQ = 0$.

First law (using ideal gas equation): $dU = \tfrac{1}{2}\alpha\left(pdV + Vdp\right) = -pdV$ since $dQ = 0$.

$$\therefore \left(1 + \tfrac{2}{\alpha}\right)pdV = -Vdp \Rightarrow \left(1 + \tfrac{2}{\alpha}\right)\frac{dV}{V} = -\frac{dp}{p} \Rightarrow \left(1 + \tfrac{2}{\alpha}\right)\ln V = -\ln p + \text{constant} \Rightarrow \ln\left(pV^{1+\frac{2}{\alpha}}\right) = \text{constant}$$

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





Example ideal heat cycles: A *Carnot cycle* (the most efficient, but difficult to achieve in reality), and a *Diesel cycle.*

Question 1

(i) A spherical weather balloon is filled with air at sea level. The balloon at launch has a radius of 0.600m, and the temperature of the air in the balloon is 15°C. The pressure of the air in the balloon is 101,325Pa, i.e. the same as the ambient air pressure, which makes the balloon a little flaccid. The balloon rises to a height of 11km at the top of the *troposphere*, where the air pressure is 22,632Pa and temperature is -56.5 °C. Assuming the air in the balloon is ideal, and nothing leaks, calculate the radius of the balloon at the top of the troposphere.

(ii) Another weather balloon is launched. This time the air pressure is 101,500Pa and the ambient temperature is 30°C. If the balloon has a radius of 0.800m, how many moles of gas are within it?

(iii) A fully inflated inner tube of a racing bicycle is 120 PSI (pounds per square inch) = 827,400Pa. Assume the (inflated) inner tube has a cross-section diameter of 2.00cm and is fitted round a wheel of diameter 62.2cm. A foot-pump is used to inflate the tyre. Assuming air is drawn into the pump at 1atm = 101,325Pa, and the pump volume for one stroke is 317cm^3, calculate the number of strokes needed to inflate the tyre. Assume the temperature of the air remains constant.

(iv) A cylindrical coffee can of diameter 12.0cm and height 20.0cm contains air at 15°C. The lid is firmly screwed on. If the air pressure was 101,325Pa, how many moles of gas are in the can? The can is now heated such that the air inside reaches 80°C. The can volume does not change (i.e. it is an isochoric process) and it does not leak. Calculate the force /N on the lid of the can (ignore the weight and thickness of the metal lid), and also calculate the heat Q transferred to the air in the can. Assume it is ideal, with $\alpha = 3$.

(v) A heat engine is 66% efficient. If it works by exchanging ideal gases from a 'hot reservoir' of temperature T_H with ambient air at 20°C, calculate the minimum possible value of T_H .

(vi) A diver blows an air bubble of radius 10.0mm at a depth of 42.0m. Calculate the bubble radius at a depth of 5.0m.

Assume water has a uniform density of $\rho = 1025\text{kgm}^{-3}$ and a uniform temperature of 10 °C. The air pressure above the water is 101,325Pa, and take the strength of gravity to be $g = 9.81\text{Nkg}^{-1}$.

(vii) A blue star emits light with a spectral peak at wavelength $\lambda_{\max} = 470\text{nm}$. What is the surface temperature of the star in K? A space probe at one astronomical unit ($1\text{AU} = 1.496 \times 10^{11}\text{m}$) from the centre of the star measures the radiation power per square metre at 5,000W/m^2 . Calculate the radius of the star in m in terms of solar radii. The radius of the Sun is: $R_\odot = 696,340\text{km}$.

(viii) 3.00 moles of gas are compressed at a constant temperature of 42°C. Calculate the work done /J on the gas if the final volume is 20% of the original volume. How much heat is released by the gas in this process?

(ix) In a diesel engine, heat is added to compressed fuel vapor as a result of combustion. Assume this occurs at constant pressure, and the volume expands from 320cm^3 to 500cm^3.

Calculate gas pressures and temperatures, and hence calculate: (a) the moles of gas; (b) the constant pressure heat capacity; (c) work done *by* the expanding gas; (d) the heat input.

Note at 101,325Pa, and 12°C, the volume of the vapor is 1000cm^3. No moles of gas are lost in this process, and assume the gas is ideal, with $\alpha = 3$.

Note for confirmation: the start and finish temperatures for the *isobaric* heating process of the Diesel cycle are: $T_2 = 609\text{K},\ T_3 = 952\text{K}$.

(x) Calculate the entropy change ΔS for the fuel vapors in (ix), as they rise in temperature (and expand) from 609K to 952K. *Hint*: you will need to do an integral. Assume the constant pressure heat capacity is: $C_p = \left(\tfrac{1}{2}\alpha + 1\right) nR$.

(xi) An ideal gas (with $\alpha = 3$) expands *adiabatically* such that it *trebles* in volume. Show that the fraction of the initial internal energy U_0 of the gas, that is done as work W as the gas expands, is: $\dfrac{W}{U_0} = 1 - 3^{-\frac{2}{3}} \approx 0.519$

Question 2

(i) Define all terms in the *Ideal Gas equation* $pV = nRT$. Briefly list the assumptions about the movement of molecules which underpin this equation.

(ii) Draw sketch graphs to illustrate (a) *Charles' Law*, (b) *Boyle's Law*, (c) *Pressure Law.* For each, be clear what quantities are constant.

(iii) A semi-sealed syringe contains 100cm^3 of air. The air pressure is 1.00 atm and the temperature is 298K.

(a) The syringe is doubled in volume. It is found that an extra 20% of the original number of moles of air is drawn in. What is the pressure in the syringe, assuming that the doubling process occurs very slowly?

(b) The original syringe (100cm^3 of air, air pressure is 1atm = 101,325Pa, 298K) is compressed rapidly. 10% of the original number of moles of air leak out, the temperature rises by 10^{o}C, and the pressure trebles. Calculate the new volume of the air in the syringe.

(c) How many molecules of air where originally in the syringe?

Question 3

An overworked *Microsoft Surface Pro* computer reaches a temperature of 42 ^{o}C. Dr French switches it off and notices that it takes 123s to cool to 30 ^{o}C. Ambient temperature is $T_a = 20\,^o\mathrm{C}$.

Assume heat flow from the Surface to the surroundings is via conduction only, and a slight breeze prevents a boundary layer of heat forming round the Surface.

(i) Sketch a graph of how the temperature of the Surface varies with time.

(ii) Calculate how long it will take the Surface to cool to 22 ^{o}C, assuming *Newton's Law of Cooling:* $\frac{dT}{dt} = -k\left(T - T_a\right)$ where k is a positive constant.

(iii) A Surface has dimensions of about 29cm by 20cm. Calculate the maximum radiative power from one of its faces. The Stefan Boltzmann constant is $\sigma = 5.67 \times 10^{-8}\,\mathrm{Wm^{-2}K^{-4}}$.

(iv) A Surface has a mass of about 0.77kg and is made of metal with a specific heat capacity of about 910J/kg/K (i.e. assuming it is mostly aluminum). Work out the average power of heat loss during the 123s cooling period. Compare this to your answer to (iii) and discuss whether you think the assumption of only considering heat conduction is a sensible one.

Question 4

A geostationary satellite faces the Sun, and receives about 1388W/m^2 of solar radiation. The satellite has a mass of $m =$ 1234kg and is, approximately, a solid mass of aluminum, which has a specific heat capacity of $c =$ 900J/kg/K. The radiating surface has an area of about $A = 20\mathrm{m}^2$. In space you can assume that heat transfer is only via radiation, and the spacecraft radiates with power (in W):

$$P_{rad} = A\sigma T^4$$

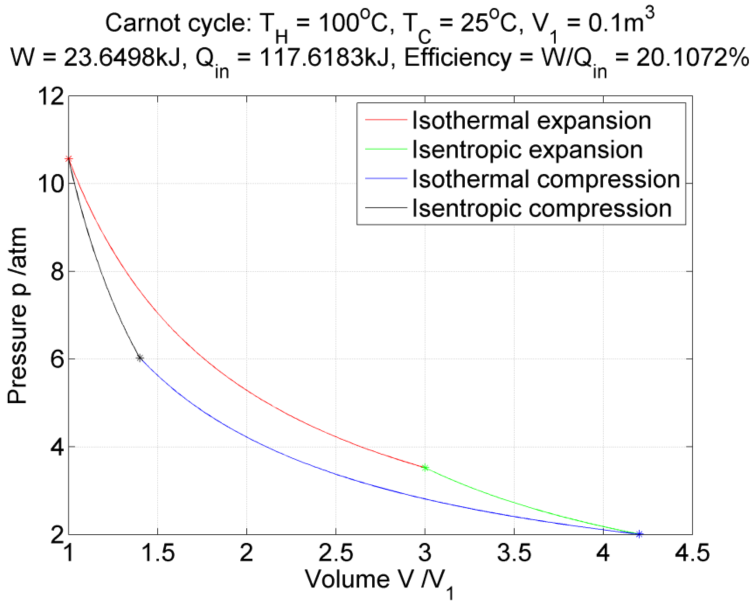
(i) Calculate the temperature /K where the radiation loss equals the power input.

(ii) When the satellite is shadowed from the Sun by the Earth, it cools via radiation. If it is in shadow for 12 hours, calculate the coldest temperature of the satellite in K. Assume it starts with the hottest temperature calculated in part (i).

You will need to firstly explain, and then use the equation: $cm\frac{dT}{dt} = -\sigma T^4$ where *t* is time in seconds.

Question 5

A *Carnot* heat cycle is illustrated by the *p* vs *V* and *T* vs *S* graphs below.



1000g of gas is used with a molar mass of 28.97g/mol.

For the *isentropic* stages $pV^{\frac{5}{3}} = \text{const}$.

(i) Calculate the number of moles *n* of gas used

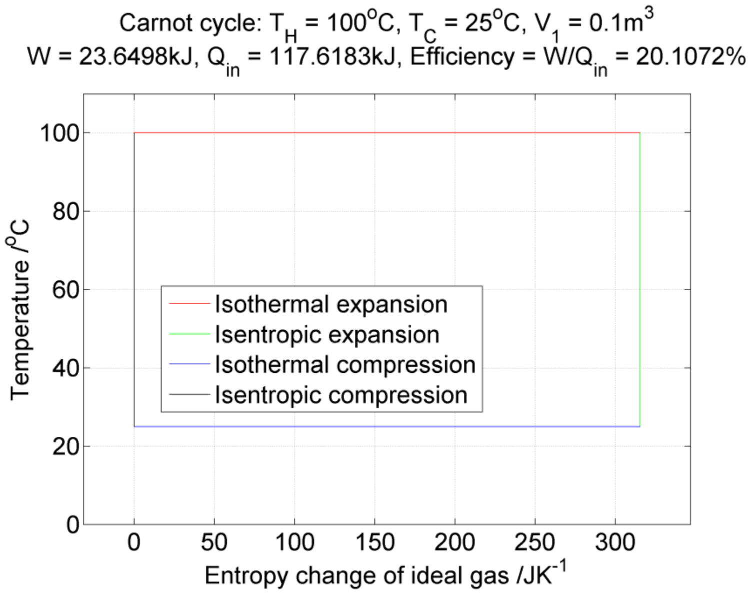
(ii) Explain in words the meaning of each stage of the Carnot cycle.

(iii) Explain why the work done *W* equals:
(a) The area enclosed by the *p* vs *V* graph
(b) The area enclosed by the *T* vs *S* graph

(iv) Explain why the *T,S* graph is *rectangular*

(v) Prove, for an ideal gas undergoing an isothermal expansion from volume V_1 to V_2, the heat added must equal:

$$Q = nRT\ln\left(\frac{V_2}{V_1}\right)$$



(vi) Hence calculate the entropy change during the isothermal stages (it should match what you can estimate from the *T* vs *S* graph).

(vii) Show by calculation that $Q_{in} = 117.6\text{kJ}$, $W = 23.6\text{kJ}$ and that the efficiency is 20.1%

Hint for Q4 (vii): Use the *T,S* graph!

(viii) Calculate (using Kelvin temperatures) $\eta = 1 - \frac{T_C}{T_H}$. What does this, and the answer to (vii) tell you about the efficiency of the Carnot engine?

EXTENSION FOR THE KEEN:

Use the p,V graph, match the pressures and volumes and show that: $V_3 = V_2\left(\frac{T_H}{T_C}\right)^{\frac{1}{\frac{5}{3}-1}}$, $V_4 = V_1\left(\frac{T_H}{T_C}\right)^{\frac{1}{\frac{5}{3}-1}}$ and then complete (vii) *without* using the *T* vs *S* graph.

Question 6

The gases in the pistons of a Ford 1.0 litre *Ecoboost* petrol engine can be modeled using an *Otto* heat cycle. An Otto cycle consists of:

- Stages 1 to 2: *Adiabatic* compression
- Stages 2 to 3: *Isochoric* heating (where heat Q_{in} is absorbed)
- Stages 3 to 4: *Adiabatic* expansion
- Stages 4 to 1: *Isochoric* cooling (where heat Q_{out} is removed from the system in the exhaust)

The isochoric heating stage models the rapid increase in pressure of a gas ignited via a *spark plug*, but without any significant volume change.

The engine parameters are:

- Uncompressed gas at position 1: $V_1 = 1{,}000\text{cm}^3$, $p_1 = 101{,}325\text{Pa}$, $T_1 = 293\text{K}$
- High pressure at position 3: $p_3 = 100\,p_1$ Compressed volume at position 2: $V_2 = 100\text{cm}^3$
- Molar mass of gas: $M = 28.966\text{gmol}^{-1}$. Degrees of freedom of gas: $\alpha = 3$.
- Engine rotation rate: 6,500RPM.

(i) Showing full workings, confirm the following (for one Otto cycle).

Number of moles of gas in engine	0.042
Ratio of specific heats gamma	1.667
Constant volume specific heat capacity /Jkg^-1K^-1	431
Constant pressure specific heat capacity /Jkg^-1K^-1	718

Outputs

Heat input during isochoric heating /kJ	0.814
Heat output during isochoric cooling /kJ	0.175
Total work done by gas on surroundings /kJ	0.639
Efficiency (work done / heat input)	0.785

Theoretical efficiency	0.785

Make sure you make an accurate sketch (or plot using Excel/MATLAB/Python) of the Otto cycle on a (p,V) graph.

Show that the total output power of the engine is about 69.2kW per cylinder.

(ii) Prove that the *efficiency* of an Otto cycle is: $\eta = \dfrac{W}{Q_{in}} = 1 - \left(\dfrac{V_1}{V_2}\right)^{1-\gamma}$ where $\gamma = c_p / c_V$.

Note that the theoretical efficiency is likely to be somewhat of an overestimate. Real petrol engines are more like 20% efficient.

Question 7

The gases in the pistons of the enormous MAN B&W 12S90ME-C Mark 9.2 diesel engine (one of *fourteen* cylinders powering the MV CSCL Globe, the largest container ship in 2014) can be modeled using an *Diesel* heat cycle. An Diesel cycle consists of:

- Stages 1 to 2: *Adiabatic* compression
- Stages 2 to 3: *Isobaric* heating (where heat Q_{in} is absorbed)
- Stages 3 to 4: *Adiabatic* expansion
- Stages 4 to 1: *Isochoric* cooling (where heat Q_{out} is removed from the system in the exhaust)

The idea is that diesel fuels spontaneously ignite (and hence combust) when compressed sufficiently. Therefore diesel engines *don't* require a spark plug like a petrol engine.

The diesel engine parameters are:

- Uncompressed gas at position 1: $V_1 = 1{,}820{,}000\text{cm}^3$, $p_1 = 101{,}325\text{Pa}$, $T_1 = 25^\circ\text{C}$
- Compressed volume at position 2: $V_2 = 79{,}000\text{cm}^3$
- Compressed volume at position 3 after isobaric heating: $V_3 = 170{,}000\text{cm}^3$
- Molar mass of gas: $M = 28.966\text{gmol}^{-1}$. Degrees of freedom of gas: $\alpha = 3$.
- Engine rotation rate: 84 RPM.

(i) Showing full workings, confirm the following (for one Diesel cycle).

Number of moles of gas in engine	74
Ratio of specific heats gamma	1.667
Constant volume specific heat capacity /Jkg^-1K^-1	431
Constant pressure specific heat capacity /Jkg^-1K^-1	718

Outputs

Heat input during isobaric heating /kJ	4267
Heat output during isochoric cooling /kJ	710
Total work done by gas on surroundings /kJ	3557
Efficiency (work done / heat input)	0.834

Theoretical efficiency	0.834

Make sure you make an accurate sketch (or plot using Excel/MATLAB/Python) of the Diesel cycle on a (p,V) graph.

Show that the total output power of the engine is about 69,700kW for all fourteen cylinders working simultaneously.

(ii) Prove that the *efficiency* of an Diesel cycle is: $\eta = \frac{W}{Q_{in}} = 1 - \frac{1}{r^{\gamma-1}}\left(\frac{s^\gamma - 1}{\gamma(s-1)}\right)$ where $\gamma = c_p / c_V$,

$r = \frac{V_1}{V_2}$, $s = \frac{V_3}{V_2}$.

Note that the theoretical efficiency is likely to be somewhat of an overestimate. Real diesel engines are more like 40% efficient.