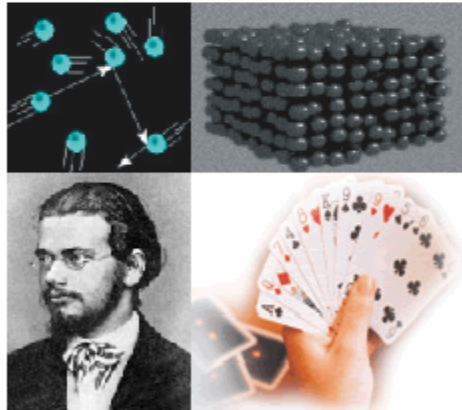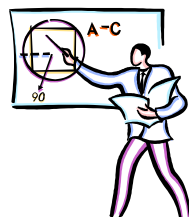# Introduction to Thermodynamics and Kinetics

F31ST1

School of Physics & Astronomy

Spring Semester 02-03

Lecture Notes
Set 4c: Heat engines and
the Carnot cycle

Introduction to heat engines

In the following sections the fundamental operating principles of the *ideal* heat engine, the Carnot engine, will be discussed. This ideal engine has the highest possible efficiency, i.e. no engine can perform better than the Carnot engine in terms of converting heat energy into useful mechanical work. However, even for the Carnot engine, we'll find that the efficiency is not 100% - we can never convert heat entirely into work. As we'll see, this is fundamentally due to the 2nd law of thermodynamics.

4.7 Reversible and Irreversible Processes

The Carnot engine involves *reversible* processes and in the discussion that follows we'll spend a considerable amount of time ensuring that irreversibility is eliminated from the Carnot cycle. A reversible process - and the Carnot engine itself – is an *idealisation.* Irreversible processes play a role in any *real* engine. There are two key types of irreversible process that we need to be sure to eliminate when we construct a Carnot cycle:

(i)   ***Friction***. We will construct a simple engine comprising a piston, gas and container. Friction must be eliminated because it will convert the kinetic energy of the piston's motion into heat energy and thus increase the total entropy of the Universe ($dS = dQ/T$).

(ii)   ***Thermal energy transfer with a large temperature difference.*** As we covered in some detail in Section 3 of the notes, thermal energy transfer between two objects increases the total entropy of the Universe. If we bring two blocks of material together, *the smaller the original temperature difference between the blocks the closer to a reversible process we get* (Coursework 7). Hence, to ensure a reversible, ideal Carnot cycle there can be no large temperature differences during transfer of heat energy.
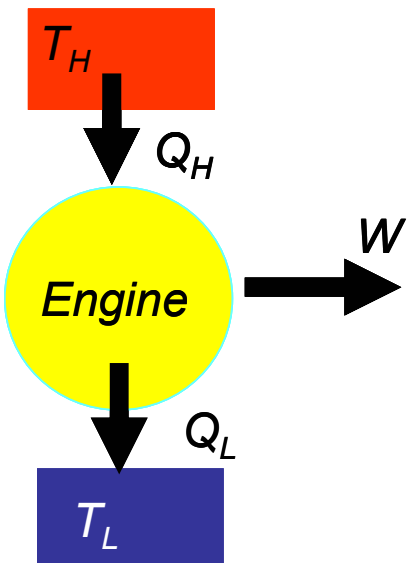

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You might then ask why we can't use very small temperature differences in the real world to approach a reversible process and thus have very efficient heat engines. The problem is that the rate of heat transfer (heat current) is dependent on the temperature difference:

$$\frac{dQ}{dt} = kA\frac{\Delta T}{\Delta x}$$

where dQ/dt is the rate of heat transfer, k is the thermal conductivity, A is the cross sectional area, and $\Delta T/\Delta x$ is the temperature gradient. If the temperature difference, ΔT, approaches 0 (as it does for a reversible process) then so too does the rate of heat transfer which means that the engine will run incredibly slowly. So, although a reversible engine has maximum efficiency in terms of converting heat to work it operates very, very slowly.

4.8 Efficiency of a reversible heat engine

The key question we will address is: how easily can heat ('disordered' thermal energy) be converted into work? The Kelvin-Planck statement of the 2nd law of thermodynamics may be worded as follows (taken from Grant & Phillips, p.435):

If work is to be obtained from a heat engine by removing heat from a hot reservoir, all of the heat cannot be converted into work.

We'll investigate why this is the case in the following sections. Let's first define what we mean by the efficiency of a (reversible) heat engine. The heat engine shown in Fig. 4.12 takes in heat from a hot reservoir, converts some of that heat into mechanical work, and rejects the remainder into a cold reservoir. The efficiency, η, of the engine is given by:

Fig. 4.12 Schematic illustration of a heat engine.

$$\eta = \frac{|W|}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

(Note that |W| = Q_H − Q_L due to the conservation of energy).

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4.9 The Carnot cycle[†]

The first stage: a reversible isothermal expansion

In addition to our engine (which we take as the piston + ideal gas + container system we've discussed throughout the module), for the first stage of the Carnot cycle we need a heat reservoir so large that extracting energy from it causes a negligible decrease in the reservoir temperature. We will couple the gas engine to this reservoir, the gas will then expand and do work on the surroundings. To have a Carnot engine we must ensure that there are no large temperature differences (otherwise we won't have reversible processes). Hence, before coupling the gas engine to the reservoir we must ensure that the temperature of the engine is only infinitesimally lower than T_H.

When the engine is placed on the reservoir there is a flow of heat into the gas and it reversibly (and isothermally) expands. In the isothermal expansion, the entropy change of the reservoir, $dS_{reservoir}$, is given by the following expression:

Fig. 4.13 A reversible isothermal expansion

$$dS_{reservoir} = -\frac{Q_H}{T_H}$$

where dQ_H is the heat that has flowed into the gas. Note that the entropy change of the reservoir is negative because heat has left the reservoir. The entropy change of the gas is:

$$dS_{gas} = +\frac{Q_H}{T_H}$$

Note that the net change in entropy is 0, as it must be for a reversible process. A potentially confusing issue here is related to the fact that the gas expanded isothermally. Therefore, as this is an ideal gas, there is no change in the internal energy and you might ask how the entropy of the gas can increase. Note that the volume of the gas increases and thus there are more ways to arrange the molecules in the larger volume. It is this volume change that gives rise to the increase in entropy.

At this point a consideration of the 1st law (i.e. conservation of energy) produces the following argument. The expansion was carried out isothermally, therefore $\Delta U = 0$. Hence, from the 1st law $|dQ| = |dW|$ i.e. all the heat has been converted into work. Does this not contradict what was said earlier – it appears that our engine *thus far* is 100% efficient?
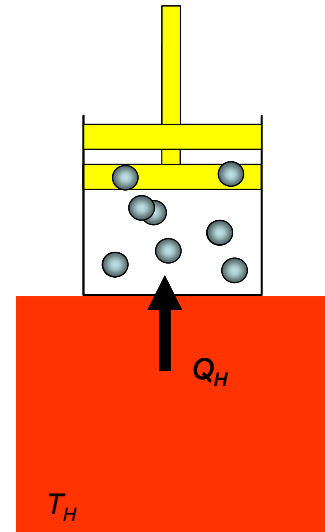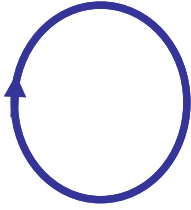

[†] Although in the following we'll focus on the piston + ideal gas + container system that we've discussed in detail throughout this section of the module, it's important to realise that the working substance in a Carnot engine need not be an ideal gas.

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An engine must operate in a cycle

Although the engine thus far is apparently 100% efficient, any engine must operate in a cycle. We need to be able to continually repeat a process with the gas being returned to its initial state at the end of each cycle. So, let's recompress the gas back to its original state and complete the cycle…..

Unfortunately, if we simply carry out a reversible isothermal compression of the gas (i.e. exactly reverse the isothermal expansion) then there is no NET thermal energy transfer and thus no NET work done. Carnot realized that heat cannot be taken in at a single temperature and converted into work *with no other change in the surroundings*.

We need to devise a scheme whereby we can run the engine in a cycle so that the piston is raised to do useful work but where it requires less work to return the piston to its original position (and thus return the gas to its original state). To do this we need to cool the gas.

Completing the cycle

However, to cool the gas we need a second, cold reservoir. Also, bear in mind that we're constructing a *reversible* heat engine. Just as we needed to ensure that the difference between the temperature of the engine and that of the heat reservoir was infinitesimally small in the reversible expansion at the start of the cycle, we'll need to ensure that we don't have a large temperature difference when we couple the engine to the cold reservoir. If we wish to reversibly compress the gas we must ensure that its temperature is almost exactly that of the cooler reservoir *before* we make contact with the reservoir. To do this a reversible adiabatic expansion is required (to cool the gas) before connecting to the cold reservoir.
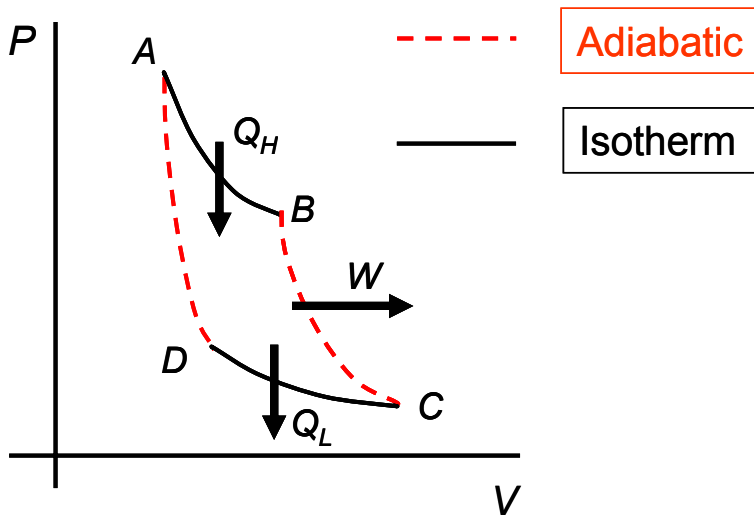
Steps in the Carnot cycle

The entire cycle we need to follow is:

1. An isothermal expansion in contact with a reservoir at temperature T_H
2. An adiabatic expansion (no contact with reservoir) – the temperature of the gas falls to T_L.
3. An isothermal compression in contact with the reservoir at T_L.
4. An adiabatic compression (no contact with reservoir) to increase the temperature of the gas to just below T_H.

See the slides for Lecture 16 for an animation of this process.

> **NOTES**

The Carnot cycle represented on a PV diagram.

Fig. 4.14 *A PV diagram for the Carnot cycle*

A PV diagram for the Carnot cycle is shown in Fig. 4.14. Note that the gas is taken cyclically round a loop involving an isothermal and adiabatic expansion followed by an isothermal and adiabatic compression. In CW Set 8 you were asked to calculate Q, W and ΔU for each step of the cycle. In addition, you should note that there are a number of questions in previous examination papers for the Heat and Properties of Matter course that are concerned with cyclic processes such at that shown in Fig.4.14. You should attempt these questions.

? *In the isothermal expansion of the gas (step A to B in Fig. 4.14), the change in internal energy is?*

? *If the volume at point B is twice that at point A, derive an expression for the work done in the isothermal expansion.*

? *...hence the value of Q_H is?*

NOTES *(see the slides for lecture 16 for the answers to the questions above)*

Functions of State

The internal energy is a *function of state* i.e. it is path independent which in turn means that the net change in internal energy in a reversible cycle is 0. This must be the case because we return the gas to its original state. However, heat and work are NOT functions of state – the net changes in these quantities around a Carnot cycle (or another cyclic process involving adiabatic and isothermal changes) will not be 0. It is also important to realise that entropy is a function of state. As for the internal energy, the net change in entropy around the Carnot cycle shown in Fig. 4.14 is 0. It is because entropy is a function of state and, therefore, changes in entropy are path independent that we could calculate the change in entropy for the process discussed in Section 3.8 of the notes.

Entropy in a cycle of the Carnot engine

The entropy change of the high temperature reservoir is $dS_{high} = -Q_H/T_H$. The entropy change of the low temperature reservoir is $dS_{low} = +Q_L/T_L$ (positive entropy change because heat is rejected from the engine *into* the lower temperature reservoir). The Carnot engine is a reversible engine and therefore there can be no change in the total entropy of the Universe, so:

$$-\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \Rightarrow \frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

Using the equation above and the expression for η, the efficiency of a reversible heat engine, given earlier ($\eta = \frac{|W|}{Q_H} = 1 - \frac{Q_L}{Q_H}$) we can show that no engine running between the temperatures T_L and T_H can be more efficient than a reversible engine.

A Carnot engine has the maximum possible efficiency

Imagine an inventor claims to have made a cyclic engine that has a higher efficiency than $1 - \frac{Q_L}{Q_H}$ when running between T_L and T_H. In that case, for a given Q_H the engine must reject a *smaller* amount of heat Q_L into the lower reservoir (so that η is closer to 1). This would mean that:

$$-\frac{Q_H}{T_H} + \frac{Q_L}{T_L} < 0$$

However, this cannot be the case because the total entropy of the Universe would decrease and this violates the 2nd law of thermodynamics. Hence, no other engine can be more efficient than a reversible (i.e. Carnot) engine.

Running a reversible heat engine in reverse: a refrigerator

If we run the Carnot cycle in reverse the net result will be that we do work on the gas. However, *we will also have transferred heat from the low temperature reservoir to the high temperature reservoir*! Hence, by doing work on the gas we can cause heat to flow from cold to hot. This is not a violation of the 2nd law of thermodynamics because, although heat is flowing in a direction contrary to our expectations, the total entropy increase associated with the entire cycle is positive.

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4. 10 Maxwell's demon

In Lecture 17 I'll spend a little time discussing Maxwell's demon. This is not part of the examinable syllabus for the Thermal & Kinetic module but for those of you who are interested in learning about this creature and its impact on the 2nd law of thermodynamics, I've provided a couple of links on the module website to relevant web pages. You should also consult the slides for Lecture 17.

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4. 11 Phase diagrams and real gases

In the final part of Section 4 of the module we'll briefly consider systems that are not ideal gases, i.e. real gases and other substances which exhibit changes of phase. When discussing phase diagrams and real gases (including the van der Waals equation of state) I will follow p. 460 – p. 463 of Grant & Phillips. No material other than that covered in Grant & Phillips will be introduced. You may find it helpful to consult the slides for Lecture 17 which are available on the module website (www.nottingham.ac.uk/~ppzpjm).

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