Department of Physics, Durham University

Foundations of Physics 2B/3C 2019-2020

THERMODYNAMICS

Among the hundreds of laws that describe the universe, there lurks a might handful. These are the laws of thermodynamics, which summarise the properties of energy and its transformation.............When in due course you emerge.......with your brain more sinewy and exercised, you will have a profound understanding of the role of energy in the world. In short, you will know what drives the Universe.

Peter Atkins, The laws of thermodynamics

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1. Motivation

Thermodynamics is a really interesting subject and it is applications in many areas of physics. The second law is one of the most fundamental laws of science, which determines whether a process will happen even if all conservation laws are obeyed. Indeed, the novelist and Scientist CPE Snow in his 1959 Rede Lecture *The Two Cultures*, given in Cambridge said:

> *A good many times I have been present at gatherings of people who, by the standards of the traditional culture, are thought highly educated and who have with considerable gusto been expressing their incredulity at the illiteracy of scientists. Once or twice I have been provoked and have asked the company how many of them could describe the Second Law of Thermodynamics. The response was cold: it was also negative. Yet I was asking something which is the scientific equivalent of: Have you read a work of Shakespeare's?*

In this course, we will get to see the excitement of this subject, and how a few simple relations and differential equations allows us to work out properties and behaviours of many materials, not just gases, and also how we can look to make engines as efficient as possible to enable us to turn energy into work.

Starting from a few basic properties of materials it allows us to describe how they behave, and in particular we can look at how one thing changes under the influence of something else. The subject emerged before atoms, so deals with bulk properties of materials. These can be thought of as the macroscopic properties of a "black box," paying no interest as to what is inside that box. Whilst useful, this approach is very general, so it can sometimes difficult to see the point as a physicist e.g. it is all well and good having relationships between heat capacities and thermal expansions of materials, but they don't help us understand magnitude and temperature dependence of actual heat capacity for a material. However, when atoms came along we can now open the black box for the microscopic picture. This enriches our understanding, but can quickly become too detailed (1 mole ~ 10^{24} atoms), so we then employ statistical mechanics to look at this more molecular scale, investigating the behaviour of constituent atoms and statistically deriving macroscopic properties. We can now look at bulk properties are looked at in molecular terms. If we can define what is known as a material's Partition function we can then work out all the thermodynamic properties, and the two subjects are inextricably linked!

2. Thermodynamics and Statistical Physics Overview

Thermodynamics deals with properties of matter and changes in these due to the effects of heat and work. It originated in the 19th Century, with engineers' desire to understand heat and heat engines by obtaining the maximum possible work from them as well as to improve their power and efficiency. However, the subject is not only about steam engines, it is much richer. It takes very much a macroscopic approach making observations on bulk materials in a "black box" sort of way Boltzmann and Gibbs developed statistical mechanics to provide methods of describing the underlying microstates of a system. This molecular interpretation immensely enriches the subject. A good understanding of thermal physics is crucial to almost all modern physics and underpins many current day technological challenges.

Thermodynamic Limit and Terminology

Thermodynamic systems contain large numbers of molecules, thereby allowing us to treat macroscopic systems by considering their properties statistically. A mole is defined as the quantity of matter that contains as many objects as exactly 12 g of ^{12}C. The **thermodynamic limit** arises when we are able to ignore small scale fluctuations in the properties of the system. This happens when the system becomes large and the number of particles tends to infinity.

> **Example 2.1 & 2.2**

Thermodynamic systems and states

Thermodynamic systems, the thing that we are interested in, contain a finite amount of matter, which is separated from its surroundings. The condition of the system is known as its **state**, which is determined by various thermodynamic **properties** or **variables**. System properties can either be **extensive** or **intensive** depending upon whether or not they scale with the system size. The system is **open** if it can exchange matter with its surroundings (fuel provided or via an exhaust) and **closed** if it cannot. The surroundings are really the rest of the world, from where observations on the system can be made. Often we simplify the surroundings to be a reservoir of constant temperature (e.g. a bath of water). The system and surroundings then constitute the Universe. An equation of state relates the system properties, whose general form is given by $f(p, V, T, \dots.) = 0$. The ideal gas law, $pV = nRT$, is the most widely known. If the corresponding states of two properties are equal, the states are identical; otherwise they are joined by a path.

> **Example 2.3**

3. Thermal Equilibrium, Heat and Temperature

Heat is actually defined as thermal energy in transit. Under its own action, it always moves from a hotter to a colder body. Heat can travel the other way, but a source of energy is required to make this happen. The rather badly-named concept of heat capacity allows us to measure the ability of a substance to hold heat energy. If an amount of heat, δQ, is required to raise the temperature of a body by the infinitesimal amount, dT, the **heat capacity, C**, is defined via $\delta Q = CdT$. Specific heat capacities, represented by lower case letters, c, deal with the heat capacity per unit mass or per mole – the context usually makes it clear which is being referred to. Heat capacities are often measured at constant volume (pressure), so we have

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = mc_V.$$

When **heat** is supplied to an object, it is positive, and when heat is removed, it is negative.

> **Example 3.1**

> **Exercise 1**

Thermal Equilibrium

From our everyday experiences two bodies in thermal contact with one another exchange energy. We are also aware of the concepts of hot and cold from e.g. fire and ice. However, our senses can let us down: a block of metal feels colder than block of wood of the same temperature due to the difference in their thermal conductivities. Two systems are in **thermal equilibrium** if and only if they

have the same temperature. Furthermore, some irreversible process must have taken place to get to this state if the systems were originally not in thermal equilibrium. Thermal processes thus define an arrow of time. Note that a system in thermal equilibrium is also in mechanical equilibrium but the reverse is not necessarily true.

4.   Zeroth law of Thermodynamics

IF TWO SYSTEMS ARE SEPARATELY IN THERMAL EQUILIBRIUM WITH A THIRD SYSTEM, THEY MUST BE IN THERMAL EQUILIBRIUM WITH EACH OTHER.
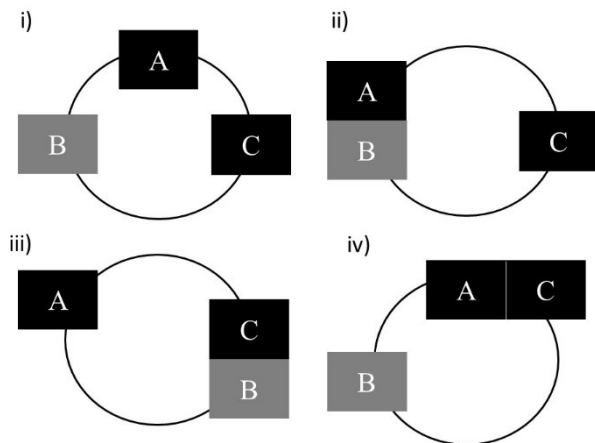

Figure 1: Representation of the Zeroth Law of Thermodynamics.

This law provides the experimental foundations upon which the thermodynamic property of temperature is founded. Unfortunately, it was originally deemed such an obvious thing, that until the early twentieth century it wasn't named. When a name was needed, everyone already knew about the first and second laws so they couldn't be renumbered! Figure 1 depicts this law for three systems that can be brought into thermal contact individually with each other (top left, (i)). If A and B, when brought into contact are and found to be in thermal equilibrium (top right (ii)) and a similar situation is found for B and C (bottom left (iii)), then we can conclude that A and C are also in thermal equilibrium without needing to perform the experiment (bottom right (iv)). The law thus provides the basis of the thermometer and forces the concept of temperature upon us.

Temperature and Thermometers

Temperature is the measure of whether two bodies are in thermal equilibrium. Values can be assigned to a temperature scale by selecting an appropriate thermometer, having some independent property to indicate if the two bodies are in thermal equilibrium. Any parameter that defines whether the bodies are in thermal equilibrium can be used. To ensure that the thermometer works, it must have a much lower heat capacity than the object that is wanted to be measured; this is so that very little heat energy is required to change the temperature of the thermometer as it comes into thermal equilibrium with the body and consequently, the bodies temperature will remain constant in this process. An absolute definition of temperature based on fundamental physics would be beneficial, and this can be defined using the Carnot cycle. Further, it should be noted that temperature can also be defined statistically.

5.   Relevant Mathematics

Thermodynamics deals with situations in which various system properties can change with respect to one another and so differential methods are required to describe things mathematically. In particular, it is often the case that one state variable changes with respect to another, whilst a further thermodynamic co-ordinate remains constant. Hence we need to use partial derivatives.

Example 5.1

Basic Concepts for partial derivatives

The total differential of a single valued function, $z = f(x, y)$ is defined by

$$dz = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = M(x,y)dx + N(x,y)dy.$$

It gives the total variation in z for changes in the x and y coordinates. In other words, how does the "height" change of a surface as you move around a plane.

> **Example 5.2**
>
> **Example 5.3: Consider the function** $z = x^2 y^3$ **We calculate** $\left(\frac{\partial f}{\partial x}\right)_y = 2xy^3$ **and** $\left(\frac{\partial f}{\partial y}\right)_x = 3x^2 y^2$**. Thus**

$$dz = 2xy^3 \, dx + 3x^2 \, y^2 dy \quad \Rightarrow$$

$$\frac{dz}{x^2 y^3} = \frac{2xy^3 dx}{x^2 y^3} + \frac{3x^2 y^2 dy}{x^2 y^3} \quad \Rightarrow \frac{dz}{z} = \frac{2dx}{x} + \frac{3dy}{y}.$$

If $f(x, y, z) = 0$ we know that $x = x(y, z)$ and $y = y(x, z)$. The following relationships can then be obtained about partial derivatives

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1 \quad ; \quad \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y \quad ; \quad \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1.$$

> **Proof 5.1**

The first is called the **reciprocal theorem** and the third the **reciprocity** theorem or **cyclic relation**.

Exact and Inexact Differentials

These mathematical relations allow path dependences of differentials to be expressed. An exact differential is independent of the path taken and can be used to represent a conservative force. The total differential, dZ, is exact if $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$, which is true if and only if x and y are independent. If x and y are independent variables, the order in which we take derivatives with respect to both variables does not matter, i.e. $\left(\frac{\partial^2 f}{\partial y \partial x}\right) = \left(\frac{\partial^2 f}{\partial x \partial y}\right)$. This is equivalent to saying that,

$$I = \int_1^2 dz(x,y) = \int_1^2 M(x,y)dx + \int_1^2 N(x,y)dy = z_2 - z_1.$$

The integral only depends on the end points and dZ defines a surface which is independent of the path taken. In other words Z, is a point function. All thermodynamic system properties (e.g. p, V, T, U, S) are such functions, and are hence represented by exact differentials.
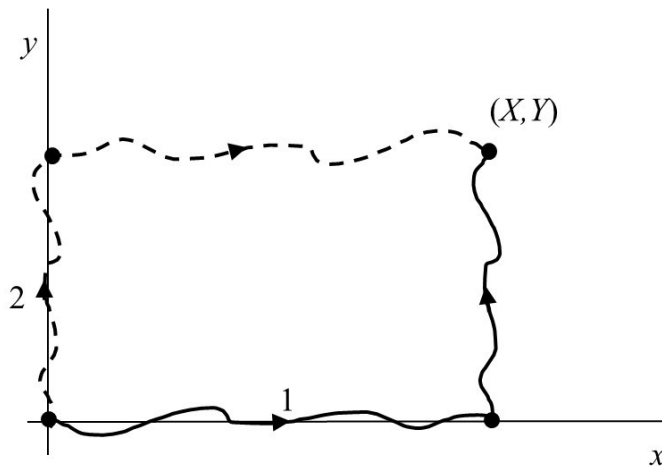
Figure 2: Integration paths considered in the problem.

Example 5.4: Consider the inexact differential represented by the infinitesimal change

$$\delta F = xdx + xdy.$$

If we compare this expression with total differential

$$dF = M(x,y)dx + N(x,y)dy,$$

we have $M(x,y) = N(x,y) = x$.

To be exact $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$, **but we find**

$$\left(\frac{\partial M}{\partial y}\right)_x = 0 \quad \text{and}$$

$$\left(\frac{\partial N}{\partial x}\right)_y = 1 \quad \text{so this is}$$

inexact.

Path A: $(0,0)$ to $(X,0)$ to (X,Y)

Path B: $(0,0)$ to $(0,Y)$ to (X,Y)

Path A from $(0,0)$ **to** $(X,0)$: $\int \delta F = \int_0^X xdx + \int xdy|_{dy=0} = \frac{X^2}{2}$.

Path A from $(X,0)$ **to** (X,Y): $\int \delta F = \int xdx|_{dx=0} + \int_0^Y xdy = XY$

Total Path A from $(0,0)$ **to** (X,Y): $\int_A \delta F = \frac{X^2}{2} + XY$.

Path B from $(0,0)$ **to** $(0,Y)$: $\int \delta F = \int_0^Y 0dx|_{dx=0} + \int 0dy = 0$.

Path B from $(0,Y)$ **to** (X,Y): $\int \delta F = \int_0^X xdx + \int xdy|_{dy=0} = \frac{X^2}{2}$.

Total Path B from $(0,0)$ **to** (X,Y): $\int_B \delta F = 0 + \frac{X^2}{2}$.

If this equivalence doesn't hold, dZ is known as an inexact differential. It requires knowledge of the path taken to be computed. I use the notation, δZ to describe inexact differentials, as it is clearer to write during lectures, but Blundell and Blundell tend to use đz. To coin this in simpler terms, inexact differentials are infinitesimals that are not the differentials of actual functions. They are known as path functions and include Q and W.

Relationship between differentials and thermodynamics

A thermodynamic system, surrounded by an environment, is in thermal equilibrium if its macroscopic observables no longer change with time. These macroscopic observables take a definite and fixed value, independent of how the system got to the state it is currently in. We term these **functions of state** and each function takes a well-defined physical value for each state of the system. They do not depend on time and include: volume, pressure, temperature, internal energy and entropy. Variables that are not functions of state and include: heat input; work done and particle position.
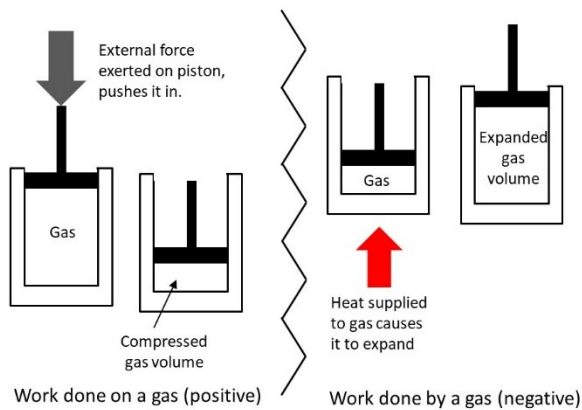
6.   Work and Internal Energy

Figure 3: Sign conventions used during this course, adopted from Blundell and Blundell.

Work, W, is like heat and is a form of energy. It gets done when a system is displaced under the action of a force. When an external force acts on a system, doing work, this work is positive. When a system acts on the environment, doing work on it, the corresponding work is negative. Figure 2 illustrates our sign conventions. Thus:

- **Forcing a cylinder shut by applying a force, and hence doing work, is positive;**
- **When a gas expands in a cylinder, forcing it outwards, displacing the air around it, the work is negative.**

The amount of work done depends upon the path taken.

Example 6.1

The **internal energy** of a system, U, is the sum of all internal degrees of freedom possessed by the system. The internal energy can be changed by the addition of heat or by doing work. Internal energy is an exact differential (function of state) since it takes a well-defined value for each equilibrium state of the system.

In 1843 Joule discovered the mechanical equivalence of heat, by slowly dropping a mass connected to a paddle that could rotate in water. The rotation frictionally warmed the water, and Joule was able to measure the increase in the water's temperature after a number of descents. We will later see that for two objects, which are not in thermal equilibrium, they can be connected via a heat engine and work got out of them – the energy contained in a system is its capacity to do work.

Types of work

Configuration work: The work that is done in changing the system's configuration, which can be expressed in terms of thermodynamic coordinates. This is the **useful work** and can be converted to motion etc.. In general, the work is a generalised force, X (intensive variable) multiplied by an extensive generalised displacement, dx, so $\delta W = X dx$.

Mode of Work	Force	Displacement	δW
Fluid	Pressure $(-p)$	Volume (V)	$-pdV$
Elastic Rod	Tension (f)	Length (L)	fdL
Liquid Film	Surface tension (γ)	Area (A)	γdA
Dielectric	Electric field $(\boldsymbol{E})$	Electric dipole moment $(\boldsymbol{p_E})$	$-\boldsymbol{p_E} \cdot d\boldsymbol{E}$
Magnetic	Magnetic field (B)	Magnetic dipole moment (m)	$\boldsymbol{m} \cdot d\boldsymbol{B}$

Table 1: Forms of work and their respective variables. **Bold font** indicates vector quantities.

Dissipative work: This is the work that gets turned into internal energy of a reservoir and it cannot be expressed in terms of thermodynamic coordinates. If it is non-zero for a process, the process is irreversible and at least some of the work gets lost as heat, for example.

Adiabatic work: This gets done on a system in isolation.

7. First law of Thermodynamics

This law is based on empirical evidence and is a statement regarding the conservation of energy. Two equivalent statements exist:

IF A SYSTEM MOVES FROM AN INITIAL STATE, i, TO A FINAL STATE, f, VIA ADIABATIC PATHS, THE WORK DONE IS THE SAME FOR ALL ADIABATIC PATHS.

EXPERIMENTS SHOW THAT WHEN A SYSTEM CHANGES FROM STATE i TO STATE f BY DIFFERENT ADIABATIC PATHS, AS MEASURED BY A CHANGE IN THE LEVEL OF A WEIGHT, THE WORK DONE IS ALWAYS THE SAME.

Mathematically, it can be stated as $\Delta U = \Delta Q + \Delta W$ or, more usefully written in terms of infinitesimal quantities

$$dU = \delta Q + \delta W.$$

Here, we are referring to the heat supplied to a system (ΔQ is positive) and the work done on the system (ΔW is positive).

Heat capacity

This concept allows us to understand how the addition of heat can change the internal energy of a gas. In general, the internal energy is a function of volume and temperature, $U = U(V, T)$. By undertaking various mathematical operations we find that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \text{and} \qquad C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p.$$

Warning: The heat capacity is only a function of internal energy, U, when the volume is constant. In all other cases, we must write it is a function of heat energy, Q!

> **Proof 7.1**

> **Exercise 2**

We also find, for an ideal gas, that $C_P = C_V + R$ and can define the adiabatic index as $\gamma = C_p/C_V$.

8. Quasi-static processes and Reversibility

A quasi-static process is one that takes place sufficiently slowly that it is close to thermal equilibrium at all points. It is really a mathematical trick that ensures that proper thermodynamic coordinates can describe the state of a system at all times. Various types of such processes exist:

- **Isobaric:** Takes place at constant pressure;
- **Isochoric:** Takes place at constant volume;
- **Isothermal:** Takes place at constant temperature.

Reversible and Irreversible Processes

The laws of physics are reversible, but many processes in nature seem to be irreversible. For example, consider an egg dropping off a table and smashing on the floor. Conservation of energy does not preclude us from using the heat dissipated by the egg on smashing to reassemble it and move it back on the table, but it is never seen to happen. This is because the statistical nature of large systems means that some outcomes are more likely to happen than others. In a real process, energy gets converted to heat and is dissipated to the environment - there are always more ways to dissipate heat energy than anything else. This caused trouble for the engineer pioneers of thermodynamics who wanted to make engines as efficient as possible and get work and not heat out.

A process is **reversible** if:

- No frictional or dissipative forces exist;
- No heat conduction is present due to finite temperature differences;
- The process is quasi-static.

In an irreversible process, dissipative work is done that has the same effect on the system as heat flow in reversible work. It should be noted that the first law applies in both cases.

Exercise 3

Adiabatic and Diathermal Walls

An **adiabatic** process takes place in isolation from its surroundings. Only work can be done in an adiabatic process. The word comes from adiathermal which means that heat doesn't flow becoming adiabatic if the process is also reversible. An **adiabatic wall** means no heat can be exchanged through it whilst a **diathermal wall** does allow the passage of heat. The equation of state for an ideal gas under adiabatic conditions is,

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

Example 8.1: Show that the above relation denotes the equation of state for a gas under adiabatic conditons

The First Law of thermodynamics is, $dU = \delta Q + \delta W = \delta Q - pdV$ & if the process is adiabatic it is isolated, so $\delta Q = 0$. From proof 7.1 we have that $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. So, the first law becomes

$$C_V dT + pdV = 0 \quad \Rightarrow \quad dT = -\frac{pdV}{C_V}. \quad (1)$$

Using $C_p = R + C_V$ allows us to write the expression above as

$$0 = (C_p - R)dT + pdV = C_p dT - RdT + pdV. \quad (2)$$

For an ideal gas, $pV = RT$, and the total differential of the temperature is

$$dT = \frac{1}{R}[pdV + Vdp], \quad (*)$$

obtained by using the chain rule for $dT = d(pV/R)$, and using the fact the R is constant. Substituting $(*)$ into (2) (the term RdT) gives

$$0 = C_P dT - p dV - V dp + p dV \quad \Rightarrow \quad dT = \frac{V dp}{C_p}.$$

Any two infinitesimal temperature changes must be equal, so $\frac{V dp}{C_p} = -\frac{p dV}{C_V}$. **We can separate the variables in this differential equation and integrate,**

$$\int \frac{dp}{p} = -\int \frac{C_p}{C_V} \frac{dV}{V}$$

$$\ln p = -\gamma \ln V + C.$$

$$\ln p = \ln(V^{-\gamma} \times \text{Const}) \quad \Rightarrow \quad pV^\gamma = \text{Const}.$$

9. Heat Engines

The concept of turning work into heat is familiar to us, for example using a resistive heater. It is relatively easy to accomplish and can be up to 100 % efficient. On the other hand, the conversion of heat into work is somewhat harder, requiring the presence of a **heat engine**. These are machines that produce work using a temperature difference between two **heat reservoirs,** known as a heat source and a heat sink. A heat reservoir is a body that is large enough to be considered to have an

essentially infinite heat capacity. Here, we will discuss ideal engines that convert heat to work in a cyclic process, and thus always return to their initial state. In a heat engine, like that in figure 4, heat is received from a high temperature source with some then being converted to work. The remaining waste heat is rejected to a low temperature sink. The cycle then begins again. During the cycle, heat is transferred to or from a **working fluid**, for example an ideal gas. Within engines, **regenerators** can be used to accept heat from the working fluid at one point in the cycle before returning the heat to the fluid in some other part.
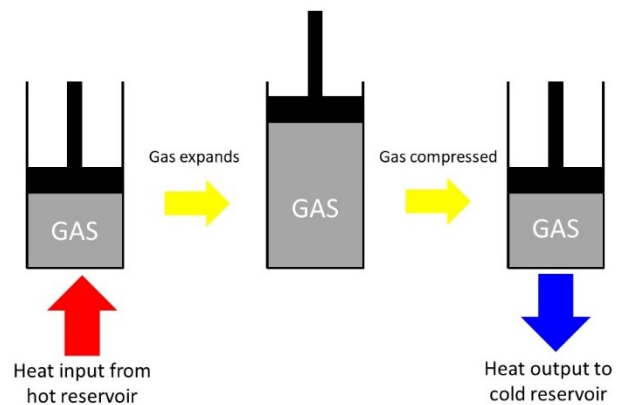

Figure 4: A basic Heat Engine.

Heat engines operating in reverse

Ideal heat engines are cyclic so can operate in reverse, using work to transfer heat from one place to another. A refrigerator takes in work and causes heat to flow from a cold to a hot reservoir, whilst a heat pump is used to pump heat from a hot reservoir to warm-up a colder place.

Efficiencies

The efficiency of a device is defined as the ratio of "what you want to achieve" to "what you put in". In the case of engine, you want to obtain work from the heat which you input, since in a cycle there is no internal energy change, whilst for a refrigerator of heat pump uses work to transfer heat.

$$\text{Efficiency} = \eta = \frac{\text{Product}}{\text{Expense}}.$$

For a heat Engine: $\eta = \frac{|\text{Work Done}|}{\text{Heat Input}} = \frac{Q_H - Q_L}{Q_H};$

For a fridge: $COP_L = \dfrac{\text{Heat from cold Reservoir}}{\text{Work Supplied}} = \dfrac{Q_L}{W}$;

For a heat pump: $COP_H = \dfrac{\text{Heat to hot Reservoir}}{\text{Work Supplied}} = \dfrac{|Q_H|}{W}$.

Engines always have efficiencies less than one, fridges can have coefficients of performance less than or greater than one, depending upon how much heat is removed for a given amount of work supplied, whilst heat pumps always have coefficients of performance greater than one.

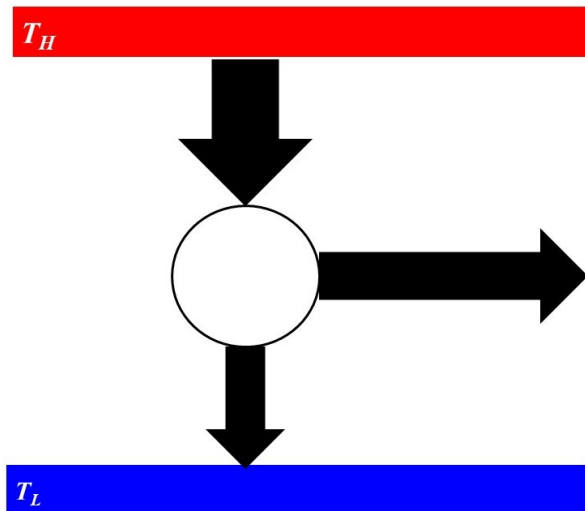Figures 5 and 6 illustrate how such efficiencies can be calculated.

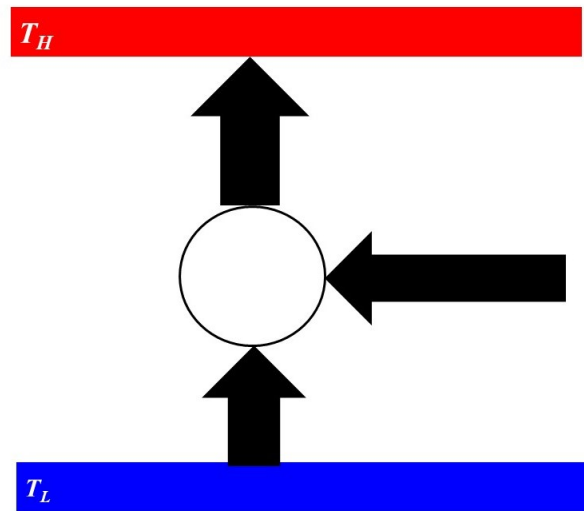
Figure 5: Efficiency of a Heat Engine.

Figure 6: Coefficient of performance of a Refrigerator/Heat Pump.

Proof 9.1

Exercise 4

Example 9.1: To maintain a fridge at $4\,°\text{C}$ heat removed at $360\ \text{kJ/min}$ using $2\ \text{kW}$ power.

$$COP_L = \frac{\dot{Q}_L}{\dot{W}_{in}} = \frac{360}{2}\left(\frac{1\ \text{kW}}{60\ \text{kJ/min}}\right) = 3.$$

Heat rejected to room (energy conservation)

$$\dot{Q}_H = \dot{W} + \dot{Q}_L = 2\ \text{kJ s}^{-1} \times 60 + 360 = 480\ \text{kJ/min}.$$

Heat removed from fridge and energy supplied eventually show up room air & become part of internal energy.

Heat pump, $COP_H = 2.5$, to keep house at $20\,°\text{C}$. When $-2\,°\text{C}$ outside, the house loses $80,000\ \text{kJ/h}$. Work supplied to heat pump

$$W_{in} = |\frac{\dot{Q}_H|}{COP_H} = \frac{80,000}{2.5} = 32,000\ \text{kJ/h} \quad (8.9\ \text{kW}).$$

To maintain the house temperature, heat must be delivered at the rate it is lost:

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = 80,000 - 32,000 = 48,000\ \text{kJ/hour}.$$

48,000 kJ of heat gets removed from the cold outside air per hour, but an electricity bill of 32,000 kJ per hour is required to be paid to run the heat pump. A resistive heater would require the full 80,000 kJ per hour to heat the room.

10. Second law of thermodynamics

This came about when the pioneers of thermodynamics considered heat engine efficiency. The first law, a statement regarding the conservation of energy, can be applied to any closed or open system. However, the first law is not a sufficient condition to ensure that a process will occur. We know from experiment that some processes only proceed in one direction, for example heat only flows (in isolation) from a hot body to a colder one, and this is related to the arrow of time. This inadequacy in the first law can be addressed by another general principle, the **second law of thermodynamics.**

- Clausius Statement

IT IS IMPOSSIBLE TO DEVISE A PROCESS WHOSE SOLE RESULT IS THE TRANSFER OF HEAT FROM A COLD TO A HOT RESERVOIR.

An alternative formalism comes from considering how easy it is to change energy from one form to another, for example work to heat. In fact, the complete conversion of heat to work is impossible. Equivalently, we can ask the following question about engines. Can a heat engine exist, operating in a cycle that produces positive work when only interacting with one heat reservoir? The answer is in the following statement of the second law.

- Kelvin-Planck Statement

IT IS IMPOSSIBLE TO CONSTRUCT A DEVICE THAT OPERATES IN A CYCLE PRODUCING POSITIVE WORK THAT ONLY INTERACTS WITH ONE HEAT RESERVOIR.

These two laws are logically equivalent as shown in the following proof and exercise, depicted in figures 7 and 8.
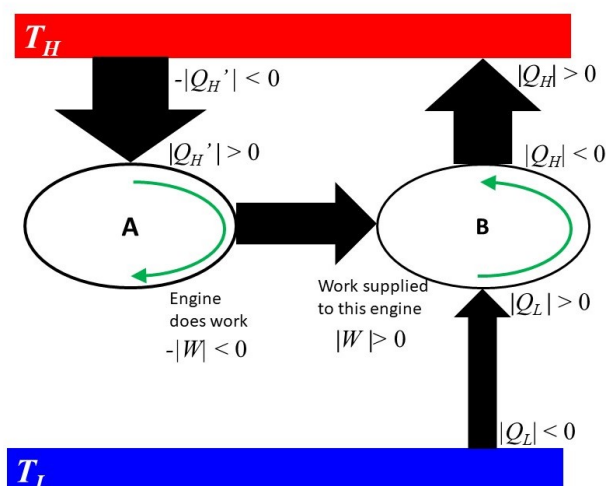

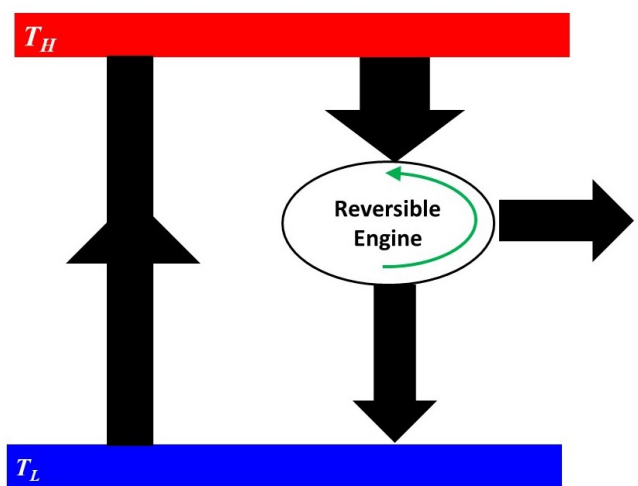Figure 7: If the Kelvin-Planck statement of the *Second Law* is violated, so is the Clausius.

Figure 8: If the Clausius statement of the *Second Law* is violated, so is the Kelvin-Planck.

Proof 10.1

Exercise 5

More on reversibility

A process is reversible if a complementary process exists that will bring the system and its environment back to their original states. We note that truly reversible processes do not exist in nature. However, it is possible to design processes that reduce the effects of irreversibility to a minimum and these processes are reversible in principle. An internally reversible process can be made reversible by making it interact with a different environment:

- To show a process is reversible it is sufficient to show a reversible process exists;
- To show a process is irreversible, it is sufficient to show that it violates the second law.
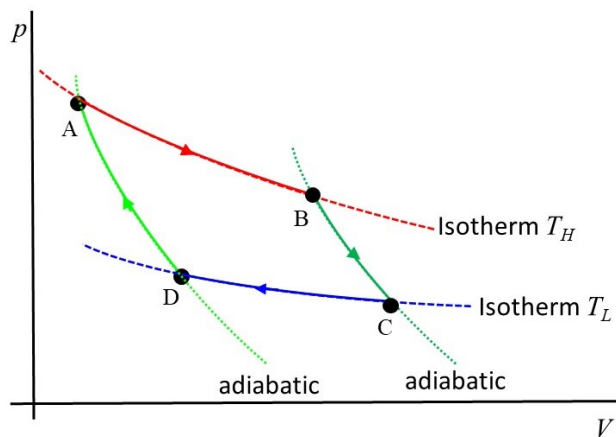
Carnot Engines

Figure 9: pV diagram for a Carnot Cycle.

A **Carnot cycle,** shown in figure 9, is an idealised cyclic process that provides an important conceptual model in thermodynamic theory, and forms the basis for a simple engine. It can be applied to any system, but is easiest to understand when an ideal gas is used as the working fluid. A Carnot cycle consists of four reversible processes: two isothermal processes, at the temperatures of the two reservoirs, linked by two adiabatic ones. Since the processes are reversible, we could construct a Carnot engine or a fridge using the cycle. From this, we find the following relationship

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L}.$$

This allows Carnot cycle(engine efficiencies (and Refrigerator or Heat pump Coefficients of performance) to be written in terms of temperatures as

$$\eta = 1 - \frac{|Q_L|}{Q_H} = 1 - \frac{T_L}{T_H} \quad ; \quad COP_L = \frac{T_L}{T_H - T_L} \quad ; \quad COP_H = \frac{T_H}{T_H - T_L}.$$

The relationship of heats and temperatures is also how thermodynamic temperature is defined.

> **Proof 10.1: Show that the Carnot relation of heats and temperatures holds. The Carnot cycle operates on one mole of Ideal Gas.**
>
> **AB: Isothermal expansion, when working fluid placed in contact with hot reservoir at $T_A = T_B = T_H$. On the isotherm there is no internal energy change $dU = 0$, since the temperature doesn't change, and internal energy of an ideal gas is a function of temperature. From the first law, we have $\delta Q + \delta W = 0$, so $Q_{AB} = Q_H > 0$ in, with $W_{AB} < 0$ (done on)**
>
> **BC: Adiabatic expansion, T_H to T_L (no heat), so $\delta Q = 0$. Negative work, as an expansion, and from the first law $dU = \delta W$, with $W_{BC} < 0$**

CD: Isothermal compression, when fluid in contact with cold reservoir, $T_C = T_D = T_L$. Again, there is no internal energy change and $Q_{CD} = Q_L < 0$ (heat given out,) $W_{CD} > 0$ is done on the gas in a compression.

DA: Adiabatic compression, T_L to T_H $W_{AB} > 0$. Gas has work done on it in a compression, with $\delta Q = 0$ again.

The engine operates in a cycle at steady power, so no internal energy change around the cycle, $\oint dU = 0$, so $W = -(Q_H - |Q_L|)$.

Work done on Isotherm at temperature T_H, $-\delta W_{AB} = \delta Q_{AB}$ (from the first law).

$$Q_H = -\int_A^B -p dV = \int_{V_A}^{V_B} \frac{RT_H}{V} dV = RT_H \ln\left(\frac{V_B}{V_A}\right).$$

$$Q_L = -\int_C^D -p dV = RT_L \ln\left(\frac{V_D}{V_C}\right) = -RT_L \ln\left(\frac{V_C}{V_D}\right).$$

The ratio of the heats is therefore given by,

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L} \frac{\ln(V_B/V_A)}{\ln(V_C/V_D)}.$$

Using the equation of state for an ideal gas under adiabatic conditions is, $pV^\gamma = $ const,

$$p_A V_A^\gamma = p_D V_D^\gamma \qquad ; \qquad p_B V_B^\gamma = p_c V_C^\gamma$$

but $pV = RT$, so we can eliminate the pressures above and right in terms of temperatures

$$p_A V_A = RT_H = p_B V_B \qquad ; \qquad p_C V_C = RT_L = p_D V_D.$$

Thus, $RT_H V_B^{\gamma-1} = RT_L V_C^{\gamma-1}$ and $RT_H V_A^{\gamma-1} = RT_L V_D^{\gamma-1}$.

Hence, writing the volume ratios in terms of temperatures

$$\frac{T_H}{T_L} = \left(\frac{V_C}{V_B}\right)^{\gamma-1} \equiv \left(\frac{V_D}{V_A}\right)^{\gamma-1}$$

So, simplifying the powers $V_C V_A = V_D V_B \Rightarrow \frac{V_C}{V_D} = \frac{V_B}{V_A}$. This tells us the volume rations are the same, which simplifies the expression for the heats as given below,

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L} \qquad \Rightarrow \qquad \eta = 1 - \frac{T_L}{T_H}.$$

It is only possible to express efficiencies in terms of temperatures for Carnot cycles and this is how it is possible to define a thermodynamic temperature scale. Since the heat flows are necessarily positive, so are temperatures, and the lowest temperature on the scale is absolute zero.

From the second law, Q_L can never be zero, and engine must always reject some heat to the cold reservoir, so no engine is ever 100 % efficient. This raises the interesting question that asks 'what the highest efficiency of an engine operating between two heat reservoirs can be?' It is found that an engine based on a Carnot cycle is the most efficient possible, so the above efficiencies are best case scenarios! This is encapsulated in the two **Carnot Principles**.

Carnot Principles

OF ALL THE HEAT ENGINES WORKING BETWEEN TWO TEMPERATURES, NONE IS MORE EFFICIENT THAN A CARNOT ENGINE.

These principles can simply be proved, using the engine cycles below in figures 10 and 11.
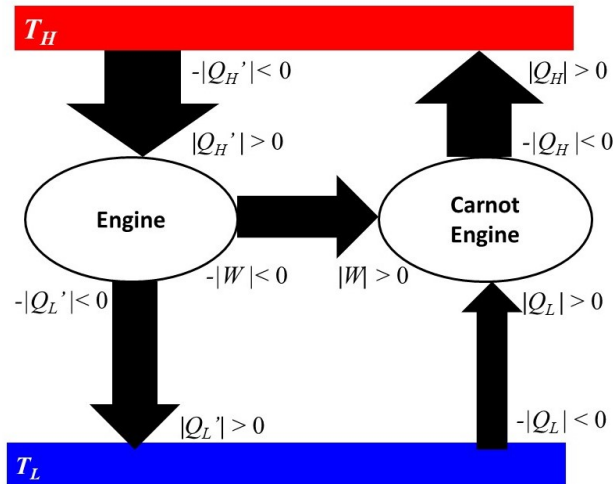
Figure 11: Carnot's First Theorem.
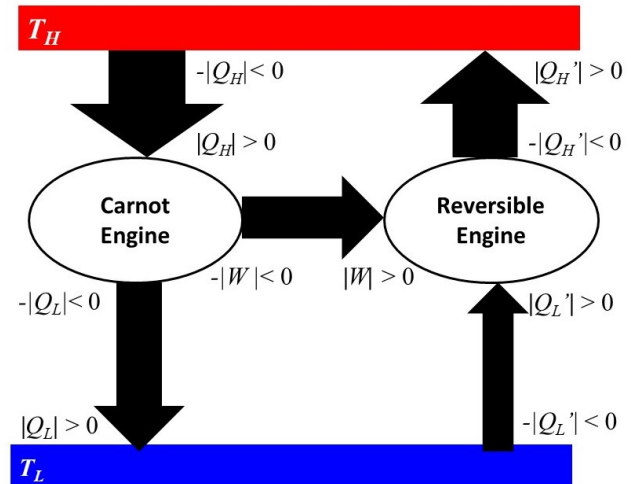
Figure 10: Carnot's Second Theorem.

> **Proof 10.2**
>
> **Exercise 6**

11. Real Engines and Refrigerators

For the interested student, more details on all of the engines and refrigerators covered (and others) can be found in chapters 8, 9 & 10 of Thermodynamics, an Engineering Approach, by Çengel and Boles. Note, I don't expect you to memorise all of the details from this. Instead, you should be able to describe basic principles of engines/refrigerators, draw cycles and derive efficiencies given a good starting point.

Reversible engines are the most efficient we can possibly design and any reversible engine, operating between two given temperatures, will have the same efficiency as the corresponding Carnot cycle.

Real Carnot Cycles

In practice it is very difficult to produce a cycle that consists of alternate adiabatic and isothermal processes having an ideal gas as its working fluid. The work done in a theoretical Carnot cycle is actually the difference between the large expansion and compression works along the two isotherms (workshop 2), since the work along the two adiabatics is in fact equal and opposite. However, a real engine, these constant entropy processes don't exist. Consequently, the nett work output from the cycle is much decreased. By changing the working fluid to a vapour, the above problems can be much reduced because a vapour is much easier to compress.

Real Engine cycles

Many cycles have been developed in an attempt to overcome the above problems, but they are always less thermodynamically efficient than Carnot cycles. They can't be modelled using a Carnot cycle because they consist of different thermodynamic processes. Some use a vapour as the working fluid, which undergoes a phase change in the cycle. Others use a fluid that can be approximated by an ideal gas. An engine can be closed whereby the working fluid is returned to its initial state at the

end of the cycle or open. In an open cycle, the working fluid gets replaced at the end of each cycle. In an internal combustion engine, for example an automobile, fuel is burnt within the engine boundaries to produce heat and hence work. An external combustion engine has energy supplied to the working fluid from an external source, for example a steam engine. In all cases, real engines can be modelled if the complexities are kept manageable, with any internal irreversibilities removed. Note, external irreversibilities will still exist that are not present in a Carnot cycle.

Gas Cycles

These engines use a gas as the working fluid, and tend to work in an open cycle since the combustion products must be got rid of through an exhaust. They become much easier to analyse if what are known as the air standard assumptions are made:

- The working fluid is air that continuously circulates in a closed loop, always behaving as an ideal gas;
- All processes must be internally reversible;
- The combustion process is replaced by heat addition from an external source;
- The exhaust is replaced by heat rejection to restore the fluid to its original state.

Reciprocating engines

A piston moving up and down within a cylinder – have found many applications, and the basic design is shown in figure 12. The cylinder moves between two positions: TDC (tod dead centre) – the position of the piston when at is smallest volume in cylinder, the clearance volume; BDC (bottom dead centre) – the position of cylinder when it is at its largest volume, the displacement volume; stroke the distance between these two positions.
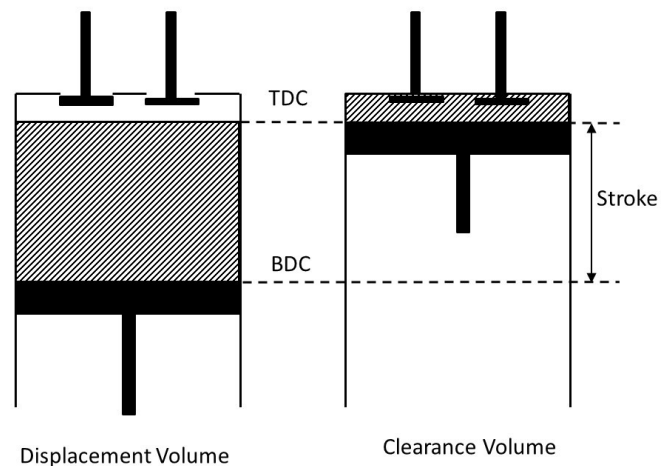

Figure 12: How a reciprocating piston moves.

Otto and Diesel cycles

The **Otto cycle**, developed in Germany in 1876, forms the basis of internal combustion engines. Most Otto cycles are four-stroke with the piston moving four times during the cycle, causing two rotations of the crank. The basic mechanism of the four-stroke cycle is shown in figure 13. With the intake and exhaust valves closed and the piston at maximum extension, the piston closes compressing the air-fuel mixture. Shortly before reaching TDC the sparkplug fires, igniting the fuel. This increases the
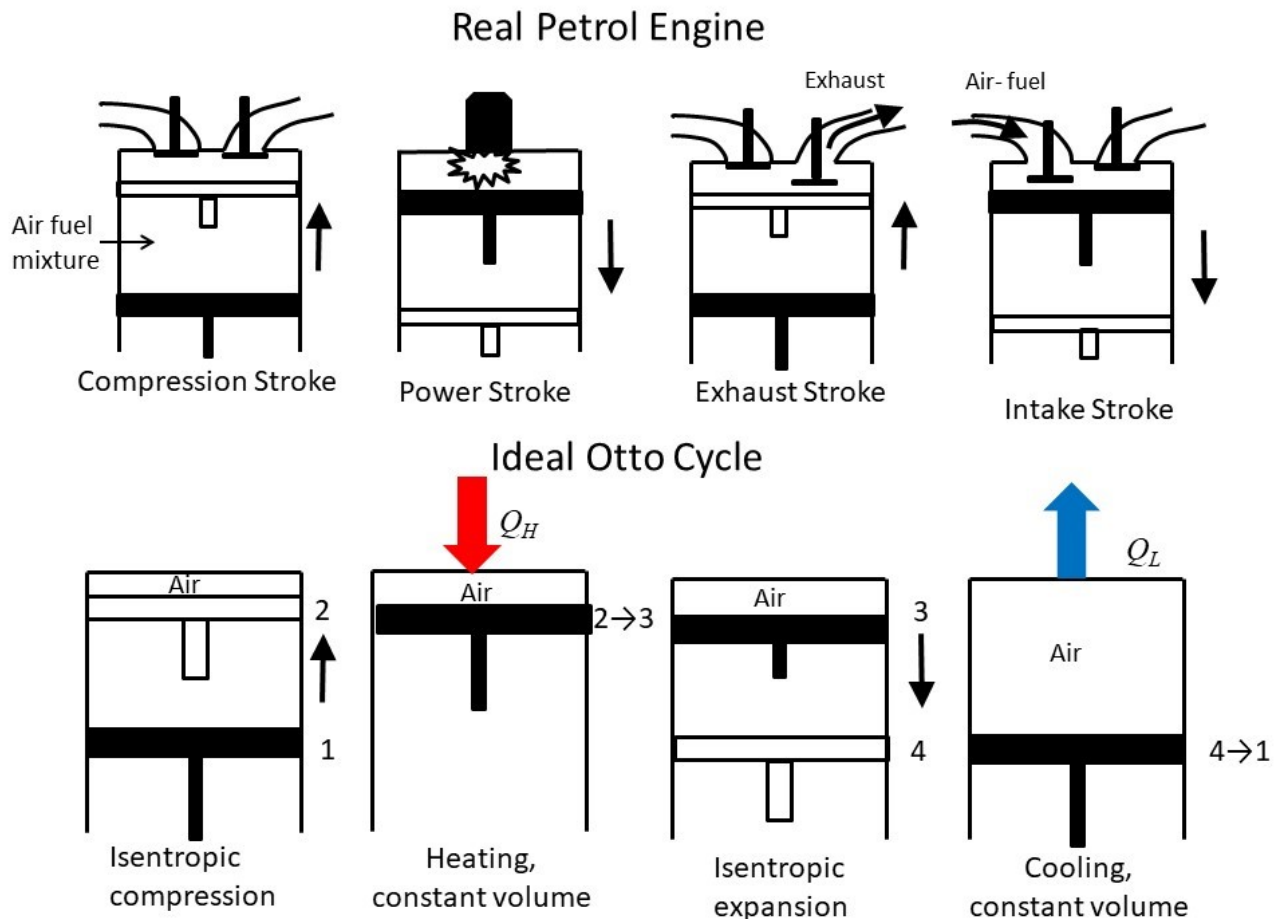

Figure 13: Ideal and real petrol engines, operating with 4 strokes per cycle.

pressure and temperature forcing the cylinder to open, causing the crank to rotate to give useful work. As the piston reaches it maximum extent it is filled with the combustion products. Closing the cylinder purges it through the exhaust before a new air-fuel mixture is input opening the cylinder a second time. Such engines require an even number of pistons, which run out of phase so that the power stoke from one cylinder can drive the compression of another etc. The crankshaft thus rotates twice in each cycle. A simpler version is a two-stroke engine, where all four processes take place in just two strokes. As the cylinder opens, it moves past an exhaust port allowing the combustion products out, before a new air-fuel mixture is allowed in through another port later in the stroke. This is less efficient than above because the exhaust is not fully expelled, but is simpler and less expensive so is okay for applications which require high power to weight ratios e.g. a lawn mower.
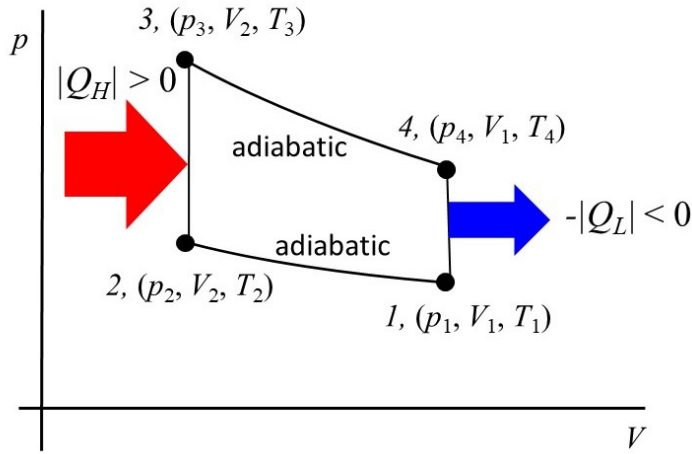
Figure 14: pV diagram of ideal Otto cycle.

The Ideal Otto Cycle consists of four internally reversible processes. Isentropic (adiabatic) compression; heat input at constant volume; adiabatic expansion; heat rejection at constant volume. Its pV diagram is depicted in figure 14 and it has efficiency is given by

$$\eta_{Otto} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \left(\frac{V_1}{V_2}\right)^{1-\gamma}$$
$$= 1 - r^{1-\gamma},$$

where r is the compression ratio, which is typically between 7 and 10.

Proof 11.1: Derive the efficiency of the Otto cycle

Considering each process for the Ideal Otto cycle in turn, and knowing that for an Ideal gas $pV = nRT$.

1→2 is Adiabatic compression: At either end of the adiabatic, we must have $p_1 V_1^\gamma = p_2 V_2^\gamma$ ⇒ $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$, the second relation has used the Ideal gas law to eliminate p for T.

2→3 is Isothermal heating with heat Q_H absorbed from an infintie series of reservoirs between T_2 and T_3.

$$Q_H = \int_{T_2}^{T_3} C_V dT = C_V(T_3 - T_2) > 0.$$

3→4 is Adiabatic expansion: $p_3 V_3^\gamma = p_4 V_4^\gamma$ ⇒ $T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1}$ ⇒ $T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$

4→ is Isothermal cooling with heat Q_L rejected from series of reservoirs between T_4 and T_1.

$$Q_L = \int_{T_4}^{T_1} C_V dT = C_V(T_1 - T_4) < 0.$$

The efficiency is

$$\eta = 1 - \frac{|Q_L|}{Q_H} = 1 - \frac{T_4 - T_1}{T_3 - T_2}.$$

Considering the adiabatic parts, we can write $T_1 = \frac{T_2 V_2^{\gamma-1}}{V_1^{\gamma-1}}$ and $\frac{T_3 V_2^{\gamma-1}}{T_4} = V_1^{\gamma-1}$ ⇒ $\frac{T_1}{T_4} = \frac{T_2}{T_3}$.

Rearranging the efficiency, we get

$$\eta = 1 - \frac{T_1\left(\left(\frac{T_4}{T_1}\right) - 1\right)}{T_2\left(\left(\frac{T_3}{T_2}\right) - 1\right)}.$$

The two bracketed terms are equal, which allows us to write the efficiency as

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

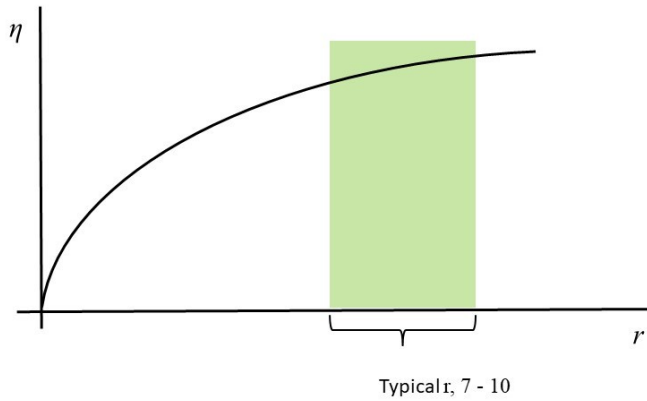**If $r = V_1/V_2$ is defined as the compression ratio, $\eta = 1 - r^{1-\gamma}$.**

Figure 15: How the efficiency varies with compression ratio for an Otto cycle.

The behaviour of the efficiency with the compression ratio – how much the gas gets compressed in the cycle before it is heated - is shown in figure 15; the typical compression ratios indicated lead to efficiencies of around 30 % If r becomes too high, the temperature of the air-fuel mixture rises above the auto ignition temperature in the compression stroke, causing an early and rapid burn of the fuel. This is termed knocking and it reduces the engine efficiency and causes damage. To increase the value of r, fuel with additives is needed – this increases its octane rating. Leaded petrol used to serve this purpose, but since its ban, engines have to be designed to operate at lower compression ratio. However, other improvements in car and engine design have increased fuel efficiency in recent years.

The **Diesel Cycle** (figure 16), developed in the 1890's by Rudolph Diesel, is the ideal cycle for a compression ignition engine. In diesel engines, air is first compressed, raising its temperature above the fuel's auto ignition point. When fuel is then sprayed into the engine, combustion begins on contact with the hot air. Thus, the carburettor and sparkplug are replaced by a fuel injector. Diesel engines to not suffer from knock because only air is compressed, this allows them to operate at much higher compression ratios (12 – 24) and use less refined fuels. Since combustion takes place over a longer time period than in the Otto cycle, it can be approximated by an isobaric heat addition process in the ideal cycle. The efficiency of such a cycle can be determined as

$$\eta_{Diesel} = 1 - 1/r^{\gamma-1}\left[\frac{(r_c^\gamma - 1)}{\gamma(r_c - 1)}\right],$$

where $r_c = V_3/V_2$ is the cut-off ratio. Note here that in the limit that $r_c \to 1$, this then becomes the same as the efficiency of the Otto cycle. Diesel cycles operate at much higher compression ratios, so even though the cut-off ratio is lower than 1, they have a higher efficiency.
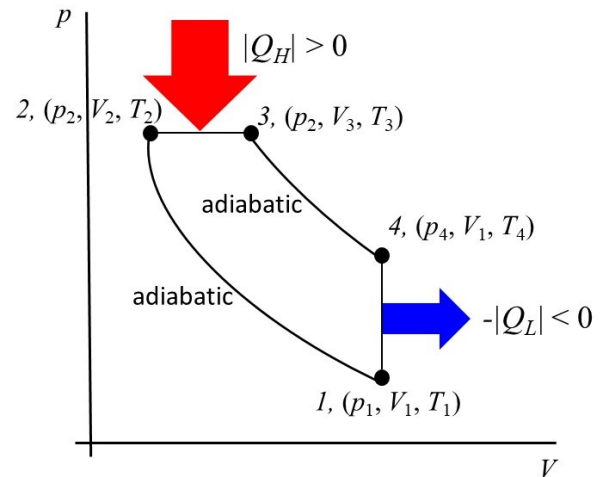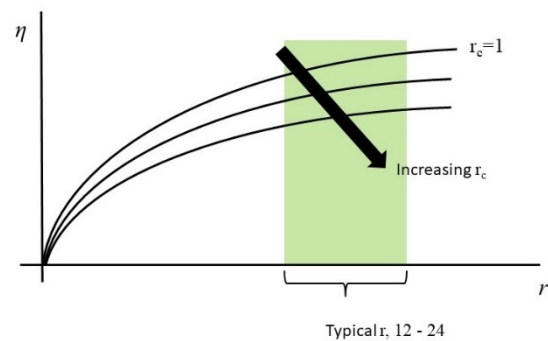

Figure 16: pV diagram of ideal Diesel Cycle.

Figure 17: Efficiency of a Diesel cycle with cut-off and compression ratios shown.
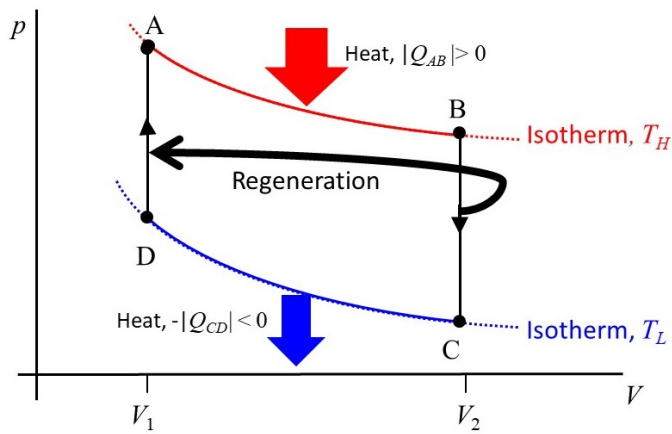
Figure 18: A Stirling Cycle, showing regeneration.

Stirling and Ericsson cycles

The Otto and Diesel cycles are what are termed as "*internally reversible cycles,*" so have a lower efficiency than a Carnot cycle operating between the same two temperatures. Two other cycles exist that are totally reversible like the Carnot engine, the ideal Stirling and Ericsson cycles whose heat interactions take place isothermally. They contain regenerators where heat gets transferred to a thermal energy storage device and reintroduced into the cycle at some later point. Figure 18 is a pV diagram for the Stirling Cycle. The heat rejected isochorically is identical to the heat input isochorically since the isochoric processes are between the same two temperatures. The rejected heat is stored in a regenerator until it is re-input, so the isochoric heating requires no further additional heat input.
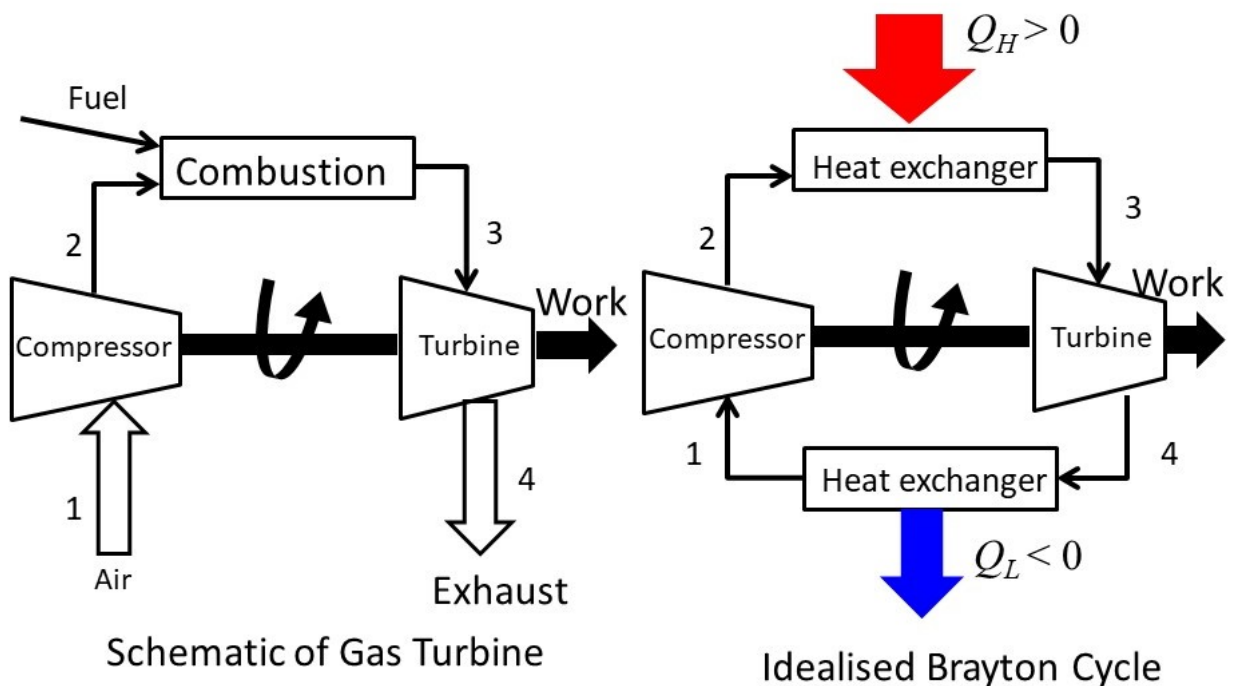
Gas Turbines

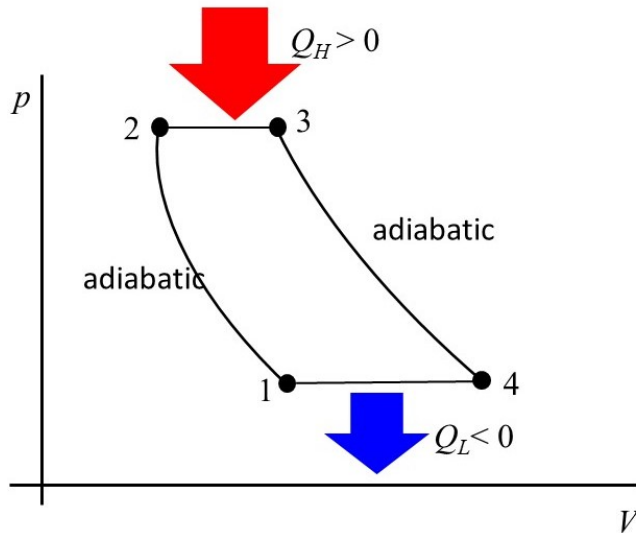Figure 19: Gas turbine schematic and how an ideal cycle can be modelled.

Figure 20: Brayton cycle pV diagram.

These operate based on the Ideal Brayton Cycle and allow expansion and compression processes in rotating machines to be examined. They are depicted in figures 19 and 207. In a real turbine, air at atmospheric pressure is drawn into a compressor, which pressurises it, raising its temperature. This hot air moves to a combustion chamber, where fuel is burned at constant pressure, further increasing T. The high temperature gases then enter a turbine where they expand to atmospheric pressure producing power, with the hot gases being cooled by an exhaust. An ideal cycle is closed with the expansion and compression as before, but with heating taking place at constant pressure, whilst the exhaust is a constant pressure rejection to ambient air. The efficiency is

$$\eta_{Brayton} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = \frac{1}{r_p^{(\gamma-1)/\gamma}},$$

where $r_p = p_2/p_1$ is the pressure ratio. In a real aircraft jet engine, the hot gases only partly expand in the turbine, producing just enough power to drive the compressor and provide any ancillary power required. The high pressure gases leaving the turbine are then accelerated through a nozzle as their pressure drops, providing the necessary forwards thrust.

Vapour cycles

In these cycles, the working fluid is alternately vaporised and condensed and they form the bases of steam power plants. Their development was as an innovative modification to Carnot cycles to improve the efficiency of real engines. Steam is the most commonly used vapour. At some point within the cycle, the steam turns a turbine, rotating a shaft attached to a generator. The limitations of the Carnot vapour cycle are overcome in the Ideal Rankine Cycle. Such a cycle consists of adiabatic compression (using a pump), before heat is added at constant pressure (via a boiler). The adiabatic expansion takes place through a turbine, before waste heat is rejected at constant pressure in a condenser.

Refrigeration cycles

We know that the flow of heat from low to high temperatures is counter-intuitive and doesn't match our everyday experiences. However, it is possible for this to happen in a fridge since work is used to do this. The working fluid of a fridge is known as the **refrigerant**. A fridge, see figure 19, is used to maintain an environment at some low temperature, the discharge of heat to the atmosphere just being a by-product. Work is done to compress a gas, raising its temperature above that of the atmosphere. As the gas passes through a condenser, it rejects

Figure 21: Schematic of a refrigeration cycle.

heat to the environment, cooling it. Further expansion in a throttle cools the gas more, so that its temperature is below that of the refrigerator. As the gas passes through the refrigerator it can absorb heat, removing it from the refrigerated space thus cooling it. A heat pump is really the same as a fridge but with a different objective. It is used to maintain the temperature of a heated space by removing heat energy from a cold reservoir and supplying heat to the warmer medium. Thus the best way to heat a building is to refrigerate the outside.

An ideal fridge would operate using a reversed Carnot cycle, but in the real world it is difficult to find processes that approximate the adiabatic compression and expansions since compressing a mixture of liquid and vapour is hard, whilst expansion of a high moisture content refrigerant is difficult. Thus the ideal cycle (figure 23) is based on a modified version of the reversed Rankine cycle, but throttling, not a turbine, is used to reduce the fluid pressure. The ideal cycle has been plotted on what is known as a temperature entropy diagram (see section 14), which are more useful when discussing heat interactions, the thing of interest – how much heat is moved out of the cold space, as opposed to the work supplied to do this.

In a fridge, the refrigerant is compressed causing a temperature rise, until its temperature is greater than that of the environment. This enters a condenser as super-heated steam, where it cools rejecting heat and becomes a saturated liquid. At the condenser exit, the temperature is still above that of the surroundings. The high temperature saturated liquid expands through the throttle which lowers its temperature to below that of the refrigerated space. On
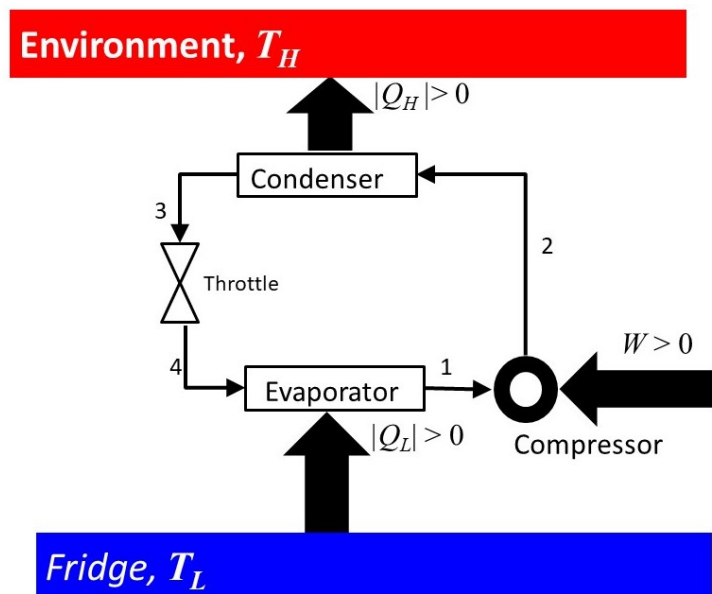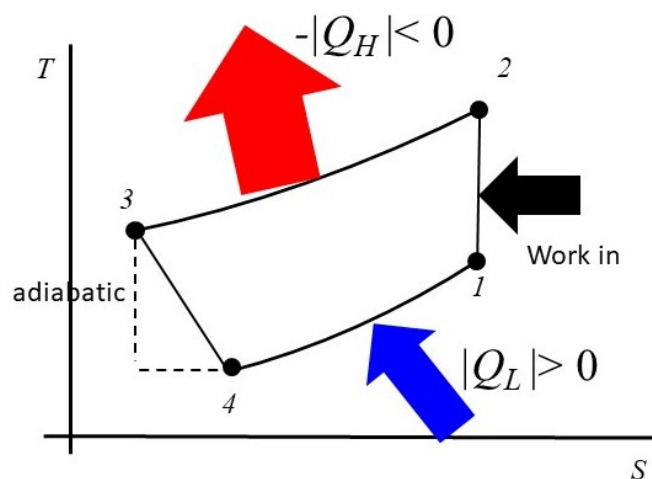

refrigerators.

23

passing through the refrigerated space, the refrigerant can take in heat and evaporate before the cycle starts again.

In a real fridge, the tubes in the refrigerated compartment serve as the evaporator, whilst the coils on the back are the condenser. In each case, these are coiled round to increase their overall length in the space available, so as to have the maximum distance to take-in/reject heat.

12. Clausius Inequality

The second law tells us that some processes may only proceed in one direction (e.g. a device operating in a cycle with one heat reservoir cannot deliver work, but it can receive work whilst rejecting heat). This can be summarised by the **Clausius Inequality**. It tells us that the integral, $\delta Q / T$, is never positive, or mathematically $\oint (\delta Q/T) \leq 0$. Heat is thus not conserved in a thermodynamic process, unless it is reversible. This inequality provides a mathematical explanation of the second law and allows us to determine whether or not a cyclic process is reversible, and the proof can be derived from figures 23 and 24.
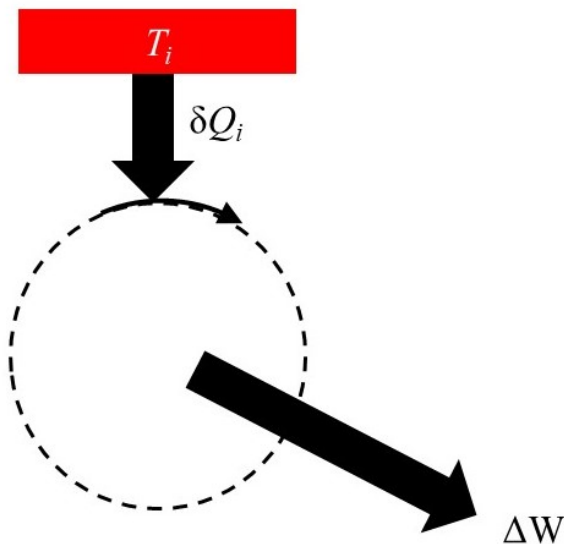
Figure 23: Heat entering through one part of an engine cycle.

Proof 12.1
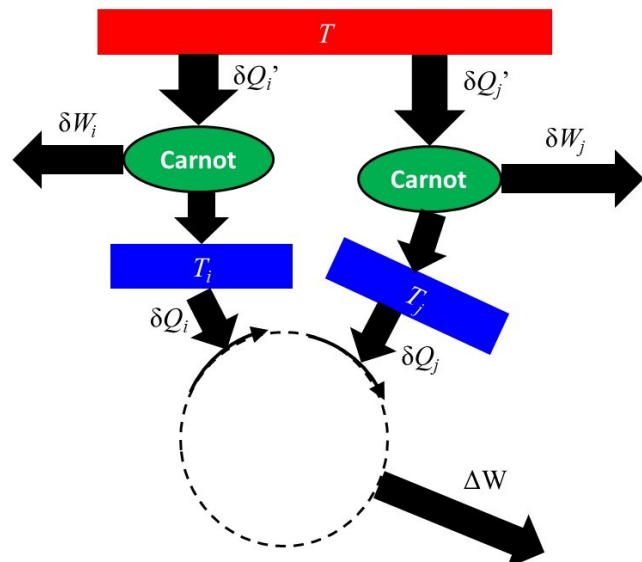
Figure 24: Heats entering a cycle from a number of Carnot cycles that are all connected to a single hot reservoir.

13. Entropy

The change in heat energy for a Carnot cycle is given by $\Delta Q = Q_H + Q_L$; here $Q_H > 0$ as heat is taken in and $Q_L < 0$ for the rejected heat since it represents the heat expelled from the engine. Therefore, by considering absolute heats in our Carnot cycle relation from section YY, we find $\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$. Writing in terms of infinitesimal heat changes, $\oint \delta Q/T = 0$, we can now evaluate for any arbitrary, reversible cycle. This means that the integral, $\int_A^B \frac{\delta Q_{rev}}{T}$ must be path independent. It is thus an exact differential and represents a system property, called **entropy**. The entropy change between the two thermodynamic states A and B is

$$dS = \frac{\delta Q_{Rev}}{T} \quad \text{so} \quad S(B) - S(A) = \int dS = \int_A^B \frac{\delta Q}{T}.$$

An adiabatic process has no heat change, ($\delta Q = 0$), so it must take place at constant entropy. They are known as **isoentropic processes.** Entropy is an extensive property, but it only makes sense to talk about the entropy change between two states. The temperature, T **MUST BE IN KELVIN!**

Example 13.1: Simple entropy calculations

Adiabatic Expansion: By definition, there is no heat transfer in an adiabatic process, so $\delta Q = 0$. Therefore, $\Delta S = \int \frac{\delta Q}{T} = 0$, i.e. there is no entropy change.

Isothermal Expansion: For a body at a temperature T_0 (so e.g. a heat reservoir) the entropy change is simply

$$\Delta S = \int_A^B \frac{\delta Q_{rev}}{T} = \frac{1}{T_0} \int_A^B \delta Q_{rev} = \frac{(\Delta Q_{rev})}{T_0}.$$

Here, ΔQ_{Rev} is the heat added/removed reversibly along the isotherm.

For a temperature change at constant volume, the differential heat for a small temperature change is given via heat capacity, using $\delta Q = C_V \, dT$. This can be substituted into the entropy equation, which is integrated between the temperatures of interest,

$$S_B - S_A = \int dS = \int_A^B \frac{C_V dT}{T} = C_V \ln\left(\frac{T_B}{T_A}\right).$$

Entropy Change for any process

It is not possible to calculate the entropy change between two states in an irreversible process by simply integrating $\delta Q/T$. Instead, it is possible to show that for any reversible or irreversible process

$$\Delta S = \int_A^B \frac{\delta Q_{rev}}{T} \geq \int_A^B \frac{\delta Q}{T},$$

with the equality holding for a reversible process. As this statement is true for any process between the states A and B we see that for an infinitesimal change, $\delta Q \leq T dS$. Furthermore, since $\delta Q = 0$ in thermally isolated systems, entropy change must always be positive.

Example 13.2

Example 13.3

Principle of increase of entropy

In the previous equation, the equality only held for a reversible process, otherwise entropy must always increase. This means that we can assert that there must be some limit on the entropy increase of an isolated system and once that system reaches equilibrium no further changes can take place. Therefore, processes only take place on an isolated system if they bring it close to equilibrium. These processes are irreversible so increase the system's entropy. Since no process is truly reversible, some amount of entropy will be created in any process, and the entropy of the Universe – that can be considered as an isolated system - will always increase. Furthermore, Clausius said that the energy of the Universe must remain constant (from the first law) whilst entropy will

tend to a maximum (second law). We can put all of this together to use entropy to give another statement of the second law.

IN EVERY PROCESS TAKING PLACE IN AN IDEAL SYSTEM, THE ENTROPY CHANGE OF THE SYSTEM EITHER INCREASES OR REMAINS CONSTANT.

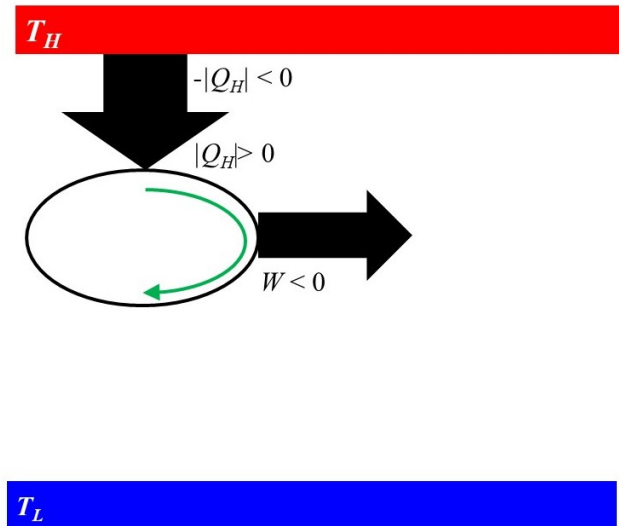This is equivalent to the Kelvin and Clausius statements, as depicted in figures 25 and 26.

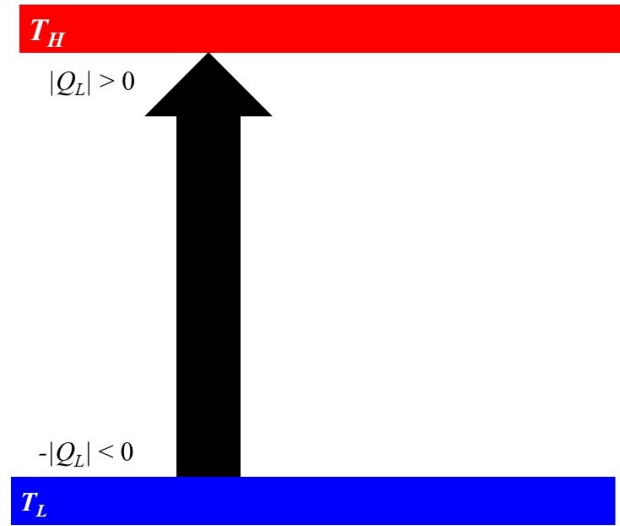Figure 25: Equivalence of Entropy and Kelvin Statements of Second Law.

Figure 26: Equivalence of Clausius and Entropy Statements of the Second Law.

Proof 13.1

Exercise 7

Entropy and Disorder

Entropy is related to disorder and nature will always tend to a more disordered state. In any irreversible process, internal energy in fact gets dissipated as heat and cannot be used for useful work. Thus entropy is a measure of the quality of energy in a system and since entropy change is always positive, it tells us that processes can only move in one direction, to a more disordered state, which complies with the principle of increase of entropy.

Entropy change in reversible and irreversible processes

In a reversible process between states it is easy to calculate the entropy change between the two states A and B as $S_B - S_A = \int_A^B \frac{\delta Q_{rev}}{T}$. Here, the temperature change of the system and its surroundings is the same, so the system and the surroundings have an equal and opposite entropy change. This means that the overall entropy change of the Universe is zero. Note that reversible processes are ideal cases.

To find the entropy change of an irreversible process, we use the fact that entropy is a system property. It thus only depends on the initial and final states, A and B and not the path linking them. Hence, to find the entropy change of an irreversible process, we find a reversible path between the states of interest and calculate its entropy change. This will be the same as the entropy change of the irreversible process we wish to calculate. In an irreversible process, the entropy change is the sum of two or more parts. One of these will increase, whilst the other decreases, but their sum is always positive, in line with the principle of increase of entropy as depicted in figure 27.
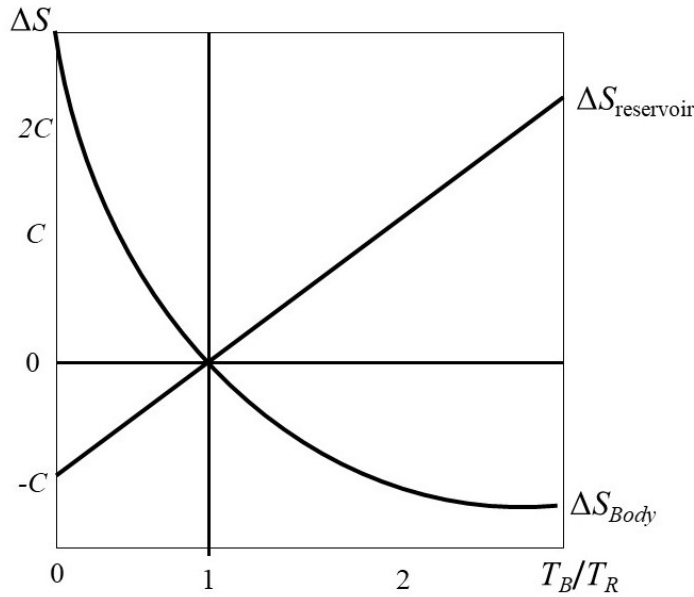
Figure 27: The entropy changes of a body and a reservoir for all temperatures. The body is initially at T_B, with heat capacity C_p, and it gets immersed in a reservoir at constant temperature T_R.

Example 13.4

A body, of heat capacity C_p at T_B is immersed in a bath of liquid at T_R. The bath's temperature remains constant throughout the process since it is a heat reservoir. This allows the temperatures to come to equilibrium. At constant pressure,

$$\Delta S_{\text{Body}} = C_p \ln\left(\frac{T_R}{T_B}\right)$$

Whilst coming to equilibrium the body takes in/rejects heat energy as its temp increases/decreases corresponding to entropy increase/decrease.

It is possible to calculate the body energy change using its heat capacity and the temperature change,

$$\Delta Q_{body} = C_p \Delta T = C_p(T_R - T_B).$$

C_P unchanged for a body!

The liquid in the bath must lose (or gain) an equivalent amount of energy to the block, and it has an isothermal entropy change

$$\Delta Q_{liquid} = -\Delta Q_{Body}.$$

$$\Delta S_{\text{Liquid}} = -\frac{\Delta Q_{Body}}{T_R} = -C_p \frac{(T_R - T_B)}{T_R}.$$

$$\Delta S_{\text{Total}} = C_P \left[\ln\left(\frac{T_R}{T_B}\right) - \frac{T_R - T_B}{T_R}\right] = C_p \left[\frac{T_B}{T_R} - \ln\left(\frac{T_B}{T_R}\right) - 1\right] \geq 0.$$

The above holds for any T_B and T_R.

It can be shown that $x - \ln x - 1 > 0$ providing $x \neq 1$ and $x \geq 0$, which is true for all $x = T_B/T_R$ (temperatures are both positive and none identical!)

First Law in terms of Entropy

The first law is defined as $dU = \delta Q + \delta W$. By considering a reversible process we find that

$$dU = TdS - pdV.$$

This actually holds for an irreversible process as well, but here $\delta Q \leq TdS$ and $\delta W > -pdV$, though the sum, dU, is the same whether the process is reversible or irreversible. The above expression holds no matter how we define our sign conventions as well! The natural variables of internal energy are thus entropy and volume, $U = U(V, S)$, and we can write $\left(\frac{\partial U}{\partial V}\right)_S = -p$ and $\left(\frac{\partial U}{\partial S}\right)_V = T$ using total derivatives.

Temperature-Entropy diagrams

Since entropy can be expressed as e.g. a function of p and V, we can describe the state of system using its entropy and one other thermodynamic function. Temperature entropy diagrams are useful for doing this. On such a plot, a reversible process is represented by $\Delta Q_{rev} = \oint T dS$ and the area under the curve is the net heat flow into the system. Note, TS diagrams of Carnot cycles are rectangular. Lines of constant pressure and volume can be plotted on these diagrams. For an ideal gas they are exponential in shape.

14. Thermodynamic Potentials

We know that thermodynamic coordinates are related via an equation of state. Further functions of state can easily be constructed by adding U to other combinations of various functions of state, providing that we always end up with dimensions of energy. These are known as thermodynamic potentials. In reality it is much easier to measure certain substance properties of a system $(p, V, T, C, \dots)$ over others $(S, U, \text{etc.})$, particularly if the experiment tries to determine these properties using their explicit definitions. Thus most potentials are useless on their own, but upon suitable mathematical manipulation they allow a whole range of thermodynamic properties to be discovered.

Internal Energy

This function of state, U, has natural variables of S and V, so we can write $U = U(S, V)$. U it is an exact differential, meaning U will always change by the same amount no matter what path is taken between two states, or $dU = U_f - U_i$. Using our knowledge of thermodynamic processes, we can furthermore prove that for a reversible isochoric process, $\Delta U = \int_{T_1}^{T_2} C_V dT$.

Enthalpy

The above result for the internal energy only holds at constant volume. To find a similar relationship at constant pressure we need to use the system **enthalpy**, which is defined via

$$H = U + pV \qquad\qquad dH = TdS + Vdp$$

Enthalpy has natural variables S and p, with $H = H(S, p)$. It represents the heat absorbed by the system in a constant pressure process, $\Delta H = \int_{T_1}^{T_2} C_p dT$. Enthalpy increases (decreases) if heat is added (removed) isobarically. This is a very useful concept since many experiments are open to the atmosphere, so take place at constant pressure. Enthalpy therefore plays the same role at constant pressure as internal energy does at constant volume.

Helmholtz Function

This function is what is termed a free energy and is defined as

$$F = U - TS \qquad\qquad dF = -pdV - SdT,$$

so has natural variables V and T, with $F = F(V, T)$. For a reversible, isothermal process $dF = -pdV$, so if F is positive it tells us that the system has work done on it by its surroundings and if it is negative, we see that work is done on the surroundings by the system. Its value is thus always less than or equal to the work that gets done so in fact it gives a limit to the maximum work that can be

got out of a system at constant temperature ($dF \leq 0$). In other words, the system does work, which is negative, on its surroundings until the Helmholtz function is minimised.

Example 14.1

Gibbs Function

This is another free energy composite function, defined via

$$G = H - TS = F + pV = U + pV - TS$$

$$dG = Vdp - SdT,$$

with natural variables p and T, so $G = G(p, T)$. These are the easiest thermodynamic coordinates to manipulate and control in an experiment. G represents the maximum mechanical work that can be done between equilibrium states and it is conserved in isothermal, isobaric processes, for example at a phase transition.

Maxwell Relations

These four relationships are derived using the above thermodynamic potentials, which tell us how we can relate partial derivatives of functions of state to thermodynamic coordinates

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_p \quad ; \quad p = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S \quad ;$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p \quad ; \quad V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T.$$

They provide a useful way to relate partial derivatives about quantities that are hard to measure, to partial derivatives about quantities that are easier to measure and understand.

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad \text{(M1)} \quad ; \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad \text{(M2)}$$

$$\left(\frac{\partial T}{\partial V}\right) = -\left(\frac{\partial p}{\partial S}\right)_V \quad \text{(M3)} \quad ; \quad \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \quad \text{(M4)}$$

Note, it is far better to be able to derive these as oppose to memorise them, but the gimmick is: p & V and S & T are always placed diagonally opposite; the lower inside parameter is the opposite outside parameter; if p and S occur together, there must be a minus sign. Jacobians can also be used to derive them – more difficult!

Proof 14.1

Example 14.2

To obtain the second Maxwell Relation, consider the Helmholtz function, $F = U - TS$. The total derivative of this is

$$dF = dU - TdS - SdT$$

(using the product rule $d(TS) = TdS + SdT$). Substituting the first law of thermodynamics $dU = \delta Q + \delta W = TdS - pdV$, yields

$$dF = -SdT - pdV.$$

Thus the Helmholtz function is naturally a function of temperature T and volume, V, so $F = F(T, V)$. Taking the total derivative of this function gives

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

and comparing terms show $\left(\frac{\partial F}{\partial T}\right)_V = -S$ and $\left(\frac{\partial F}{\partial V}\right)_T = -p.$

By the equivalence of second derivatives (the Helmholtz function is a function of state, so is defined by an exact differential), $\left(\frac{\partial^2 F}{\partial T \partial V}\right) = \left(\frac{\partial^2 F}{\partial V \partial T}\right)$ holds. Thus

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial(-S)}{\partial V}\right)_T = \left(\frac{\partial(-p)}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V.$$

Generalised Quantities

Heat Capacity: The most general form of this for a substance at some constant property, α, is given by

$$\boxed{C_\alpha = \left(\frac{\partial Q}{\partial T}\right)_\alpha = T\left(\frac{\partial S}{\partial T}\right)_\alpha.}$$

Therefore, some of the Maxwell relations correspond to real, measurable properties! **Specific quantities** are defined per unit mass and are denoted by lower case letters e.g. c, v, h, s, u. Using them makes the results of calculations only dependent upon the type of material used.

Generalised susceptibilities quantify how much something changes when a **generalised force** is applied. This force is a differential of the internal energy with respect to some other parameter, such as $= \left(\frac{\partial U}{\partial S}\right)_V$. Common ones are the isobaric and adiabatic expansivities $\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and $\beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$, which give the fractional change in volume with temperature at constant pressure and entropy respectively. Similarly, the isothermal and adiabatic compressibilties give the fractional volume changes when pressure is applied and are defined by $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ and $\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S.$

The negative sign indicates that an increase in the pressure causes a decrease in volume.

TdS and Energy Equations

The TdS equations provide another useful method for describing the behaviour of substances and are obtained by considering entropy as a function of useful pairs of thermodynamic coordinates, e.g.) $S(V, T), S(p, T)$ etc. and then by invoking Maxwell's relations

$$TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV \quad \text{(TS1)};$$

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_p dp \quad \text{(TS2).}$$

Proof 14.2

Example 14.3

The energy equations, derived from the first law, allow the internal energy change to be expressed in terms of easily measurable thermodynamic co-ordinates. The first can be used to calculate the internal energy change in terms of thermodynamic coordinates

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \quad \text{(E1)};$$

$$\left(\frac{\partial U}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T \quad \text{(E2)}.$$

Proof 14.3

General methods for solving problems

There are a number of steps that should be followed to solve calculus–type problems: write down a thermodynamic potential in terms of particular variables; use Maxwell relations to transform disgusting partial derivatives into nice ones; apply the theorems of calculus (reciprocal and reciprocity relations); see if a heat capacity can be identified; finally, identify any generalised susceptibilities.

Example 14.4

Example 14.5

Example 14.6: What does the first energy equation tell us about an ideal gas?

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p.$$

Using the Ideal gas Law, we work out the appropriate partial derivative, $\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$, so substituting into the energy equation

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{TR}{V} - p = p - p = 0.$$

Therefore, U doesn't depend on volume as previously found out in homework 2!

15. Entropy Applications

For the interested reader, a more thorough discussion of this than is given in the course text can be found in chapter 7 of Thermodynamics, an Engineering Approach, by Çengel and Boles. Beware of their opposite sign conventions though!

We have already considered entropy change in both reversible and irreversible processes, finding $\delta Q_{rev} = TdS$. It has been shown that the overall, entropy change of the Universe will always positive. **Temperature–entropy** diagrams provide a useful way for representing reversible processes, with the area under the curve being the net reversible heat flow into the system.

On a more fundamental level, entropy itself provides a measure of energy quality and is thus a very useful measure of analysing both closed and open systems – engineers for example often talk about isoentropic efficiency. All we note here is that if the overall entropy change of a process is negative (an entropy decrease) that process is not allowed to happen. However, a process can consist of two parts one of which has a decrease in entropy with the other a corresponding increase, providing that their sum is greater than or equal to zero. Therefore, the simplest way to test to see if a process is possible is to see if it violates any form of the second law (Kelvin-Plank, Clausius, or entropy).

Efficiency and Effectiveness of a process

We have already defined the **efficiency of a process**, as the ratio of what you get out of a device to what you put in, Actual Efficiency=$\frac{\text{Product}}{\text{Expense}}$ and $\eta_{engine} = \frac{|\text{Work done}|}{\text{Heat Input}}$. Obviously, it is always possible to put more heat into a device than useful work can be got out of it. In this case, some energy becomes lost, or unavailable for doing work. The **effectiveness**, or reversible efficiency, of a process is defined as the ratio of the output you would get for the best possible process running between two states (no losses or entropy change) to what is put in, so is useful for real devices,

$$\text{Effectiveness} = \eta_{rev} = \frac{|\text{Best possible Work}|}{\text{Heat in}}$$

This allows what is termed a second law efficiency to be defined as the ratio of these

$$\eta_{2nd} = \frac{\text{Actual efficiency}}{\text{Effectiveness}}.$$

Example 15.1 Consider two engines, both having thermal efficiency of 30 %. One is supplied with heat from a reservoir at 1000 K the other from a reservoir at 600 K and they are both reject heat to the environment at 300 K. The effectiveness of these two engines is given by

$$\boldsymbol{\eta_{rev1} = 1 - \left(\frac{300}{1000}\right) = 70 \text{ %};}$$

$$\boldsymbol{\eta_{rev2} = 1 - \left(\frac{300}{600}\right) = 50 \text{ %}}$$

Thus, even though both engines seem to convert the same fraction of heat which they receive to work through the standard efficiency, the first engine actually has a much greater work potential; 70 % as opposed to 50 % of the heat supplied to it could be turned to work, if the engine was perfectly reversible, so the first engine is performing poorly in reality. The second law efficiencies are then

$$\boldsymbol{\eta_{2nd1} = \frac{30}{70} = 0.43 \quad ; \quad \eta_{2nd2} = \frac{30}{50} = 0.60.}$$

16. Availability and Available Energy

It is easy to see that the work obtained from a real device is always less than would be obtained from a reversible device, since energy gets dissipated as heat in an irreversible process. The **available energy** of a device (also known as the device's exergy) tells us the maximum work that could be obtained from a system in a particular state, operating in a specific environment. If a system delivers maximum work it must end-up in a what is called a **dead state**. Such a state means that the process takes the system into thermal equilibrium with the environment, so no more work can be done. If it wasn't in thermal equilibrium, an engine could be connected between the state and the environment and used to obtain work.

Example 16.1

Consider Air - standard atmospheric conditions moves at 10 m s^{-1} has potential to do 0.05 kJ kg^{-1} of work i.e.) completely bringing 1 kg to standstill provides 50 J of energy.

A 100 kg mass at the top of the Cathedral tower has $P.E. = 6.6$ kJ. If lowered on a rope and pulley, this amount of work could be done. Once on the ground, no more work can be extracted (unless the block is carried to the top by someone expending energy from food).

The available work is not the amount of work that gets done in a process; rather it provides an upper limit on the work that a device could deliver without breaking any of the laws of thermodynamics. The difference that exists between the actual work obtained and the available work is where engineers can look to improve machines and processes – particularly apt at this time, when people are conscious about sustainability agenda. The available work and availability are defined via the following, where p_0 and T_0 are the pressure and temperature of the environment,

$$A = U + p_0 V - T_0 S \quad ; \quad dA = dU + p_0(V_2 - V_1) - T_0 (S_2 - S_1).$$

Relationship to thermodynamic potentials

The Gibbs and Helmholtz functions are known as what can be termed **free energies**. They provide constraints on what can be got out of (or input to) a system. If the Helmholtz function is considered, we can find that $\delta W \geq dF$, with equality holding in reversible processes. Thus, the addition of work to the system (doing work on it from the outside) increases the system's Helmholtz function, whereas if the system does work on the environment, the Helmholtz function falls by at least the same amount. For a mechanically isolated system, no work is done, so that means that any thermal change to the system, as it heads towards equilibrium, must decrease the Helmholtz function. At thermal equilibrium, the Helmholtz function takes a minimum value. In a more general case, the availability of the system is always negative. This means that any change to the system will decrease the amount of energy available for work $dA \leq 0$. Similarly, at thermal equilibrium, the available energy is a minimum, and is in fact zero for a dead state. The form that A takes depends on constraints of applied to the system.

> Example 16.2
>
> Example 16.3

Useful work and Irreversibility

In an engineering situation, a simple evaluation of just the availability is not good enough to see how well a system is performing. This is unrealistic because if all the available energy was supplied by the system it would end up in a dead state. In a realistic process, work also gets done on the surroundings, and this work cannot be usefully used by the system for motion etc. The **useful work** is defined as the difference between the actual work done during the thermodynamic process (total work produced by the device) and this **surroundings work** (which would be done against the atmosphere, or is dissipated as heat etc.)

$$W_{use} = W_{act} - W_{surr} \quad ; \quad W_{surr} = p_0(V_2 - V_1).$$

The **reversible work, W_{rev}** is defined as the maximum amount of useful work that can be produced by a device, or minimum work that must be supplied to a system, as it undergoes a change between two states, when operating on a reversible cycle. The difference between this work and the useful work is the **irreversibility of a process**, I, and is related to the Universe's overall entropy change

$$I = W_{rev} - W_{use} = T_0 \Delta S_{Universe},$$

where T_0 is the Universe temperature (normally that of the external environment) and $\Delta S_{Universe}$ the overall Universe entropy. Thus, the larger the entropy change, the greater the irreversibility of the process and the smaller the amount of useful work that is available.
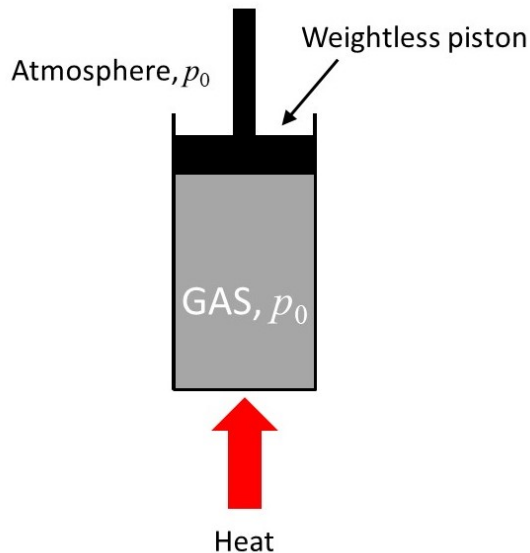
Figure 28: Available work obtained from a piston.

Example 16.4

Figure 27 shows a vertical cylinder which is fitted with a weightless, frictionless piston. The cylinder contains gas at atmospheric pressure, p_0.

When heat is input, work is done, $\delta W = -\delta Q$ (if the process is isothermal) and the gas expands. Atmospheric pressure will be maintained inside the piston.

As the piston rises, no boundary work is done. The work done is not useful since it is just enough to push against the atmosphere outside and move the piston outwards. (If the piston where connected to an external load, via a reciprocator, we would need to add sufficient heat to increase the internal pressure of the gas so that it was above atmospheric pressure. This would then enable us to push the atmosphere aside before doing work).

On cooling the gas, the piston falls which compresses the gas. Again, no work is done.

Example 16.5

17. Phases of a Substance

(You should be familiar with all the material below but I don't expect rote memorization of all the low temperature facts. Thus, for cooling using both the liquefaction of gases by expansion and adiabatic magnetization you should be able to describe the basic principles, but a detailed knowledge is not required.)
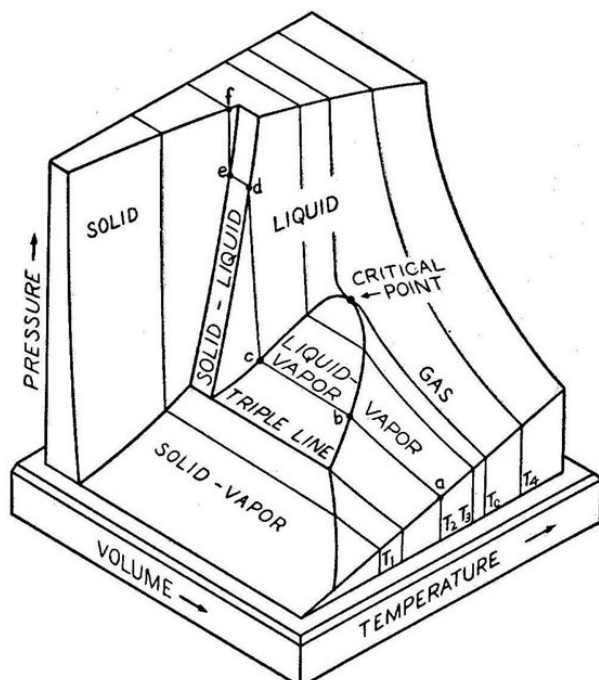

Figure 29: pVT surface for a material.

Substances can occur in one of three **phases**, solid, liquid or gas, and the phase depends upon the temperature and pressure. When the phase of a substance changes with a discontinuity, the effects can be fascinating e.g. when a small change in the temperature can produce a vast change in something else. Pressure-volume-temperature (PVT) surfaces can be sketched in three-dimensions, an example of which is shown in figure 29. They show how the phase of a substance varies with these properties. On these surfaces, there are regions where just one phase exists, others where two phases coexist, and finally along the triple-line, all three phases exist at once.

Consider a gas that is being compressed. At some pressure it begins to separate into two phases (liquid and vapour) and no further

compression can take place, though the volume will be decreased until all the vapour has become a liquid. During this coexistence the liquid and vapour are what is known as **saturated**.

Boiling, Freezing and sublimation

In an isobaric process, and above some temperature (substance dependent), the vapour phase appears with a much larger specific volume than the liquid phase. This corresponds to boiling. Note that a liquid boils when its vapour pressure equals the external pressure. Conversely, if the temperature is reduced below some value a solid phase separates out from the liquid and freezing occurs. Furthermore, a liquid cannot exist at a temperature lower than T_3 and at a pressure lower than p_3. Instead, a direct transition takes place from solid to vapour, known as sublimation.

Latent Heats

Adding heat to a substance increases its temperature and entropy. The amount of energy that must be supplied for a given temperature increase is given by the heat capacity, which relates the gradient of entropy and temperature at some constraint via $C_\alpha = T \left(\frac{\partial S}{\partial T} \right)_\alpha$. At a phase change, extra heat is usually required, known as the **Latent Heat**. However, we also know from our studies of the second law that entropy change, temperature and heat supplied are related by the integral equation $\Delta S = \int \delta Q / T$, so

$$L = \Delta Q_{rev} = T_0 \Delta S.$$

In other words, at a phase change the entropy changes from $S_1 \to S_2$ at constant temperature, T_0.

Phase Transitions

The Gibbs function provides a useful method for describing phase transitions. It is easy to show that the Gibbs function of a substance in equilibrium is the same in both phases over that phase transition (i.e. it is continuous). However, the derivatives of the Gibbs function may not be identical in the different phases i.e.) they are discontinuous. The first derivative of the Gibbs function with respect to temperature (at constant pressure) is the entropy, whilst the second derivative, gives the heat capacity. If the first derivative is not continuous, latent heat must be generated or absorbed at the phase change, and we have a first order phase transition. If the second derivative is discontinuous, we have a second order phase transition and the heat capacity of the substance must be different in the two different phases.

n_2 moles vapour

n_1 moles liquid

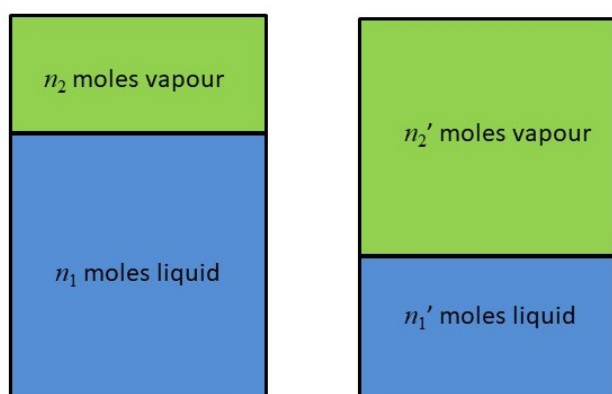n_2' moles vapour

n_1' moles liquid

Figure 30: Gibbs function for a fixed amount of material that coexist between two phases, with the amount of each phase changing with respect to each other.

Example 17.1 We know that total differential of the Gibbs function is $dG = -SdT + Vdp$ (see section 14). At a phase change the pressure and temperature are constant on either side of change, so $dG = 0$ or $G_i = G_f$, the Gibbs function must be the same before and after the phase change, when liquid changes to vapour.

Now consider the system shown and use specific Gibbs functions (defined per unit mass, so use lower case letters).

The iquid and vapour have Gibbs functions g_1 and g_2 before and g_1', g_2' after the system undergoes a volume change (so that we end up with more vapour and less liquid). The total Gibbs functions for each system, before and after the expansion are then

$$G = n_1 g_1 + n_2 g_2 \quad ; G' = n_1' g_1' + n_2' g_2'.$$

Since $n_1 + n_2 = n_1' + n_2'$ (total amount of the material is unchanged in the phase change) and $G = G'$, (from $dG = 0$) the pair of equalities can only be satisfied if Gibbs function takes same value in both phases in each system, i.e. $g_1 = g_2$ and $g_1' = g_2'$.

Example 17.2

Clausius-Clapeyron Equation

This equation describes how pressure changes with temperature for a system having two phases which are in equilibrium, and can be derived by considering a reversible isothermal and isobaric change for a substance moving between two phases, the initial, i, and the final, f, phase

$$\left(\frac{\partial p}{\partial T}\right)_{i \to f} = \frac{L_{i \to f}}{T(V_f - V_i)},$$

where, $L_{i \to f}$ is the specific heat of transformation on going from phase i to phase f. This equation can also be derived using the Gibbs function. This equation is most useful since it tells us the slope of the equilibrium line between two phases in a PT diagram.

Proof 17.1

Example 17.3

Consider the phase change between a liquid and an ideal gas, so $V_f = \frac{RT}{p} \gg V_i$.

$$\left(\frac{\partial p}{\partial T}\right)_{l \to g} = L/T \left(\frac{RT}{p}\right) = \frac{Lp}{RT^2}.$$

Integrating,

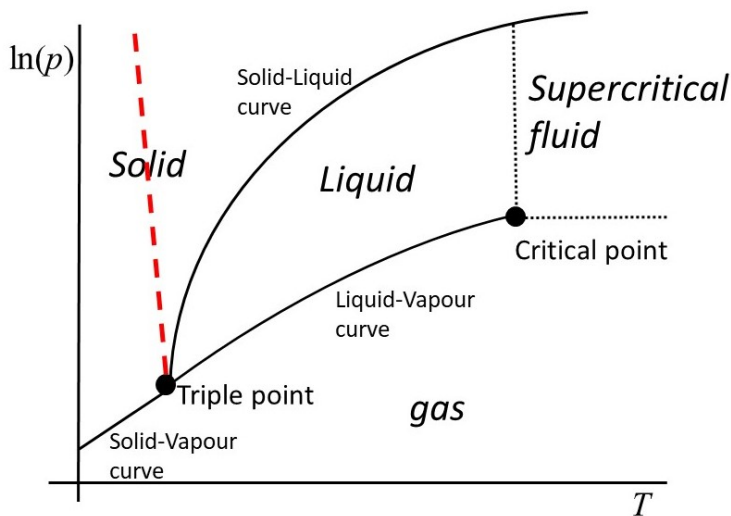$$\ln p = -\frac{L}{RT} + \text{constant}.$$

Figure 31: Phase diagram in the pT plane, including showing the positions of the critical and triple points.

Projections of PVT surfaces give the well known PT and PV curves on **phase diagrams**, an example of which is shown in figure 31. Two specific points of interest exist: the **critical point**, above which the densities of the saturated liquid and saturated vapour are the same; here these two states cannot be distinguished from one another. The other is the **triple point**. At this single point, all three phases coexist but below either the temperature or pressure of this point the liquid phase cannot exist. It is interesting to note that the solid-liquid

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curve is very steep because the entropy change is large but the volume change is small, and it also normally has a positive gradient since volume increases on melting. The line is also pressure dependent.

18. Low Temperatures

Many interesting and remarkable effects occur at low temperatures, for example superfluidity, superconductivity and Bose Einstein Condensation. Low temperatures are also used in the operation of e.g. MRI scanners. Much research work has been carried out in both the above areas, as well as elsewhere, for example, in spectroscopic analysis can be undertaken at cryogenic temperatures to help isolate and resolve the frequencies of vibrational modes. Handy temperatures to know are: $77\,\mathrm{K}$ (liquid nitrogen), $20\,\mathrm{K}$ (liquid hydrogen) and $4\,\mathrm{K}$ (Liquid Helium).

Various methods exist that allow us to access low temperatures, with one of the most common being the liquefaction of gases by the **Joule-Kelvin effect**. This is much more useful in the real world that the simpler **Joule effect**. Of course, liquefied gases can also be used as the coolant in a refrigeration cycle to cool other substances. Adiabatic cooling is another method of cooling. Once these methods are exhausted, further cooling from low temperatures, is possible by the evaporation of liquid under reduced pressure.

Joule-Kelvin Effect

A gas expands through a porous plug in a process known as throttling at constant enthalpy. In this process, we are interested in the Joule-Kelvin coefficient, a measure of how the temperature changes with respect to the pressure, which can also be expressed in terms of heat capacity,

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right].$$
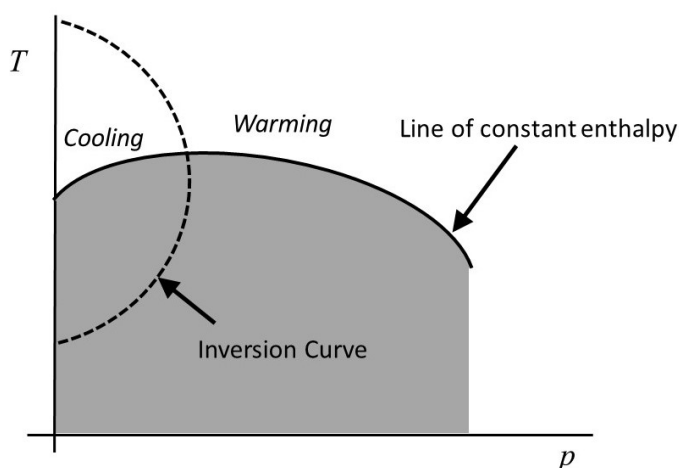
Proof 18.1

Figure 32: The inversion curve in the Joule-Kelvin (constant enthalpy) expansion.

This coefficient changes sign at the inversion point, whose temperature depends on the pressure of the gas before expansion. The locus of these points defines the inversion curve as shown in figure 32. Furthermore, since pressure always decreases during the expansion of a gas, the temperature change can be positive or negative depending upon whether the gas is initially above or below the inversion temperature. This means that some gases must be pre-cooled to a temperature below their inversion temperature before they can be liquefied (cooled) using this method. For an ideal gas, this coefficient is zero, which therefore neither cools nor warms on expansion at constant enthalpy.

Adiabatic Expansion

This process, shown in figure 33, always reduces the temperature of the substance of interest, no matter where we start. However, the lower the initial temperature, the smaller the temperature drop achievable is. The process is cyclic and involves an isothermal compression, followed by an adiabatic expansion. It is easy to see that returning to the initial pressure (point c) results in a temperature decrease, because those points on the adiabatic expansion curve must lie on a lower temperature isotherm than the initial one, along which expansion took place.

Figure 33: pV diagram of an adiabatic cooling process via expansion.

Example 18.1

Getting below $4.2\,\mathrm{K}$

Once we have reached the temperature of liquid helium we cannot continue to liquefy a gas and further lower its temperature by either of the above two methods, so how do we cool below $4.2\,\mathrm{K}$? First, we note that any other sample can easily be cooled to the temperature of liquid helium by placing it in a cryostat surrounded by liquid helium that acts as the coolant in a refrigerator. **Pumping** on this liquid helium bath, which lowers the pressure, allows a further decrease in temperature to just below $1\,\mathrm{K}$, ($0.7\,\mathrm{K}$ for ^{4}He and $0.3\,\mathrm{K}$ for ^{3}He). **Dilution refrigerators** can be used to reduce the temperature down to a few milli-Kelvin. These operate using a mixture of ^{3}He and ^{4}He which are of different densities. At sufficiently low temperatures, a mixture of the two spontaneously separates with ^{3}Hemoving to the top. The more dense ^{4}He atoms are more closely packed since the inter-atomic forces are greater. This means that all helium atoms want to be preferentially surrounded by ^{4}He. Therefore the heavier ^{4}He is actually only $94\,\%$ pure. Thus, it is what is termed a dilute phase of ^{3}He. Cooling works by moving a ^{3}He atoms from the highly ordered concentrated phase to the more disordered dilute phase and to do so, it must absorb heat, cooling the surroundings (this is rather like molecules of hot tea/coffee moving across the water air phase boundary at a liquid surface, removing energy and cooling the liquid!)
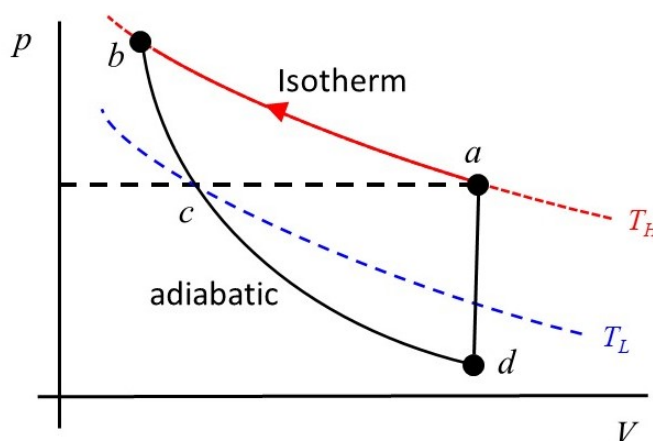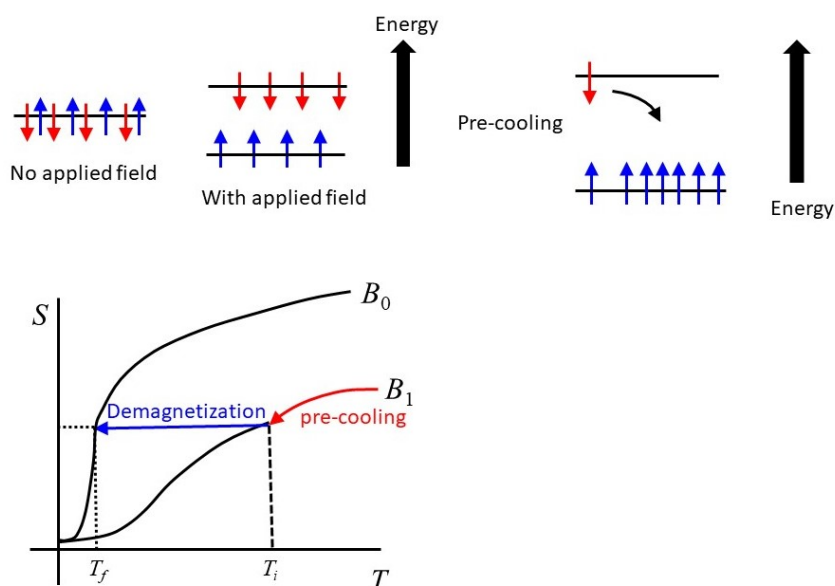
Figure 34: Adiabatic demagnetisation: both the process and the TS diagram.

Adiabatic Magnetisation

A sample is surrounded by metal plates, connected to a dilution refrigerator, which can be cooled magnetically to very low temperatures. Without the presence of an applied field the metal contains approximately equal amounts of spin-up and spin-down atoms. When a magnetic field is applied, the spin-up states become energetically more favourable (lower energy) as shown in figure 34. Cooling of the metal by dilution refrigeration removes energy. This depopulates the upper energy level of spins in favour of the lower energy level in a process known as pre-cooling. After thermally decoupling the metal from the dilution refrigerator, the magnetic field can be slowly reduced, forcing the highly populated, lowest energy level to increase in energy. As the metal is now isolated, energy must be absorbed from the surroundings, cooling both it and the sample. During demagnetisation the entropy, and hence disorder, do not change, so the process is adiabatic.

Example 18.2

Low Temperature Records

We would like, if possible, to answer the question: how low a temperature can we actually reach? The answer is set by the **Third Law of Thermodynamics**. The current lowest temperature recorded is $100\,\text{pK}$ by a research group in Finland investigating the magnetism of a piece of rhodium metal Laser cooling, using the interaction of matter with light fields - available at Durham - can be used to cool to just a few nano Kelvin. At such low temperatures, interesting quantum effects manifest themselves. We want to see if we can describe general thermodynamic properties at such low temperatures.

The second law of thermodynamics tells us that we can only ever measure the entropy change between two states of system. We note here, that statistical mechanics can be used to describe the actual entropy, but in a classical sense it would be nice if we knew the entropy of a system at some temperature. The **third law of thermodynamics** provides this information.

19. Third Law of Thermodynamics

Various statements exist; the first was given by Walter Nernst in 1920. Based on experimental evidence of changes in the Gibbs function and enthalpy, he postulated

THE ENTROPY CHANGE OF ANY REACTION IN A SYSTEM IN INTERNAL EQUILIBRIUM IS ZERO NEAR ABSOLUTE ZERO.

Example 19.1

Max Planck improved this by hypothesising the following about perfect crystals

THE ENTROPY CHANGE OF ALL SYSTEMS IN INTERNAL EQUILIBRIUM IS THE SAME AT ABSOLUTE ZERO, AND MAY BE TAKEN TO BE ZERO.

It is believed that this is valid for any system, not just perfect crystals, providing that it is in internal equilibrium. A further generalisation was made by Francis Simon in 1937, who looked at the contributions to a system's entropy from the various subsystems contained in it (electrons, nuclear spins etc.) that are all weakly coupled. This statement allows us to concentrate on the thing we are interested in, knowing that its entropy goes to zero as the temperature approaches absolute zero, while also allowing us to ignore system aspects that we are not bothered about, whose entropy might only go to zero at some temperature much closer to absolute zero.

Third Law Consequences

THE CONTRIBUTION TO THE ENTROPY OF A SYSTEM BY EACH ASPECT OF THE SYSTEM WHICH IS IN THERMODYNAMIC INTERNAL EQUILIBRIUM TENDS TO ZERO AS $T \to 0$.

There are many of these. At absolute zero: heat capacities tend to zero; thermal expansion stops; gases do not remain ideal; Curies Law breaks down; and absolute zero is unattainable. The final statement has almost been elevated to another statement of the third law

IT IS IMPOSSIBLE TO REACH $T = 0$ IN A FINITE NUMBER OF STEPS.

Example 19.2

By definition,

$$C_\alpha = T\left(\frac{\partial S}{\partial T}\right)_\alpha \quad \Rightarrow \quad \Delta S(p,T) = \int_{T_1}^{T_2} \frac{C_p dT}{T} \quad = C_P(\ln(T_2) - \ln(T_1)).$$

As $\lim_{T_1 \to 0} \ln(T_1) \to -\infty$ and because $\Delta S = 0$ we must have a heat capacity of zero or we have a contradiction of Nernst's theorem!

20. Thermodynamics of other Systems

For the interested student, more details on all Similarly, I don't expect you to memorise any of the equations to describe thermodynamics of real systems or real gases. However, as we did in our discussions on ideal gases you should be in a position to manipulate them, using relevant partial derivatives etc., and thus calculate system properties from a given starting point. The material on atmospheric and biological thermodynamics is not examinable.

Thermodynamics in Action

Thus far, we have mainly considered the thermodynamic properties of ideal gases, but the tools at our disposal also describe many other systems such as rods, bubbles and magnets. In each case, we start from the first law of thermodynamics ($dU = TdS + \delta W$), with the appropriate formalism of work. The work is always a generalised force (intensive variable) multiplied by a generalised displacement (extensive variable). This means, for example, that you can mathematically show that a rubber band placed under tension will cool when it is released. In paramagnetic behaviour, the magnetic moments line up in an applied field and Curie's law, $\chi \propto 1/T$, is obeyed.

Example 20.1

Real Gases

If the ideal gas equation is used to describe real gases it breaks down when the pressure is high or the volume is small, because all real gases actually do interact with each other. For example, if no interactions took place, we would not be able to liquefy gases via expansion. The simplest way to describe a real gas is through the van der Waals equation which describes both the molecular interactions and accounts for the gas molecules having a finite size. Even though it is a model, it describes more physical properties of real gases compared to the ideal gas law. Its equation of state is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT.$$

Other models of real gases also exist, such as the Dietrici equation, $p(V_m - b) = RT \exp(-a/RTV_m)$, which contains a Boltzmann term to correct the pressure since molecules in a real gas lose some kinetic energy each time they hit the wall of the container they are in. Another correction to the ideal gas law is by using a Virial Expansion. Here, a power series is used to modify the ideal gas law, $\frac{pV_m}{TR} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \cdots$ If the coefficient $B(T) = 0$, we obtain the ideal gas law and this happens at the Boyle temperature. The additional terms provide information on the intermolecular interactions.
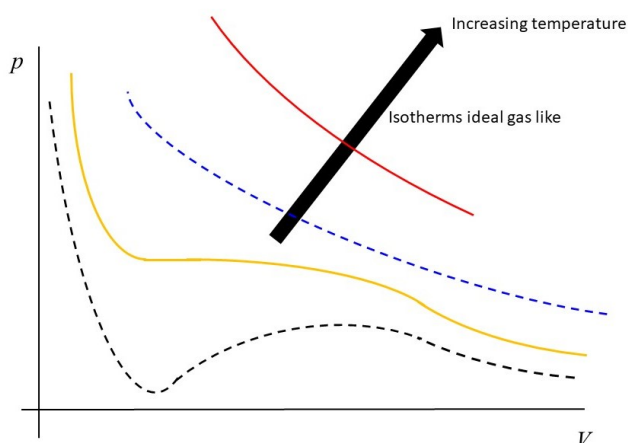

Figure 35: Isotherms for a van der Waals gas

Example 20.2 Consider a van der Waals gas

Isotherms go from ideal gas shaped in top right, to 'S' shape at low volume and pressure.

What does this mean for isothermal compressibility, $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$?

For an Ideal gas, $\kappa_T > 0$ since $\left(\frac{\partial V}{\partial p}\right)_T < 0$ always.

For a van der Waal, this must change sign in the horizontal 'S-shaped' region, we actually have a negative compressibility here (i.e. increasing pressure increases volume!) This means pressure increases can increase volume, so in a pressure fluctuation, work can be done by the gas causing expansion (energy is provided to amplify fluctuations).

The gas behaviour is okay to critical temperature, where we have a point of inflection. Here, have $\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$.

Atmospheric Thermodynamics

The atmosphere of the earth, gases gravitationally bound to the earth (of mass $\sim 5 \times 10^{18}$) can exchange thermal energy with the oceans (of mass $\sim 10^{21}$) and space. Solar energy from the sun and radiation emitted from the earth cause the atmosphere to have a temperature profile that can be modelled using energy arguments.

Greenhouse effect and Climate Change

The earth receives short wavelength radiation from the sun and reradiates it a longer (infrared) wavelengths. Some of this surface radiation is absorbed by certain molecules (CO_2, H_2O) in the atmosphere and radiated upwards or downwards, leading to surface warming. Consequently, radiation that would pass straight out of an atmosphere of purely diatomic molecules (N_2, O_2 etc.) is absorbed by these molecules causing an increase in temperature. Obviously, this is good to a certain extent otherwise the earth would be cold all of the time, but it can elevate the temperature too much. Since the industrial revolution, the concentrations of greenhouse gases have changed immensely. Due to the large heat capacity of the oceans, the full effects of these increases on the climate may not become apparent for many years, so there is much research work to be done.