Imperial College
London

Thermodynamics

Second year lecture notes

Vijay Tymms
Version 5
October 2019

Contents

0. Course overview

0.1 Lecturer details

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There will be two office hours per week arranged on the Friday, emailed and noted on Blackboard

0.2 Lecture details

Timetable: No fixed timetable but usually three lectures per week

Duration: The course runs from week 2 to week 8 in the 1st term

Number of lectures: 18 lectures at 50 minutes each plus one revision lecture in term 2

Sections: The course is split into 18 sections

Course notes: Course notes are given out for the whole course and put on Blackboard.

Study handout sheets: In the final lecture of each week from 2 to 8 you will be given a study worksheet will be uploaded to Blackboard. Each contains material designed to consolidate understanding from the preceding week's lectures. These state learning objectives for the study, contain some suggested sources for further study (often basic reading but occasionally other audiovisual material) and problems related to the lectures. There will be a range of problems for you to do in your own time, an assessed problem for that week (if there is one) and the tutorial discussion problem (which you should not attempt prior to the tutorial). Hints and solutions to all the problems on the study sheet will be made available on Blackboard a maximum of one week after release.

Summer exam: The majority of the summative assessment for the course comes from the Thermodynamics and Statistical Physics exam in term 2

0.3 Course overview and learning outcomes

This course covers the zeroth, first, second and third laws of thermodynamics in detail appropriate for core university physics in the UK. It introduces entropy formally for the first time at university level. Much of the material follows on directly from the year 1 Structure of Matter course. Knowledge of the course is essential for starting the Statistical Physics course that follows on from it.

On completing the Thermodynamics course, students will:

1. recall, understand and use the zeroth, first, second and third laws of thermodynamics
2. appreciate that the four laws can be phrased in different ways, why these different ways are important in their own right and know how to prove that seemingly different statements are equivalent
3. know that thermodynamics is a macroscopic theory that exists independently of atomic and subatomic theory
4. appreciate that according to contemporary understanding there are no known exceptions to the four laws
5. understand the ideas of thermodynamic systems and thermodynamic equilibrium
6. understand, appreciate and use the varied definitions of temperature and entropy
7. recognise equations of state and use an unseen equation of state to predict properties of a thermodynamic system
8. use the first law to analyse basic thermodynamic process with the use of PV and TS diagrams
9. use the first law to derive several general expressions for the heat capacity of materials
10. recognise the concept of a thermodynamic cycle and use cycles to compute efficiencies of heat engines and coefficients of performance of heat pumps and refrigerators
11. recall and state the Kelvin and Clausius statements of the second; prove one statement from the other by consideration of an ideal heat engine of heat pump
12. recall and state the mathematical formulation of the second law in terms of entropy
13. compare and contrast reversible, quasistatic and irreversible processes
14. argue why the Carnot cycle is the most efficient possible thermodynamic cycle operating between two heat reservoirs and why such it is a theoretical ideal that can never be attained
15. recall the formula for the Carnot efficiency
16. generalise the Carnot cycle to thermodynamic systems other than an ideal gas
17. recall and understand the Clausius inequality and appreciate its derivation from a multi-stage cyclic process on an arbitrary system
18. appreciate the importance of derived thermodynamic potentials and know how internal energy, enthalpy, Helmholtz free and Gibbs free energy can be used to interpret thermodynamic systems in more detail than by merely using the first and second laws
19. derive other thermodynamic potentials from first principles
20. derive the Maxwell relations
21. use the Maxwell relations in conjunction with the first and second law to compute changes in temperature, volume, pressure and entropy in thermodynamic systems
22. understand the subtleties in the expansion of real gases, notably in free expansion and throttling processes and calculate temperature changes for these processes
23. appreciate the need for a chemical potential when dealing with phase changes and use chemical potential in new expressions for free energy
24. appreciate the concepts of generalised force and displacement in thermodynamics
25. appreciate the difference between phases of matter and states of matter
26. use PT diagrams in conjunction with PV diagrams to understand the nature of phase changes for materials
27. calculate the changes in specific Gibbs function, specific heat capacity, specific volume and specific entropy for first order phase changes
28. use the Clausius-Clapeyron relation to compute the change in melting and boiling point with temperature for materials
29. appreciate the different ways of stating the third law and how they all relate to an absolute zero of temperature
30. provide a thermodynamic proof the absolute zero is unattainable
31. appreciate that thermodynamics ceases to be useful to understand the physics of materials near absolute zero and that the atomic hypothesis and subatomic physics are needed
32. show how thermodynamics shows that properties of material either become zero or have no temperature dependence close to absolute zero
33. appreciate how thermodynamics means energy degrades and leads to the heat death of the universe
34. explain the paradox and resolution of the paradox of Maxwell's demon

0.4 Assumed prior knowledge

All of the core first year course material, including both the mathematics and the physics. Structure of Matter is the physics course that most directly relates to this one and much of the material will follow on directly. Regarding the mathematics Functions is probably the most applicable course.

0.5 Recommended texts

Sears and Zemansky's University Physics with Modern Physics, 12th Edition, Young and Freedman – the recommended text for the core degree course. It has hundreds of problems to work through on the basics of thermodynamics.

Heat and Thermodynamics, Zemansky and Dittman, (McGraw-Hill)

Thermal Physics, Finn (Nelson Thorne)

The Feynman Lecture on Physics, Volume 1: Mainly Mechanics, Radiation and Heat, 2nd Edition (2005), Feynman, Leighton and Sands, Addison Wesley – chapter 39 to 46 contain material relevant to this course, Structure of Matter and Statistical Physics

I will often also provide sources for further reading and inspiration during the course, often in the study handouts.

1. An overview of thermodynamics

This section provides an overview of what thermodynamics is – and what it isn't – relevant to second year degree level physics. It provides some alternative, though overlapping, definitions of the discipline and highlights its positions within all of physics. Thermodynamics is governed by just four laws that are introduced in a readily understood format. The second half of the section introduces some essential concepts and vocabulary most notably to do with equilibrium.

1.1 What thermodynamics is

A basic statement with qualifications

Broadly speaking, thermodynamics is the study of the transfer of heat energy on a macroscopic scale. More specifically, it deals with physical systems – well-defined volumes in space that contain any number of components – and studies the exchange of heat energy between both the components of the system and the system's surroundings, plus the conversion of heat to other forms of energy and vice-versa.

Going further still, thermodynamics considers not just the heat flow regarding the system, but also the work done by each of components the system on each other and on the surroundings. All components of the system can be defined by a set of macroscopic variables that are all related to temperature.

The four laws of thermodynamics

Actually, just two principles can, more or less, summarise all there is to know about thermodynamics, and indeed all processes that occur in the macroscopic world. These are:

(i)	Energy is conserved
(ii)	Entropy increases

You haven't met entropy formally yet but for now think of simply as the amount of disorder in a system. A nicely stacked Jenga tower has high order, low disorder and thus low entropy, whereas a collapsed Jenga tower has low order, high disorder and thus high entropy.

Although that's not quite enough to describe the whole subject all of thermodynamics can be expressed by just four laws. These laws can be, and are, expressed in a variety of ways, which may well appear quite different on first viewing; this introduction provides some easily accessible statements of them:

> **The zeroth law of thermodynamics** states that if two objects are both in thermal equilibrium with a third, then they must be in thermal equilibrium with each other
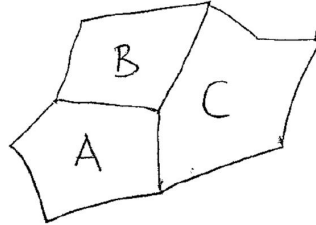
Figure 1.1 If object *A* and object *B* are both in thermal equilibrium with object *C* then they must be in thermal equilibrium with each other. This is almost the same as stating that the objects are all at the same temperature.

The law is useful as it helps us understand heat, temperature and concepts of equilibrium in more detail. There will be no separate section dedicated to the law itself but it will be mentioned and used many times in the course.

> **The first law of thermodynamics** states that the <u>change</u> in internal energy of a closed system equals the heat supplied <u>to</u> the system plus the work done <u>on</u> the system.
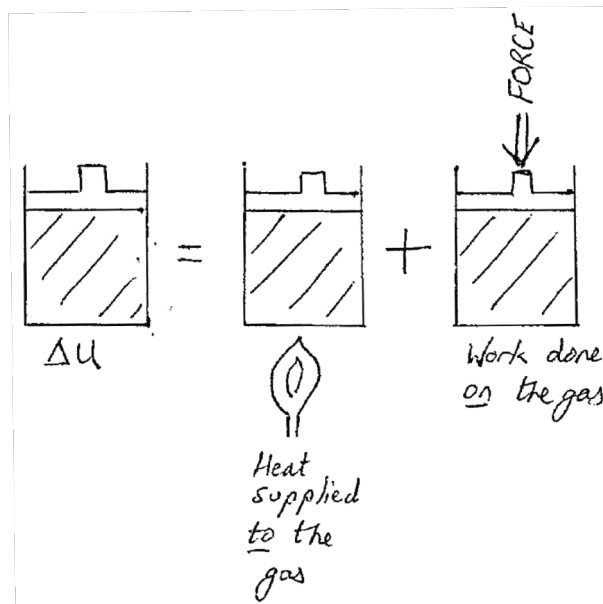
Figure 1.2 Many thought experiments in thermodynamics will use the concept of a gas in a piston; here the increase in internal energy of the gas equals the work done on the plunger plus the heat supplied by the flame

The law is a specific way of stating the conservation of energy. Section 4 is entirely devoted to the first law and it will be invoked many times throughout the course. You have already met the law formally in the Structure of Matter course.

The second law of thermodynamics states that heat energy will always flow from a hotter object to a colder object when they are in thermal contact.

This is one of many forms of the second law which can, at first sight, seem very disconnected. Another simplified statement of the law is merely that "entropy increases". How the various forms are related is one of the fundamental parts of this course, with section 6 itself being specifically dedicated to the second law.

The third law of thermodynamics states that it is impossible for an object to reach an absolute zero of temperature.

The third law is discussed in detail in sections 16 and 17.

Thermodynamics is a macroscopic theory

One of the many remarkable things about thermodynamics is that it is an entirely macroscopic theory of matter and energy meaning it doesn't involve any consideration of the graininess of the world - atomic and subatomic behaviour is not relevant to the four laws nor their ramifications. Note that the theory was largely developed in the 19th century – before the discovery of quantum mechanics and even before the existence of atoms was universally accepted. It is remarkable that the theory holds so true; of course the test of any good theory is by experiment and indeed all of the four laws of thermodynamics have, thus far, been well verified by experiments: in the whole of history no repeatable experiment has been conducted that contradicts any of the four laws. Einstein himself once (allegedly) said

> **"It is the only physical theory of universal content, which I am convinced, that within the framework of applicability of its basic concepts will never be overthrown".**

Even with the discovery of quantum mechanics and the astounding theoretical and practical advances across science of the last 110 years where we are now able to manipulate individual atoms and their structures have flaws or modifications to the four laws been discovered; indeed the fact that they have been tested rigorously in a realms far beyond those that the founding fathers could ever have dreamt of is a tribute to their success.

That said, atomic and subatomic theory is, of course, relevant to thermodynamics, and indeed can go a long way to explaining some or perhaps all of the laws on what may be considered a more fundamental level. Broadly speaking, the branch of physics that deduces the laws of thermodynamics from our

understanding of atoms, with the necessary application of physics (quantum mechanics and classical mechanics as and when appropriate) and mathematics (probability theory and statistics) is statistical physics. Kinetic theory (as met in year 1 Structure of Matter) is often a student's first introduction to statistical physics and this course leads straight on to the first such course of your degree (and the only one that forms part of the core curriculum).

That said, it would be a little odd in this day and age to give a course on thermodynamics without any reference to explanations of the laws and their results without a reference to the graininess of matter at all – in fact this course will often make reference to microscopic scale physics when appropriate.

Thermodynamics doesn't use distance and time as independent variables very much

Think of all the equations you know in physics. These will tend to be <u>constitutive equations</u> i.e. those that define a property of a substance, like $density = \frac{mass}{volume}$ or how something responds to a stimulus of some kind, like $resistance = \frac{potential\ difference}{current}$ or differential equations that explain how the rate of change of something depends on something else like $F = ma$ or any of Maxwell's equations. Most of the differential equations that you have formally met so far use either time or distance themselves – or time-related or distance-related variables (like frequency and wavenumber) as the independent variables. A simple way of looking at it is that when we plot graphs in physics it often either time/frequency or distance/wavenumber goes along the x-axis.

Thermodynamics is different because although differential equations do dominate the mathematics of the discipline the independent variables are <u>state variables</u> like temperature, pressure, and volume. While the direction in which a process occurs (e.g. which way heat flows, which direction a chemical reaction goes in, or the which way matter moves) is fundamental to the subject the <u>rate</u> at which it flows ($\frac{dQ}{dt} \equiv \dot{Q}$) or the <u>gradient</u> ($\frac{dQ}{dx} \equiv Q_x$) is of secondary importance (or even of nil importance depending on the problem under scrutiny).

1.2 Thermodynamic systems

A central concept in the study of thermodynamics is the concept of a system. A system is made of a volume in space with a defined boundary and a surroundings:
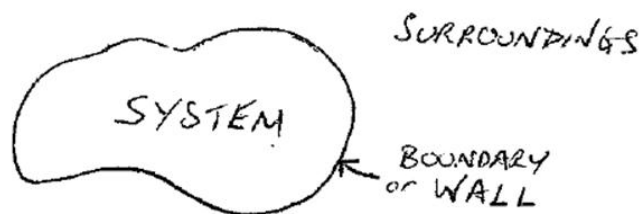
Figure 1.3 A generic thermodynamic system

The system is essentially the thing we are interested in. It can consist of any number of components that can interact with each other and with the surroundings. As the course progresses the nature of systems and their surroundings will be qualified in greater detail but for now it is important to remember that there are three types of system:

An <u>open system</u> is a system where some part of the boundary permits an exchange of both matter and energy.

A <u>closed system</u> is a system where some part of the boundary permits an exchange of energy but the whole of the boundary is prevents an exchange of matter.

An <u>isolated system</u> is a system where the whole of the boundary prevents and exchange of matter and of energy.

1.3 Equilibrium in thermodynamics

Although the word "equilibrium" didn't appear in any of the statements of the four laws in this section in fact thermodynamics is all about equilibrium. A central tenet of the subject is that a system, or a set of connected systems, always moves towards <u>thermodynamic equilibrium</u>. And once a system, or set of connected systems is in thermodynamic equilibrium, it will remain in that state until it is disturbed by an external agent.

To define it simply, thermodynamic equilibrium is the state in which there is no net macroscopic flow of matter or energy either within a system or between sets of connected systems.

To define it more rigorously other types of equilibrium need to be defined:

Two systems are said to be in **thermal equilibrium** if they are in thermal contact and no heat flows between them. As the second law implies this means the two systems have the same temperature so in fact saying two objects are in thermal equilibrium with each other is equivalent to saying they have the same temperature (though there is actually a subtlety to this explanation that will be revisited when temperature

is more formally defined in section 2.) A system is in thermal equilibrium with itself when it its temperature is spatially and temporally uniform and no macroscopic heat flows with the system itself.

A system is said to be in **mechanical equilibrium** when it experiences no resultant external force nor a resultant external torque thus its linear momentum and angular momentum are constant relative to any inertial reference frame. In thermodynamics when considering two connected systems a simplified version of this is to say that the two systems are in mechanical equilibrium when their pressures are the same.

A system is said to be in **chemical equilibrium** when the reactants and products are present in concentrations where there is no net change in the amount of each with time. All chemical reactions can be considered as reversible reactions and chemical equilibrium in a reaction is reached when the forward rate equals the reverse rate. In thermodynamics the system is said to have a uniform **chemical potential** when it is in such a state. Chemical potential is discussed in detail in section 14.

Two systems are said to be in **phase equilibrium** when there is no net change in the amount of material in each separate phase.

For two systems to be in thermodynamic equilibrium they must be in thermal, mechanical, chemical and phase equilibrium. If two systems are *not* in thermodynamic equilibrium they will move towards that state. Thermodynamics is all about deciding which direction the movement is in (but doesn't consider the rate at which the movement occurs).

2. Temperature, internal energy and entropy

In thermodynamics we will meet several state variables – physical parameters that describe the current physical state of a system without consideration of what has happened to the system before it arrived at that state, nor what will happen to it after. The three most important are temperature, internal energy and entropy. Essentially these are the fundamental parts of the zeroth, first and second laws. In this section all three quantities are defined in a little more detail; a more complete understanding of all the quantities, especially entropy, will develop as the course progresses and beyond into the Statistical Physics course.

2.1 Temperature

We all know what temperature is. We know the difference between a hot day and a cold day, and what it means to say one object has a higher temperature than another. We're also all comfortable with the idea that thermometers can measure temperature, and that several temperature scales exist of which the most well-known everyday scale is the Celsius scale (with the freezing point of water at $0\ °C$ and the boiling point at $100\ °C$ with linear steps between and beyond) and the Kelvin scale (also known as the absolute scale or thermodynamic scales) as being a linearly shifted version of this with $0\ K \cong -273\ °C$ and so on. And most of us are reasonably happy to take on board that there exists an absolute zero of temperature that can never be attained.

2.1.1 Defining temperature

But how do you <u>define</u> temperature? Beyond what we have said above and recognising that it is a scalar quantity how do you give a rigorous definition to temperature? You can't just say that it is a measure of how hot something is. Or can you? In fact, that <u>is</u> one possible definition of many. The usefulness of each definition really depends on what you want to use it for though each ought to be consistent with the others within the limits of how they are explained.

Aside from the difficulty of merely articulating something that we already feel we understand in a formal language, one further issue is a question of scale. This can be summarised by asking what the temperature of a system is a single point inside the volume under consideration. This is comparatively easy to answer when the system is considered macroscopically but on a microscopic scale it become intractable. If the system is a gas for example, on a microscopic scale a single point is likely to be in between the atoms that make the gas. Does it make sense to ask what the temperature is there? A similar question can really apply to any other intensive variable applied to the system (e.g. density) but does indicate a further issue.

Definition 1: temperature is what a thermometer reads

This of course seems like a completely circular – and trivial - definition at first sight but it depends on what is more fundamental – the quantity itself or the device (the meter) that measures it. At first sight one might say the quantity itself is the more important thing but one school of thought does state that for a quantity to be fully defined a way of measuring it must be defined. Thus, to define a set of thermodynamic parameters the meters that measure things are described initially then the quantities themselves are assigned to the meters.

This forms part of larger concept – that of thermodynamic instruments – where an instrument is either a meter, which measures a thermodynamic parameter or a reservoir, which forms the surroundings to a system and retains a constant value of the parameter in questions.

Definition 2: temperature is the degree of hotness

This ties directly in with the zeroth and the second law of thermodynamics – and the qualifying statement made in subsection 1.2 that saying that two objects are in thermal equilibrium is more or less equivalent to saying they are the same temperature but can go some way to qualifying a subtle difference.

We can say that if two objects are in thermal contact then if one has a higher temperature than the other then the heat must flow from hotter to colder and thus we are implicitly saying that temperature is a proxy for "hotness". Hotness isn't normally such a well-defined concept in physics but for certain systems it is better to define the hotness of adjacent components rather than the temperature in the case that the temperature cannot be well defined. This could be the case in an inhomogeneous physical system with irregular changes within. It may be impossible to measure the temperature at any one time in a system that is not in thermodynamic equilibrium with itself. But placing it next to another system will still cause heat to flow from hotter to colder.

Definition 3: in terms of the average kinetic energy

Another definition, or rather, another interpretation of temperature that has been seen in the Structure of Matter course and follows from the theorem of the equipartition of energy and kinetic theory is that the temperature of an object is directly proportional to the average kinetic energy of the molecules comprising the objects. For monatomic ideal gases this leads to the important, well verified, law that

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T \qquad \textbf{Equation 2.1}$$

where m is the mass of each atom, $\overline{v^2}$ the mean square speed of the atoms, $k_B \approx 1.38 \times 10^{-23}$ JK^{-1} is Boltzmann's constant and T is the temperature in Kelvin.

Definition 4: as a reciprocal of thermodynamic beta

Boltzmann's constant was also seen in the Structure of Matter course, and will be seen detail in the Statistical Physics course as a measure of the probability that a particle has a certain energy, E - it turns out to be directly proportional to $e^{-\beta E}$ where $\beta = \frac{1}{k_B T}$. Expressions of this type can also be seen, for example, in equations involving rates of chemical reaction – they are often also proportional to $e^{-\beta E}$. When dealing with equations of this type it becomes more natural to stop dealing with T as the fundamental quantity and instead consider β as the fundamental quantity and define temperature as a consequence of that.

2.2 Internal energy and heat

At GCSE level heat is sometimes stated to be the amount of thermal energy contained with an object. Though suitable for GCSE this definition is not suitable for university level physics study – it is almost the way we define internal energy – so it is worth defining heat properly before defining internal energy

2.2.1 Heat

Heat has been mentioned in connection with both the first and the second law. In both instances it involved a discussion of a transfer of energy either into or out of a single closed system (the first law) or from one body to another in thermal contact (the second law). The key point is to do with the transfer of energy between objects – **heat can be defined as the energy transferred between two objects in thermal contact**. It is a scalar quantity with units of joules. In these lecture notes it will be usually given the symbol Q and as it is associated with a change in energy will often be prefixed with some form of delta. e.g. if two objects are put in thermal contact and transfer $10\,\text{J}$ of heat between them then we could write $\Delta Q_{hot \rightarrow cold} = +10\,\text{J}$ and $\Delta Q_{cold \rightarrow hot} = -10\,\text{J}$.

A transfer of heat is always associated with a change in entropy of the objects in contact.

2.2.2 Internal energy

The internal energy (U) of a system is defined as the total energy contained within a system. It is scalar with units of joules and is an extensive quantity (i.e. the magnitude of the internal energy of an object depends on its size).

The internal energy of the system does not include the kinetic energy it has relative to another inertial reference frame (so a cup of tea of internal energy $500\,\text{J}$ that is stationary has the same internal energy as an identical cup of tea travelling in a fast moving car).

The internal energy of a system does not include the potential energy it has by virtue of its position in a conservative force field (so the same cup of tea has the same internal energy whether it is on the floor or placed on a table).

Microscopic view

From a microscopic view the total energy of a system is entirely comprised of:

- the kinetic energy of all its constituent particles

plus

- the energy required to bring them into place i.e. the internal potential energy of all the particles.

For an ideal gas, none of the particles experience any forces of attraction or repulsion so the internal energy is entirely kinetic. As the average kinetic energy is proportional to temperature only this means the internal energy of an ideal gas must also be simply be proportional to temperature; in fact it can be proved (as in the Structure of Matter course) that

$$U_{ideal\ gas} = \frac{3}{2}Nk_BT \qquad \textbf{Equation 2.2}$$

where N is the number of atoms in the gas.

For real gases the particles feel some forces of attraction when far apart and repulsion when squashed together so there should be some volume dependence as well. For a van der Waals gas for example,

$$U_{vdW} = \frac{3}{2}Nk_BT - a\frac{N^2}{V} \qquad \textbf{Equation 2.3}$$

where a is a constant.

Internal energy is one of the <u>thermodynamic potentials</u> – scalar quantities that define the state of a system. There are five important thermodynamic potentials related to energy that are seen in this course (introduced in sections 9 and 12) that all prescribe how much energy can be extracted from a system in different ways. Internal energy is a measure of how much energy can be removed from a system as work plus how much can be removed as heat.

2.3 Entropy

As stated in section 1 entropy can be thought of as the amount of disorder in a system. Another way of thinking about it that may seem quite different at first is that <u>entropy is the lack of energy available to do mechanical work in a system</u>. That may sound a bit of a mouthful but we can make sense of it by thinking of the Jenga blocks again. When neatly stacked into a tower each block could be lowered using some kind

of machine that used the falling gravitational potential energy to do mechanical work. When collapsed the energy is converted to heat and is not so easy to use for mechanical work. Just how much the capability to do useful work has fallen is one of the central parts of the second law.

This is generally true. The more disordered a system, the less energy available for mechanical work and the greater the entropy.

It was stated in section 1.1 that thermodynamics could be summed up by saying energy is conserved and that entropy increases. To take the entropy part further, consider an isolated system of any kind. The system always changes its nature to try and move towards thermodynamic equilibrium and will continue changing until thermodynamic equilibrium is fully attained. During this process the total entropy of the system always increases. When thermodynamic equilibrium is reached the system has attained a state of maximum entropy i.e. maximum disorder and minimum amount of energy available for work. Once in this state the system will do absolutely nothing until either (a) heat is supplied or (b) work is done to move it away from thermodynamic equilibrium i.e. increase the order. The move towards thermodynamic equilibrium and maximum entropy will thus start anew.

2.3.1 Reversible and irreversible processes

Before providing a mathematical definition of entropy now is a good time to provide two essential classifications of process in thermodynamics. These will be referred to throughout the course. Remember for any process that we discuss in thermodynamics a system:

 - starts in an equilibrium state

 - experiences some kind of changes to the variables associated with the system involving some combination of heat supplied and work done

 - finishes in an equilibrium state.

> **A reversible process is one in which the system can be restored to its original state without any change to the system and surroundings.**

What this means is that if a process is reversible, and has subsequently been reversed (i.e. brought back to its original state) then if an external observer were to measure all the properties of the system itself and the surrounding universe then they would not detect any change.

> **Correspondingly, an irreversible process is simply a process that is not reversible: bringing the system back to its original state causes some kind of change to the surroundings.**

The reversible process is a theoretical concept. All real macroscopic processes are irreversible for the simple reason that they all involve some dissipation of energy and thus some kind of measurable change to the outside world when restoring the system to its original state.

For example, consider the oscillation of a pendulum. In a frictionless world when the pendulum goes through one complete cycle it returns to its original state without any change in the surroundings. But it in the real world energy is dissipated by friction at the pivot point and with air resistance so the oscillation gets damped. An external agent is required to return the system to the same initial state. An external observer could measure a small increases in temperature of the surroundings, and a reduction in the fuel content of whatever powers the external agent.

Just as with many ideas we develop in physics, we will often, but not always, assume the reversible ideal in thermodynamics.

A reversible process can also be thought of as a process where the system and surroundings are in thermodynamic equilibrium at all times during the process.

2.3.2 The macroscopic definition of entropy

Imagine that in a single, infinitesimal, step of a reversible process a small quantity of heat, δQ_R, is transferred in or out of the system where the subscript R implies the process is reversible. The infinitesimal change in entropy, δS, of the system is <u>defined</u> by the equation

$$\delta S = \frac{\delta Q_R}{T} \qquad \textbf{Equation 2.6a}$$

where T is the system's temperature during the change. So if heat is put into the system the system's entropy increases and if heat is removed from the system its entropy decreases.

The corollary of this is that as the infinitesimal step is reversible, the entropy change of the surroundings is given by $-\frac{\delta Q_R}{T}$.

For an entire reversible process, the entropy change is given by the sum of the entropy changes of each individual step. For an infinite number of infinitesimally small steps this gives the entropy change for a whole reversible process as:

$$\Delta S = \int_{Initial\ state}^{Final\ state} \frac{dQ_R}{T} \qquad \textbf{Equation 2.6b}$$

Note that the entropy change in a reversible process depends only on the initial and final thermodynamic states and not the thermodynamic path taken. This concept will be revisited later in the course during and after discussion of the First Law.

The entropy change of the surroundings in a complete reversible process is thus $-\int_{Initial\ state}^{Final\ state} \frac{dQ_R}{T}$.

For a reversible process the entropy change of the system is always equal and opposite to the entropy change of the surroundings. If the system is reversed and brought back to its original state an observer would not be able to measure any change in entropy anywhere in the universe.

For irreversible processes the entropy change of the system plus surroundings is always positive. Entropy is not therefore a conserved quantity and the entropy of the universe always gets bigger. This will be reinvestigated many times in the course.

Note that regardless of whether or not a process is reversible, equation 2.6b can be adapted to find the change in entropy of any component of a system which is simply given by

$$\Delta S_{system} = \int_{Initial\ state}^{Final\ state} \frac{dQ}{T} \qquad \textbf{Equation 2.7}$$

Entropy is a scalar quantity with unit of JK^{-1}. All standard SI prefixes are used to indicate high and low entropies and within physics it is very rare to find any non-SI units applied. If the right-hand side of equation 2.7 is actually integrable then the entropy change of a system going through a process is easy to find.

For constant temperature processes (e.g. a phase transition) then the equation simplifies to $\Delta S_{system} = \frac{\Delta Q}{T}$. So for example if $100\ J$ of heat is supplied to water (a) at its melting point and (b) at its boiling point then the entropy change of the water for case (a) is $\frac{100}{273} \approx 0.37\ JK^{-1}$ and for case (b) is $\frac{100}{373} \approx 0.27\ JK^{-1}$. This tells you that melting leads to comparatively greater disorder and reduction of energy available for useful work that boiling for identical energy inputs.

2.3.2 The microscopic view of entropy

This is the domain of the Statistical Physics course so will just be mentioned here.

Consider a monatomic gas of a fixed number, N, of atoms in a box. Imagine the box has an invisible divide down the centre. If each individual atom has an equal probability of being anywhere inside the box, what is the probability that a certain number of atoms is on each side of the divide?

First of all consider the concept of all N atoms being on one side of the divide as represented in figure 2.1a
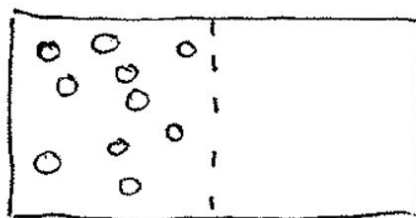
Figure 2.1a A gas with all atoms being on one side of an imaginary divide

Now consider the case that $(N - 1)$ atoms is on one side of the divide and just one atom on the other as represented in figure 2.1b:
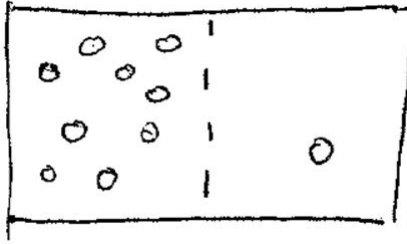
Figure 2.1b: A gas with just one atom on one side of the imaginary divide

How many ways can the two arrangements be made? As the atoms are indistinguishable this becomes a permutations problem; in the first case there is only one way for the atoms to be arranged. In the second case any of the N particles can be on the right-hand side of the box so there are N ways of arranging the system.

If the molecules have an equal probability of being anywhere in the box we can thus conclude that the second case is more likely – in fact it is exactly N times more likely.

An extension of this is that the more evenly distributed the atoms – and thus the more disordered they are the more likely the arrangement becomes.

When we say that when the entropy of an isolated system increases it means that statistical fluctuations tend to a situation where the most likely state is taken by a system.

2.3.3 Absolute entropy

You will have noticed that equations 2.6 and 2.7 referred to the change in entropy of systems. And indeed changes in entropy are what we usually deal with, rather than absolutes (just as with changes in potential energy).

However absolute entropy does have some meaning and is used. Taking the microscopic view of entropy it can be appreciated that if an object forms a perfect solid crystal where the atoms do not move then the object's entropy will be an absolute minimum. This idealised state is when the object is at an absolute zero of temperature. It thus makes sense to define this point of maximum order as being of minimum entropy. Making this universal minimum of entropy as being the zero of absolute entropy is a physics standard.

The absolute entropy of an object is thus defined as the entropy change it would experience if brought from its perfectly crystalline state at absolute zero to the state it is in now according to equation 2.6b.

2.3.4 Specific entropy

Of more use than the absolute entropy is the specific entropy i.e. the entropy per unit mass, or per unit amount of a substance. For example the molar entropy of graphite is $5.7 \, \mathrm{JK^{-1}mol^{-1}}$ and for diamond is $2.4 \, \mathrm{JK^{-1}mol^{-1}}$. This tells you diamond is more ordered than graphite and also indicates that converting diamond to graphite needs an input of useful work.

3. Equations of state and types of variable

This section looks at the difference between process variables and state variables and explains what an equation of state is. Some new mathematical notation is developed.

3.1 Equilibrium, rates and gradients

When a system is in thermodynamic equilibrium then all of its macroscopic properties are both constant in time and uniform in space.

If a system is left alone and nothing does work on it nor supplies heat to it then its macroscopic properties remain constant in time. Conversely if heat is supplied or work done then the macroscopic properties will change with time as the system tries to move towards a new state of thermodynamic equilibrium.

If no external force field (e.g. a gravitational field) acts on a system then its macroscopic properties remain constant in time. If an external field does act then the macroscopic properties can change, for example the gas in our atmosphere is denser near the ground and less dense higher up. If an external field does affect the contents of a system then its mass-energy changes and it looks for a new state of thermodynamic equilibrium; a properly isolated system needs to be impervious to the effects of any external force field. For most of this course the effects of external fields on system will not be considered as it does not add to the development of the key concepts.

As stated in section 1.1 pure thermodynamics is not concerned with the rates of change involved but rather the initial and final states.

3.2 Process and state variables (with some revision on processes)

To introduce process and state variables, consider an ideal gas. The relationship between its pressure, P, volume, V, temperature, T, and the number of molecules, N, is given by the familiar

$$PV = Nk_BT \qquad \textbf{Equation 3.1}$$

Consider the gas as held in a piston so it forms a closed system where work can be done and heat supplied while the amount of substance stays constant.

Imagine that the gas starts at a certain pressure and volume and is subject to some sort of thermodynamic process and it ends up at some other pressure and volume. We want to know what the final values of P, V, N and T are.

Let the gas start at pressure P_i and volume V_i and finish with and pressure P_f and volume V_f. Overall the gas expands so $V_f > V_i$ and let the final temperature be the same as the initial temperature $(T = \frac{P_i V_i}{N k_B} \equiv \frac{P_f V_f}{N k_B})$ thus necessitating that the pressure falls so $P_f < P_i$.

The process can happen in several different ways as shown on a PV diagram (or <u>indicator diagram</u>):
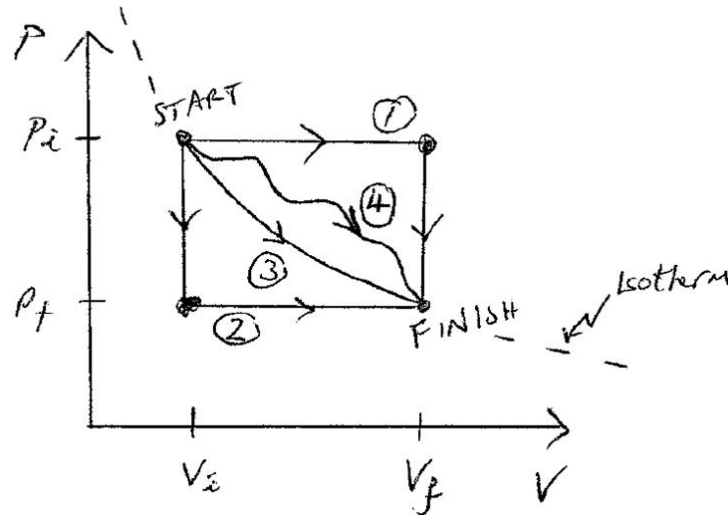
Figure 3.1 An overall expansion and pressure reduction of an ideal gas via (1) an isobaric expansion followed by an isochoric cooling, (2) an isochoric cooling followed by an isobaric expansion, (3) an isothermal expansion, (4) a general route.

The overall internal energy change of the gas is the same for each case - it is exactly zero as $U \propto T$ and the final temperature is the same as the initial one - but the routes are all different as the heat supplied and the work done is different in each case:

- In (1) the gas does some positive work on its surroundings given by $P_i(V_f - V_i)$ thus the work done <u>on</u> the gas is $P_i(V_i - V_f)$. The gas's temperature increases and thus its internal energy is also increased; the heat supplied to the gas is used to both heat the gas and do work on the surroundings.
  This is followed by a cooling of the gas at constant volume. No work is done as the gas loses heat as it cools. The net work done <u>on</u> the gas over the whole process is $P_i(V_i - V_f)$.

- In (2) the gas starts by cooling at constant volume, with no work being done but a lowering in temperature. This is then followed by the isobaric expansion with the gas doing work on the surroundings of $P_f(V_f - V_i)$ and thus the net work done <u>on</u> the gas over the whole process is $P_f(V_i - V_f)$.

- In (3) during an isothermal expansion the process occurs slowly enough for the temperature of the gas to remain the same as the surroundings; the work done by the gas is $P_i V_i \ln \frac{V_f}{V_i}$ and the net work done <u>on</u> the gas during the process is $P_i V_i \ln \frac{V_i}{V_f}$.

The amount of net work done on the gas in cases (1), (2) and (3) is different. In (4) it is different still but without further information it can't be defined without further knowledge of the path other than to say it is given by $\int P dV$ over the range.

3.2.1 Process variables

In any thermodynamic process any quantity that is path dependent for the process is known as a <u>process variable</u> (or process function, or process quantity).

In thermodynamics the most important process variables are <u>heat</u> and <u>work</u>.

3.2.2 State variables

In thermodynamics a <u>state variable</u> (or state function, or state quantity) is a variable that can be used to describe the equilibrium state of a system regardless of the way that the system acquired that state. Pressure, volume, temperature, internal energy, number of atoms, amount of substance and entropy are all state variables.

Independent state variables

When considering a thermodynamic system it is useful to know how many state variables can be varied independently, or to phrase it another way, how many variables can be altered before the others have to be completely defined.

For the gas in a piston where N is fixed, there are two independent state variables as defining two of them fixes all the other: if any two quantities from pressure, volume and temperature are known then all other state variables follow from them and cannot be varied.

3.2.3 Exact and inexact differentials

The first law of thermodynamics states that the increase in internal energy of a system equals the heat supplied to the system plus the work done on the system. For large changes this can be written in the A-level style as

$$\Delta U = \Delta Q - \Delta W \qquad \textbf{Equation 3.2}$$

where ΔW is the work done <u>by</u> the system.

But for infinitesimally small changes how do we write it? A very casual way would be to write $dU = dQ - dW$ which is (and should have always been stated to be) wrong but better would have – up till now – been $\delta U = \delta Q - \delta W$.

Now is the time to introduce some new terminology and notation. For infinitesimal quantities the first law can be written as

$$dU = \delta Q - \delta W \qquad \textbf{Equation 3.3}$$

The difference in the prefixes is important as it provides a distinction between state and process variables.

In thermodynamics consider a state variable, z. An infinitesimal <u>change</u> in the variable is written as dz. We say that dz is an <u>exact</u> or <u>perfect differential</u>. This is henceforth legitimate mathematics – but you need to be careful with using it outside of thermodynamics – this is one of the only places where it is used.

Infinitesimal amounts of a process variable are from now denoted by δQ or δW. These are <u>inexact</u> or <u>imperfect differentials</u>. Sometimes they are denoted by a barred "d" instead.

Notice that $d(something)$ refers to an infinitesimal <u>change</u> in a state variable whereas $\delta(something)$ refers to an infinitesimal <u>amount</u> of a process variable and is not to do with change.

The mathematics of exact differentials

If dz is an exact differential then it implies that $\int_A^B dz$ is independent of path and that $\oint dz = 0$ i.e. the change in z over a closed path is exactly zero.

Other familiar relations hold:

The reciprocal rule holds: $\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y}$

As does the cyclic rule: $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

And the rule for mixed derivatives: $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$

If z is a function of two variables, x and y, then the exact differential can be written as $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$.

Further discussion on the exact differential of a function of two variables

It is worth discussing how this final result is used in thermodynamics as it comes up frequently, most often pertaining to closed systems when there are just two independent state variables. Some mathematics and some physics can be clarified on this this.

First the mathematics: Let's say, as above, that z is a function of two variables, x and y so we can write $z = z(x, y)$ and $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$. Now, let us also say we can write x as a function of two other variables a and b so $x = (a, b)$ and we can also write y as a function of the same i.e. $y = y(a, b)$. The function z could now, in principal, be written as a function of any combination of two of the variables i.e. one could say that:

$z = z(x, a)$ so $dz = \left(\frac{\partial z}{\partial x}\right)_a dx + \left(\frac{\partial z}{\partial a}\right)_x da,$

$z = z(x, b)$ so $dz = \left(\frac{\partial z}{\partial x}\right)_b dx + \left(\frac{\partial z}{\partial b}\right)_x db,$

$z = z(y, a)$ so $dz = \left(\frac{\partial z}{\partial y}\right)_a dy + \left(\frac{\partial z}{\partial a}\right)_y da,$

$z = z(y, b)$ so $dz = \left(\frac{\partial z}{\partial y}\right)_b dy + \left(\frac{\partial z}{\partial b}\right)_y db,$ or,

$z = z(a, b)$ so $dz = \left(\frac{\partial z}{\partial a}\right)_b da + \left(\frac{\partial z}{\partial b}\right)_a db.$

If this seems confusing or unconvincing – and well it might do on first viewing - try experimenting with some simple functions. For example, try using $z = 3x + 2y$ with $x = a + b$ and $y = a - b$, substitute things in to get new functions and compare the exact differentials to see they are equivalent. Even try putting in numbers and small changes in numbers to see that it does work.

Now the physics. As closed systems in thermodynamics have just two independent state variables it is possible to always write down an exact differential for the change in one variable in terms of any two others.

For example we know we can write pressure as a function of temperature and volume alone, i.e. $P = P(T, V)$. Because of this we can write $dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$. The key thing to realise here is that provided we know the system is closed and there are just two independent state variables this expression holds true <u>regardless of the equation of state</u>. The expression works just as well for an ideal gas, a van der Waals gas, liquid helium, a banana or a neutron star provided it is a closed system.

We have currently formally seen the state variables pressure, volume, temperature, internal energy and entropy. You may pick any one of these, write is as function of any of the other two and write out the exact

differential and it will be absolutely and generally true for closed system. So for example if we had a problem where we were interested in a system's change in entropy and we knew something about the system's internal energy and volume then we could say immediately, let $S = S(U,V)$ and thus $dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$ and potentially use this as a starting point to investigate the problem further.

Later on we will meet several other state variables and the same principle applies to them; indeed we will use this sort of mathematics as a starting point to investigate properties of these state variables in the first place.

The mathematics of inexact differentials and direct application to the first law

None of the mathematics above applies to inexact differentials. In fact if δf is an inexact differential then there is no corresponding function where $f = \int df$.

For a reversible process in thermodynamics:

Work done <u>by</u> a system is given by

$$\delta W = PdV \qquad \textbf{Equation 3.4}$$

Heat supplied <u>to</u> a system is given by

$$\delta Q = TdS \qquad \textbf{Equation 3.5}$$

Thus $W = \int PdV$ and $Q = \int TdS$ thus the first law can be written

$$dU = TdS - PdV \qquad \textbf{Equation 3.6}$$

or

$$\Delta U = \int TdS - \int PdV \qquad \textbf{Equation 3.7}$$

and an amendment can be made to our definition of entropy in section 2.3.2 using more refined notation:

$$dS = \frac{\delta Q_R}{T} \qquad \textbf{Equation 2.6a improved}$$

3.4 Equations of state

An equation of state is any equation that expresses a relationship between the state variables of a system.

Gases

The most well-known equations of state follow from the general equation of state for an ideal gas (equation 3.1). It is also worth being aware of the equation of state for a van der Waals gas:

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_BT \qquad \textbf{Equation 3.8}$$

Real gases are often modelled as a power series in $\frac{1}{V}$ so the equation of state is:

$$\frac{PV}{Nk_BT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots$$

This is called a <u>virial expansion</u>.

A wire in tension

Equations of state don't apply just to gases. One illustrative example is the equation of state for a wire of original length L_0, Young's modulus Y, cross sectional area A, put under a tension J, offset from the surrounding temperature by $(T - T_0)$ and with a coefficient of linear expansion α. The equation of state for such a wire is:

$$L = L_0\left(1 + \frac{J}{YA} + \alpha(T - T_0)\right).$$

The concept of a wire in tension is a useful adjunct in developing understanding of thermodynamics; most discussions will start by looking at an ideal gas and often the wire in tension will be discussed as a comparator.

4. The first law of thermodynamics

The first law has been covered in most of the detail needed already required, both in Structure of Matter and in the earlier parts of the course. The bulk of this section is spent developing the theory of how the first law can be applied to ideal gases and how the heat supplied and the work done differ for the four most important processes that are applied to ideal gases.

The section also highlights an important mathematical technique in thermodynamics as applies it to derive expressions for constant pressure and constant volume heat capacities for ideal gases.

4.1 Various statements and sign conventions

Statements

As stated in section 1 the law can be clearly stated as:

> **The first law of thermodynamics** states that the <u>change</u> in internal energy of a closed system equals the heat supplied <u>to</u> the system plus the work done <u>on</u> the system.

Really, this is the only form of the law that is required. Many other forms can be seen with additional qualifying statements, for example, looking at the change in internal energy for an open rather than a closed system but they don't add much to the physics. This is in contrast to the second and third law, where there is more than one way of stating the laws that can appear totally different and one of the conceptual challenges is to appreciate why they are indeed equivalent. With the first law it is usually easy to see that everything is essentially a conservation of energy statement.

One exception is that sometimes you may see the law stated as "It is impossible to create a perpetual motion machine of the first kind". Such a machine is simply one that never stops going without having an input of energy: for example, a pendulum that never diminished the size of its oscillations; energy is always lost to friction and air resistance in real life so would need to have a source of energy to keep it going.

Sign conventions

There are various sign conventions associated with the law. In this course we will nearly always use the ones used in equation 3.3:

$$dU = \delta Q - \delta W \qquad \textbf{Equation 3.3}$$

δQ is the heat supplied <u>to</u> the system and δW is the work done <u>by</u> the system. This can cause some consternation. Isn't it better to have $dU = \delta Q + \delta W$ where δW is the work done <u>on</u> the system? This would maybe make more intuitive sense and look cleaner. Many textbooks use this notation. At the end of the day it <u>is</u> a matter of preference, but in developing conceptual understanding of pure physics (as opposed

to chemistry or engineering understanding) it probably makes things better to keep it as equation 3.3. This is because in physics we often use the law in the form given in equation 3.6:

$$dU = TdS - PdV \qquad \textbf{Equation 3.6}$$

In this equation, for a reversible process, following the macroscopic definition of entropy, the heat supplied <u>to</u> a system is given by the area under a temperature-entropy (TS) curve and the work done <u>by</u> a gas is given by the energy under a pressure-volume (PV) curve. Take the expansion of a gas that is being heated for example: the entropy and temperature increase give a positive number for the heat supplied. The volume of the gas increases as it expands thus is does work against the environment, and the pressure increases. The area under the PV curve is some positive value as the volume has increased and this positive number equals the number of joules of work done <u>by</u> the gas against the environment. The negative of this equals the work done <u>on</u> the gas.

For a compression the volume decreases and the conventional area under the graph is a negative value – once again, taking the negative of this to give a positive number gives the work done on the gas.

As the TS and the PV diagram are such stalwart tools in the development of physics concepts it makes sense to keep things so that equations 3.3 and 3.6 are the ones we use.

4.2 Thermodynamic processes

This subsection looks at the Big Four[1] thermodynamic processes: isobaric, isothermal, adiabatic and isochoric in detail using TS and PV diagrams. In all cases the development of the physics utilises the ideal-gas-in-a-piston thought experiment. Prior to looking at these processes some clarification on the ideality of thermodynamic processes is required.

4.2.1 Reversible and quasistatic processes

Consider a thermodynamic process where a gas is both compressed in a piston and heated at the same time. It starts with a definite pressure, volume, temperature and entropy and finishes with different, well defined, values of these quantities too, as shown on figure 4.1:

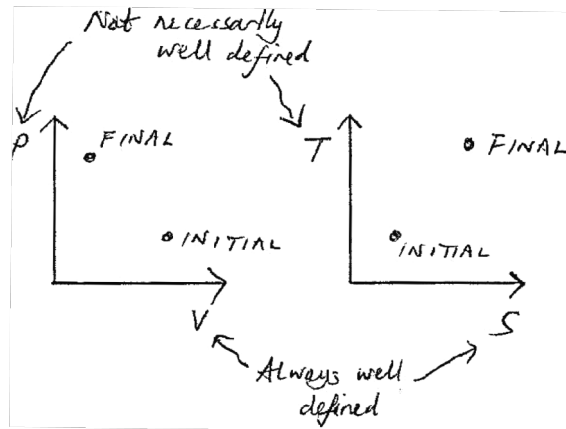[1] This is just Vijay's terminology, not a physics standard

Figure 4.1 The start and end points of a compression with heating of an ideal gas represented by PV and TS diagrams.

In such a process the volume drops, the pressure rises, the entropy may increase or decrease (but let's say it increases) and the temperature rises. But what lines can be drawn between the start and end points on the two diagrams?

Of course the processes are path dependent – the lines drawn between the initial and final points depends on the rates and intensities of compression and heating – but the more fundamental consideration is whether lines between the start and end points can be drawn at all.

In any process the volume is, of course, uniquely defined at any time during the process.

Using the microscopic view of entropy, where the value depends on the space available and the speed of each atom in the system, the entropy is also always uniquely defined.

But for a general process the temperature and pressure will vary from point to point in the gas and thus cannot be uniquely defined. This means it is impossible to draw a line of any kind between the start and end points and thus the areas under the curves

$$\Delta Q = \int_{Initial}^{Final} T dS$$

and

$$\Delta W = \int_{Initial}^{Final} P dV$$

have no meaning. Of course ΔQ and ΔW have a value – there is an amount of heat supplied and an amount of work done in the process but they can't be determined by the area under a single curve.

For the thought experiments developed in thermodynamics we often need to use an idealised system where the pressure and temperature is uniform throughout. This can only be possible when the process happens at such a slow rate that the volume change and heating occurs in infinitesimal increments so that the pressure and temperatures become equalised throughout the system after every small step. Such a process is known as a quasistatic process.

Any thermodynamic thought experiment or theoretical development that essentially uses the area under a PV or TS curve has with it the caveat that is applies to a quasistatic approximation only and is thus an unobtainable ideal. This must be considered when designing real experiments or carrying out any practical application of thermodynamics.

Really the processes need to be not just quasistatic but also reversible so as to permit the macroscopic definition of entropy - $\delta S = \frac{\delta Q_R}{T}$ to hold. For the gas-in-a-piston problems that we deal with here this simply means the piston acts in a frictionless manner so energy is not dissipated.

Quasistatic and reversible processes are revisited when studying the second law.

4.2.2.1 Isobaric processes

Consider an isobaric (constant pressure), quasistatic expansion of an ideal gas. This can be obtained by keeping the external pressure constant (easy to do) and heating the gas. The gas expands, doing work on the environment. The PV curve is simple – the pressure stays constant and the volume increases – but what about the temperature and entropy? As the pressure is constant and the volume increases the atoms in the gas must move faster to maintain the same pressure. This means the temperature must increase. As the space the gas occupies increases <u>and</u> the speed of the molecules must increase the entropy must also rise. There is no easy function relating the temperature to the entropy but the PV and TS curves are as shown below:
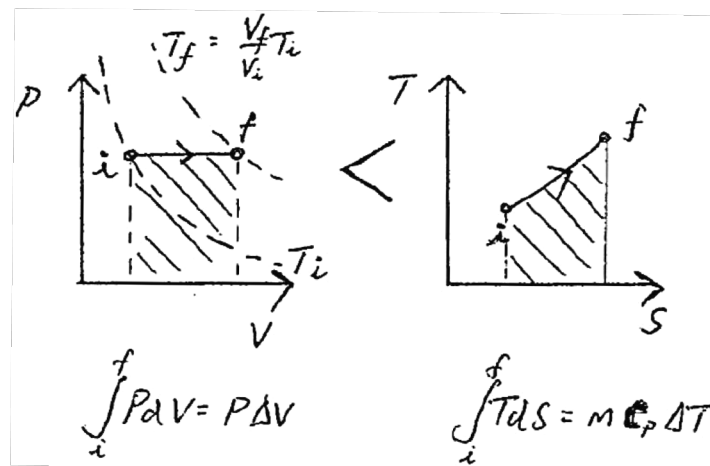

Figure 4.2: PV and TS curves for an isobaric expansion. It is often a good idea to sketch isotherms on a PV diagram.

As per the reasoning above the PV diagram clearly shows the temperature increase when the isotherms are annotated.

The work done in the process is easy to calculate as $P\Delta V$.

The heat supplied would be tricky to compute using the area under the TS graph but an easy method is to recognise that according to the definition of heat capacity at constant pressure this will be equal to $mc_P\Delta T$ where m is the mass of the gas.

Which area is bigger? It must be the area under the TS curve: the heat supplied has been used to both heat the gas <u>and</u> do work on the environment so must be larger. This is easy to see when looking at the formula for the first law:

$$\Delta U = \int TdS - \int PdV$$

thus

$$\int TdS = \Delta U + \int PdV = \Delta U + P\Delta V.$$

As the temperature has increased, and so has the internal energy, the heat supplied must be greater than the work done.

This leads us to the idea that the isobaric expansion is a heat intensive process!

Going a bit further

The general equation for the internal energy of and ideal gas is given by $U = \frac{n_d}{2}Nk_BT$ where n_d is the number of degrees of freedom of the gas molecules. This leads to $\Delta U = \frac{n_d}{2}Nk_B\Delta T$.

As $\Delta Q = \Delta U + P\Delta V$ this gives $\Delta Q = \frac{n_d}{2}Nk_B\Delta T + Nk_B\Delta T = \left(\frac{n_d}{2} + 1\right)Nk_B\Delta T$.

As the heat supplied is also given as $mc_P\Delta T$ this shows the specific heat capacity of the gas at constant pressure is equivalent to $c_P = \frac{\left(\frac{n_d}{2}+1\right)Nk_B}{m}$ as seen in Structure of Matter.

4.2.2.2 Isothermal processes

Consider an isothermal, quasistatic expansion of an ideal gas. To do this the walls of the system should be good conductors so if the process is conducted slowly enough the temperature of the gas is always the same as the temperature of the surroundings. Once again the gas does work on the environment but in this case, as the temperature stays constant the speed of the particles does not increase and correspondingly there is no change in internal energy. The pressure of the gas thus falls, and as the space available for the gas is greater the entropy increases. All this is borne out when sketching the PV and TS curves which are particularly easy to draw:
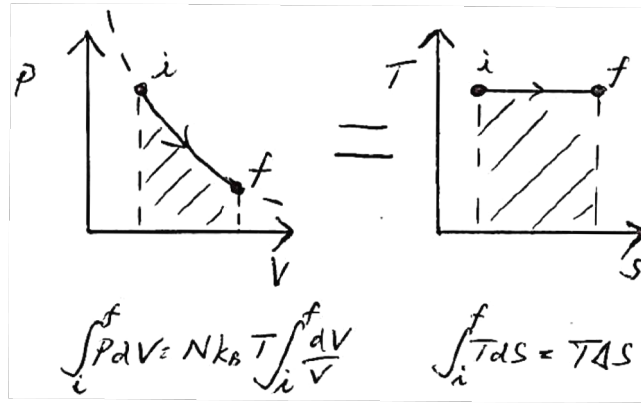
Figure 4.3: PV and TS curves for an isothermal expansion

The PV curve is just drawn along an isotherm. The area under the curve is

$$\int_i^f PdV = Nk_BT \int_{V_i}^{V_f} \frac{dV}{V} = Nk_BT \ln\frac{V_f}{V_i}$$

which is a familiar result.

The TS curve is, of course just a straight line with the area given by $T\Delta S$.

From the first law, as the process is isothermal, $\Delta U = 0$ so the simplified version becomes $TdS = PdV$ and so $T\Delta S = Nk_BT \ln\frac{V_f}{V_i}$ giving the entropy change as simply

$$\Delta S = Nk_B \ln\frac{V_f}{V_i}.$$

Note that in this case the areas under the two curves are exactly equal.

4.2.2.3 Adiabatic processes

Adiabatic processes are the most mathematically fiddly to deal with as the fiddly powers of γ and $\gamma - 1$ appear everywhere. The physics is more straightforward than many may be initially supposed however.

An adiabatic process is simply one where no heat is supplied to the system. In practice this simply means the process occurs rapidly so there isn't the time for any heat to transfer between the surroundings and the system – effectively the opposite of an isothermal process. For a reversible processes this means the entropy change is zero – as $dS = \frac{\delta Q_R}{T}$ by definition it must be. So adiabatic processes can often also be classified as isentropic i.e. constant entropy.

Note that if the process is not reversible then an adiabatic process won't necessarily be isentropic. An example is when a gas expands into a vacuum – a free expansion – when it does experience an entropy change. This is dealt with in section 11.

In an adiabatic expansion where the entropy stays constant the space available for the gas increases thus the speed of the molecules must correspondingly fall. This means the temperature and internal energy of the gas must also fall.

The PV and TS diagrams are:
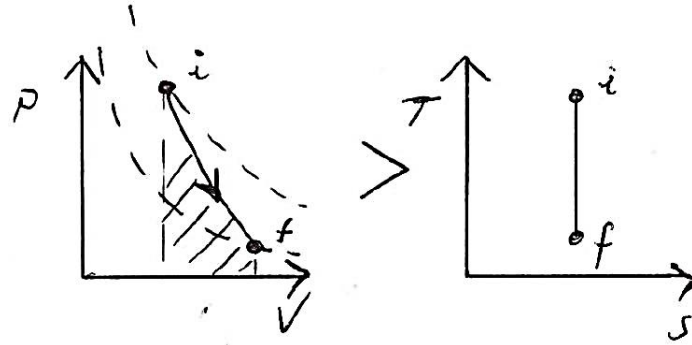
Figure 4.4: PV and TS curves for an adiabatic, isentropic expansion

The PV curve falls from one isotherm to another lower temperature isotherm. The TS curve is merely a drop in temperature.

As $dS = 0$ the specific version of the first law for this type of process is $dU = -PdV$ or $\Delta U = -\int_i^f PdV$.

The adiabatic process relations

We can use this result to derive the familiar relations for adiabatic processes for ideal gases: as $dU = \frac{n_d}{2} N k_B dT$ and $PdV = \frac{N k_B T dV}{V}$ we can write $\frac{n_d}{2} N k_B dT = -\frac{N k_B T dV}{V}$.

This reduces to $\frac{dT}{T} = -\frac{2}{n_d} \frac{dV}{V}$ which integrates and rearranges to give $TV^{2/n_d} = constant$.

Remembering that the formula for the ratio of heat capacities for ideal gases is given by

$$\gamma = \frac{n_d + 2}{n_d} \qquad \text{Equation 4.1}$$

leads to the following relations:

$$TV^{\gamma - 1} = constant \qquad \text{Equation 4.2}$$

and

$$PV^{\gamma} = constant \qquad \text{Equation 4.3}$$

which were seen in Structure of Matter.

As $\gamma > 1$ (but not by much – for a monatomic ideal gas it is $\frac{5}{3}$) this means the magnitude of the gradient of the PV curve must be greater than for an isothermal expansion (which it has to be if it drops between isotherms).

4.2.2.4 Isochoric processes

Finally, consider an isochoric (constant volume), quasistatic cooling of an ideal gas. Of course, for this to happen the piston must just be fixed in place and the outside needs to be colder than the inside. The temperature drops, the internal energy drops and the entropy drops. The PV and TS curves are:
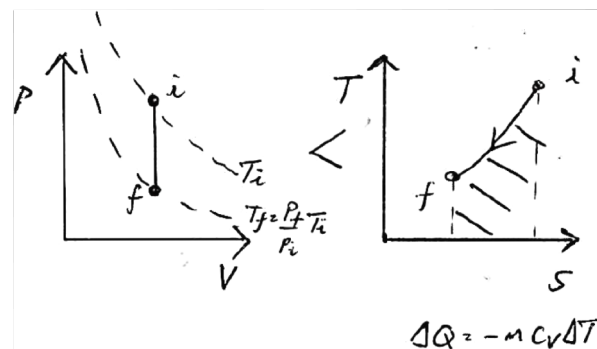
Figure 4.5: PV and TS curves for an isochoric cooling

The PV curve has zero area underneath as no work is done. As with the isobaric expansion there is no simple formula relating the temperature and entropy but from the definition of heat capacity at constant volume the heat transferred is of magnitude $mc_V\Delta T$.

The simplified formula for the internal energy change is $dU = TdS \equiv mc_V\Delta T$.

4.2.2.5 Generalising the processes

The processes has been listed in a logical order which can be demonstrated in several ways. Compare the following:

(i)   The amount of heat supplied relative to the amount of work done for the processes in the order given in the notes. For the isobaric processes – a heat intensive process – the heat supplied is greater than the work done. For the isothermal they're equal, for the adiabatic the work done is greater than the heat supplied (which is exactly zero) and for the isochoric the work done is zero but the heat supplied is actually negative.

(ii)   The gradients of the PV graphs. They go from flat, to sloped, to more steeply sloped to infinite

(iii)   The gradients of the TS graphs. They go from upwards, to flat, to straight down to "backwards".

This classification permits an intuitive feeling for how thermodynamic processes operate.

4.3 More on heat capacities

The heat capacity of an object is defined by the ratio of heat supplied to temperature change so mathematically

$$C = \frac{\delta Q}{dT} \qquad \textbf{Equation 4.4}$$

and as δQ is path dependent, hence so is C (as we have already shown in a reasonably casual way in the above analyses) - C_P is the heat capacity at constant pressure and C_V is the heat capacity at constant volume.

As we have argued that isobaric processes are heat intensive it should be expected that the constant pressure heat capacity should be higher. We will now show, in general terms, how much so.

If volume and temperature are chosen as state variables then we can write a change in internal energy as

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT.$$

From the first law, $\delta Q = dU + PdV$ hence

$$\delta Q = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + PdV = \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\} dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

At constant volume, $dV = 0$ thus $\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT$ thus giving

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \textbf{Equation 4.5}$$

and

$$c_V = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_V \qquad \textbf{Equation 4.6}$$

For constant pressure choosing volume and temperature as state variables and taking $V = V(T, P)$ we can write

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP.$$

For a constant pressure process this simplifies to $dV = \left(\frac{\partial V}{\partial T}\right)_P dT$.

Then taking $\delta Q = \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\} dV + \left(\frac{\partial U}{\partial T}\right)_V dT$ from before we can write

$$\delta Q = \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial T}\right)_V dT.$$

But as $C_P = \frac{\delta Q}{dT}$ by definition and $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ this becomes $C_P = \left\{\left(\frac{\partial U}{\partial T}\right)_T + P\right\}\left(\frac{\partial V}{\partial T}\right)_P + C_V.$

For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T$ must be zero and $\left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk_B}{P}$ thus giving

$$C_P = Nk_B + C_V \qquad \textbf{Equation 4.7}$$

thereby corroborating the earlier assertion that $C_P > C_V$. The factor γ is defined by

$$\gamma = \frac{C_P}{C_V} \qquad \textbf{Equation 4.8}$$

though would more normally be computed using equation 4.1. The greater the number the degrees of freedom of the gas particles, the closer to unity the ratio of heat capacity becomes.

5. Cycles, engines, heat pumps and refrigerators

This section looks at clockwise and anticlockwise thermodynamic cycles. Engines are studied first, followed by heat pumps and refrigerators which permits an in depth understand of various aspects of the second law in section 6. The section provides the basics of the physics only - no detail is given on the engineering of any machines.

5.1 Thermodynamic cycles

A <u>thermodynamic cycle</u> is a series of thermodynamic processes that involve work being done on or by a system, and a transfer of heat in or out of a system that alters the state variables of the system during the cycle but on completion of the cycle sees the system with same values of the state variables that it began with.

The system can be absolutely anything.

For example, consider a gas in a piston that somehow undergoes a four-stage cyclic quasistatic process so that it experiences:

(i)   Isobaric expansion (the gas does some work, plus absorbs some heat)

(ii)   Isochoric cooling (the gas releases some heat)

(iii)   Isobaric compression (some work is done on the gas, but less in magnitude than in (i) as the pressure is less, plus rejects some heat)

(iv)   Isochoric heating (the gas absorbs some heat)

So overall it should be expected that the gas does some net work on the environment and absorbs a net amount of heat over the whole cycle. Annotated PV and TS diagrams assist in the analysis:
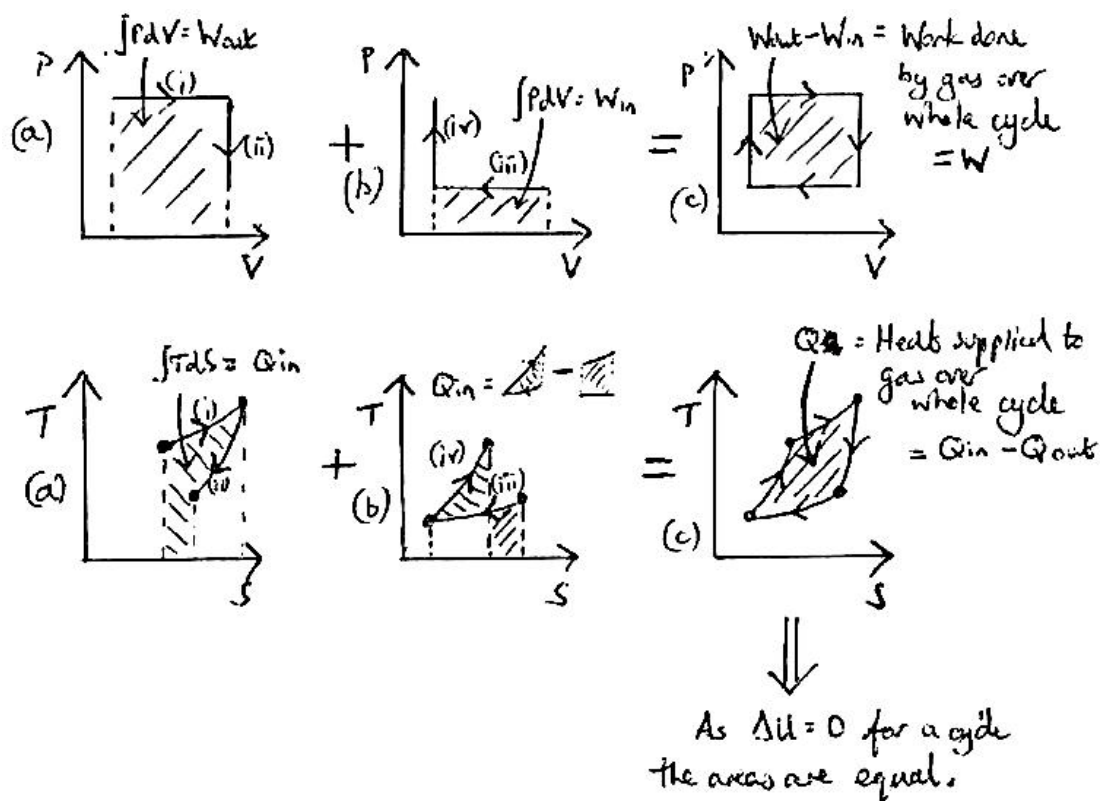
Figure 5.1 PV and TS diagrams for the four-stage thermodynamic cycle described above. Part (a) shows the expansion stage, (b) the compression stage and (c) the whole cycle with the work done on/by and supplied to/remove from the gas indicated in for each case. The PV diagrams are exact for the processes described; the TS diagrams are more schematic.

The figures highlight some important rules about thermodynamics cycles that are actually completely general:

- After one cycle all state variables return to their initial values
- The net change in internal energy of the whole system is thus zero
- Provided all the processes are properly quasistatic the PV and TS diagrams form a closed loop that start and end at a defined point
- The area enclosed by the clockwise PV loop indicates the work done by the gas over the whole cycle. This is, of course, path dependent.
- The area enclosed by the clockwise TS diagram indicates the heat supplied to the gas over the whole cycle and is also path dependent
- As the internal energy over a whole cycle sees no net change the areas enclosed by the PV and TS loops must be equal

Representation of a general process

For a generalised cycle, let:

- the amount of heat that is transferred into the system over the whole cycle be Q_{in}

- the amount of heat transferred out be Q_{out}

- and the work done <u>by</u> the system be W.

Using the first law, the net change in internal energy for the whole cycle can thus be written $\Delta U = (Q_{in} - Q_{out}) - W$.

As the internal energy change is zero by definition, this means for any thermodynamic cycle

$$W = Q_{in} - Q_{out} \qquad \text{Equation 5.1}$$

5.2 Heat engines

A heat engine is a device that converts heat into work. Broadly speaking it does this by taking a <u>working substance</u> - essentially anything with a non-zero heat capacity (usually a fluid) - and causes it to go through temperature variations. The subsequent changes in physical properties of the substance that it experiences as a result of the temperature variations are exploited to do mechanical work on the environment.

If a heat engine sees the working substance go through a series of processes that are specified by an ideal thermodynamic cycle then the engine is referred to by the same nomenclature as the cycle.

For example, the idealised thermodynamic cycle as described in figure 5.1 can be referred to as the Isochore Isobar cycle. If a fixed mass of gas were enclosed in a frictionless piston and the system were subjected to the cyclic procedures described then that would be an Isochore Isobar engine. The net output of mechanical work could, in principle, be put to some useful purpose.

Note that a heat engine certainly doesn't <u>have</u> to operate in a cycle but most of the discussion that is pursued in these notes is to do with working substances put through idealised thermodynamic cycles to operate as heat engines.

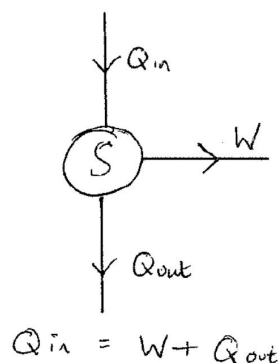A schematic diagram of a heat engine in shown in figure 5.2:

Figure 5.2 A schematic diagram for a generic heat engine

Heat engine efficiency

The work done by the engine is given by $W = Q_{in} - Q_{out}$.

Q_{out} is essentially energy that is thrown away - it doesn't do anything useful. A perfect engine would convert all of the incoming heat into work so $Q_{out} = 0$ and $W = Q_{in}$.

That this is actually impossible is essentially a simplified statement of the second law.

The efficiency of a heat engine, η, is defined as the fraction of incoming heat that is converted into work i.e.

$$\eta = \frac{W}{Q_{in}} \qquad \textbf{Equation 5.2a}$$

which, using the first law, can be written

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} \qquad \textbf{Equation 5.2b}$$

We will see later that the efficiency of a heat engine is fundamentally limited.

5.3 Two-reservoir engine

Imagine two reservoirs where one is a heat source held at a high temperature, T_H and the other a heat sink held at a lower temperature T_C. In such a setup $Q_{in} = Q_H$ is the heat transferred into the system from the heat source and $Q_{out} = Q_C$ is the heat transferred from the system to the heat sink.

A schematic diagram of such a two-reservoir engine is shown below:

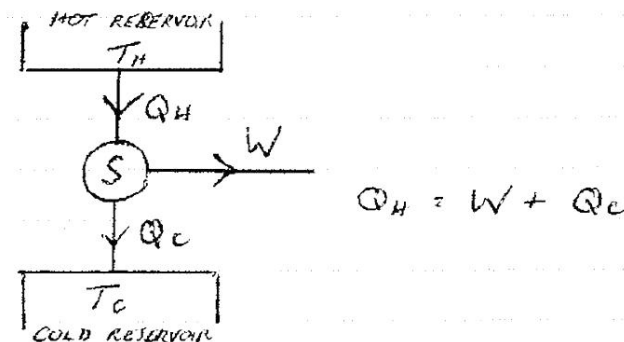**Figure 5.3 A schematic diagram of a two-reservoir heat engine**

An example of a two-reservoir is a coal fired power station. The system is essentially water which changes from its liquid to gas phase during the cycle. The hot reservoir is a furnace held at approximately 800 K and the cold reservoir the outside environment held at atmospheric temperature.

The two-reservoir system will be used many in this course.

5.4 Anticlockwise thermodynamic cycles

What about if the cycle described in section 5.1 goes in reverse?

In that case there would be a net work done <u>on</u> the gas and a net amount of heat removed from the gas. The PV and TS diagrams for the whole process are shown below:
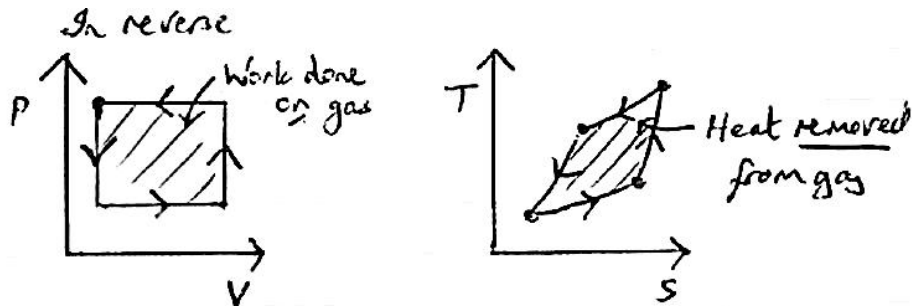
Figure 5.4 PV and TS diagrams for the reverse process to that represented in figure 5.1

This provides a general rule:

> **If a thermodynamic cycle moves clockwise on a PV diagram the net work done by the system is positive**
>
> **If a thermodynamic cycle moves anticlockwise on a PV diagram the net work done by the system is negative**

5.5 Refrigerators

A refrigerator is essentially a heat engine run in reverse: it uses work to transfer heat from a cold area to a hot area. The PV diagram for a refrigeration cycle runs anticlockwise.

For a household fridge the cold reservoir is the contents of the fridge and the hot reservoir is the air surrounding the fridge. The schematic diagram for two reservoir fridge is:
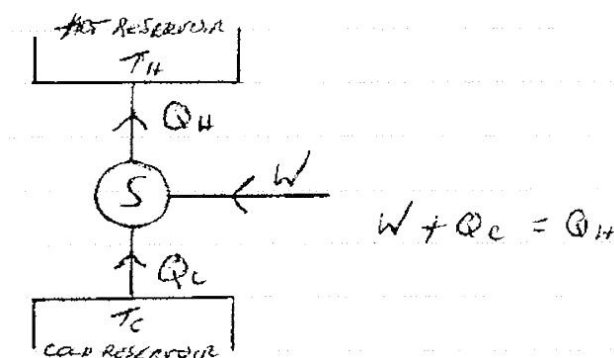
Figure 5.5 A schematic diagram of a refrigerator

A perfect fridge would transfer heat from the cold reservoir to the hot reservoir without any work being done so $W = 0$ and $Q_C = Q_H$.

As with the perfect heat engine, this is an impossible ideal that is prohibited by the second law.

The <u>coefficient of performance</u> of a fridge, ω_F, is defined as the ratio of the heat removed from the cold reservoir to the work done i.e.

$$\omega_F = \frac{Q_C}{W} \qquad \textbf{Equation 5.3a}$$

which can also be written

$$\omega_F = \frac{Q_C}{Q_H - Q_C} = \frac{1}{\frac{Q_H}{Q_C} - 1} \qquad \textbf{Equation 5.3b}$$

Note that this is <u>not</u> an efficiency and can be greater than unity; the coefficient of performance of domestic fridges ranges from about 1 to 10.


5.6 Heat pumps

A heat pump is a fridge used to heat a building. The cold reservoir is the ground outside of the building and the hot reservoir is the interior of the building.

The coefficient of performance of a heat pump, ω_P, is defined as the ratio of the heat transferred to the hot reservoir to the work done i.e.

$$\omega_P = \frac{Q_H}{W} \qquad \textbf{Equation 5.4a}$$

which can also be written

$$\omega_P = \frac{Q_H}{Q_H - Q_C} = \frac{1}{1 - \frac{Q_C}{Q_H}} \qquad \textbf{Equation 5.4b}$$

This value is always > 1. Typical building heat pumps have a coefficient of performance of between 1 and 10.

Joule heating has a coefficient of performance of unity so heat pumps are normally a better way of heating a building.

Although the definitions of heat engine efficiency and coefficient of performance of the refrigerator and heat pump are all different they are all a measure of $\frac{What\ you\ (want\ to)\ get\ out}{What\ you\ put\ in\ (i.e.the\ work\ done)}$.

6. The second law of thermodynamics

This section reintroduces the second law via the three key ways of stating it and shows how they are equivalent. This forms the centrepiece of the section. Some further detail is provided on reversible and irreversible processes.

6.1 Alternative statements

As Michael Coppins points out the second law essentially concerns a fundamental asymmetry in nature. Because this asymmetry manifests itself in many ways there are many equivalent statement of the law. Herewith the most important three:

Kelvin statement

No process is possible in which the <u>sole effect</u> is the absorption of heat from a reservoir and its complete conversion into work.

Another way of phrasing this is thus that a perfect engine is impossible.

Clausius statement

No process is possible in which the <u>sole effect</u> is the transfer of heat from a colder reservoir to a hotter reservoir.

Another way of phrasing this is to say thus that a perfect refrigerator is impossible.

Mathematical formulation in terms of entropy

The change in entropy during a reversible process is always exactly equal to the heat transferred per thermodynamic temperature and the change in entropy during an irreversible process is always greater than the heat transferred per thermodynamic temperature i.e.

$$dS \begin{cases} = \dfrac{\delta Q}{T} \ in \ a \ reversible \ process \\ > \dfrac{\delta Q}{T} \ in \ an \ irreversible \ process \end{cases}$$

As reversible processes are a theoretical ideal for a frictionless, quasistatic processes this effectively means that nearly all real processes tend to create an overall entropy increase in the universe.

This law, regardless of the way it is stated, is always true. There are no known exceptions. Though on a macroscopic scale it can be shown to have its roots in the probability of particle motions it also works on microscopic scales, for relativistic situations and indeed in all applications of physics that have been developed since its first articulation in the 19th century.

6.2 Equivalence of the Kelvin and Clausius statements

One way in which to show the two statements are equivalent is to if one of them is violated then so is the other. We show here that if the Kelvin statement is violated, then so is the Clausius statement; this week's asks you to do it the other way around.

Imagine there were such a thing as a perfect heat engine: for each joule of heat extracted from a hot reservoir, exactly one joule of work would be done. For such a heat engine $Q_C^E = 0$ so $Q_H^E = W^E$ and it could be illustrated schematically by:
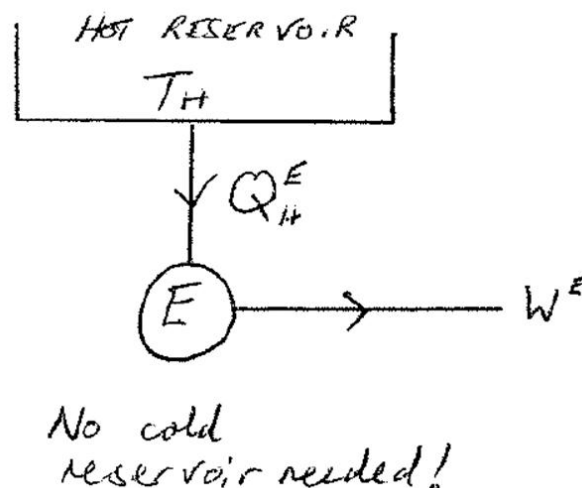
Figure 6.1 A schematic diagram of an ideal heat engine

Now suppose the work from this heat engine is used to run a refrigerator – not an ideal refrigerator, just a normal one, which can have any coefficient of performance at all – which discharges its heat into the same hot reservoir. The schematic diagram for this would look like:
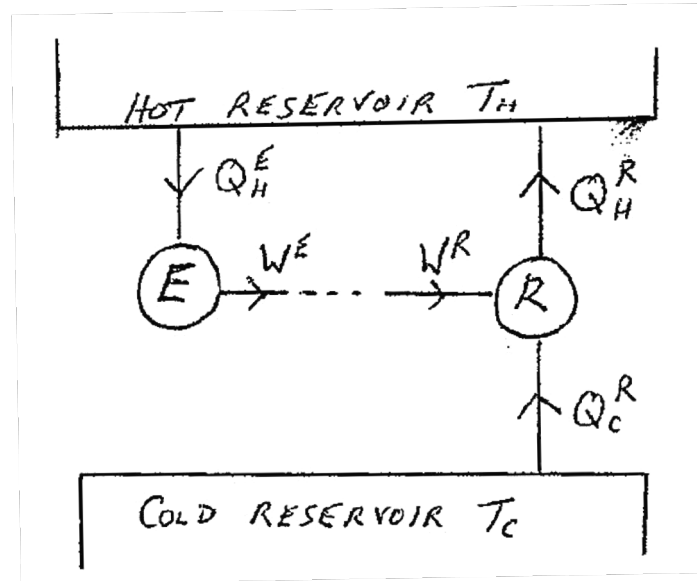
Figure 6.2 A schematic diagram of an ideal heat engine using its work to run a refrigerator

Let's say we can adjust the engine so that it produces exactly the same amount of work required to run the refrigerator so $W^E = W^R$. The net effect of this can be represented schematically as follows:
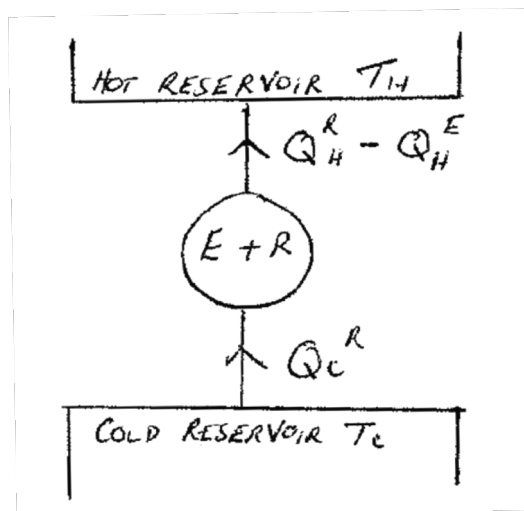
Figure 6.3 A schematic diagram showing the combined effect of an ideal heat engine running a refrigerator

Using the conservation of energy we have $Q_C^R = Q_H^R - Q_H^E$.

The net and <u>sole effect</u> of this combination is that heat is transferred from the cold reservoir to the hot reservoir. This violates the Clausius statement therefore showing the two statements are equivalent.

6.3 Reversible and irreversible processes

The macroscopic definition of entropy is that the entropy change of a system is given by $dS = \frac{\delta Q_R}{T}$ where the subscript R emphasises the heat transfer has been reversible i.e. both quasistatic and frictionless. This means, as stated and used in section 4.2.2.3, that a reversible adiabatic process is also <u>isentropic</u> i.e. $dS = 0$ so S is constant. The ideal gas law for adiabatic processes, $PV^\gamma = constant$ holds only for such isentropic processes.

For a reversible process calculating an entropy change, is, in principle, easy, as we can use $\Delta S = \int \frac{\delta Q_R}{T}$ - the equality makes it straightforward.

But for an irreversible process $\Delta S > \int \frac{\delta Q_R}{T}$ so how can ΔS be calculated? Quite easily in fact by recognising the entropy is a state variable and using a trick – look at the initial and final states of the system and choose any reversible path between the two states and calculate the entropy change along that path.

A reversible isothermal volume change

Consider an ideal gas in a piston placed in thermal contact with a heat reservoir:
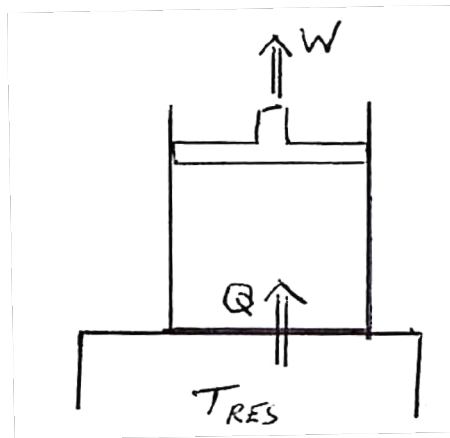
Figure 6.4 An isothermal expansion of an ideal gas in thermal contact with a reservoir

Heat flows into the gas which expands; all the work is used to expand the gas against the environment. Heat from the gas is converted completely into work. Note that this does not violate the second law as the transfer of heat into work is not the sole effect of the process as the volume of the gas changes as well.

As we know from section 4, the entropy change is given by $\Delta S = Nk_B \ln \frac{V_f}{V_i}$. Although this equation gives the entropy change for a reversible process as it only involves state variables is also applies even if the process between the two states is irreversible as is detailed in the next section.

7. The Carnot cycle and Carnot's theorem

This section looks at the reversibility again, then the Carnot cycle with more generality than proffered in many sources and then Carnot's theorem.

7.1 Reversible, quasistatic and irreversible processes again

Reversible heat

Consider an object in thermodynamic equilibrium with a reservoir at temperature T_C which is then moved into thermal contact with hotter reservoir at temperature T_H:
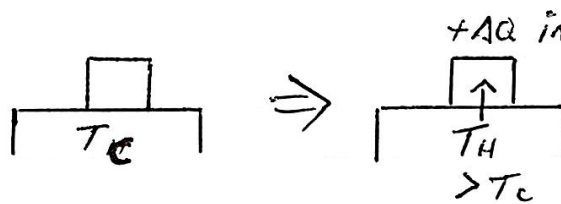
Figure 7.1a An object moved from a cold to a hot reservoir in one go

A quantity of heat, $+\Delta Q$, flows into the object until its temperature reaches T_H. The process is not quasistatic as the state variables of the system will not be uniform during the heat transfer process (if is was a gas for example convection currents would transfer the heat around).

The process is also not reversible. The object could easily be transferred back to its original state:
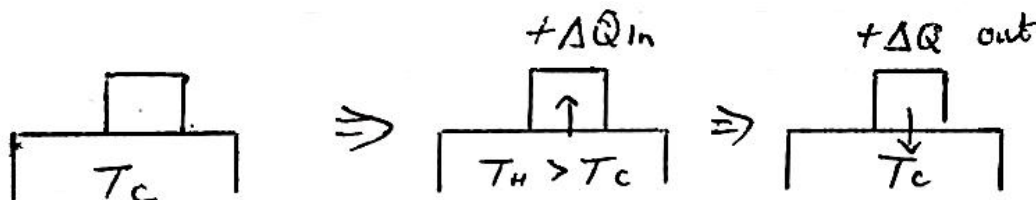
Figure 7.1b The object moved back to the cold reservoir causing a net removal of heat from the hot to the cold reservoir

This process has caused a net shifting of heat ΔQ from the hot to the cold reservoir. There is nothing amiss about this except that the process has caused the state of the reservoirs to change, therefore the process in not reversible. Returning the reservoirs back to their original state would be possible but not without a change in something else (as per the Clausius statement of the second law).

Now consider converting the object's temperature from the cold to the hot state by moving it from one reservoir to another, each with a temperature slightly higher than the other so it gradually but incrementally goes from $T_C \rightarrow T_H$:
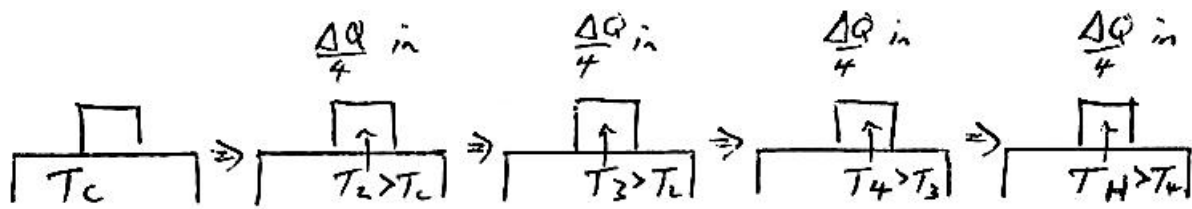
Figure 7.1c An object moved from a cold reservoir to a hot reservoir in several steps

In this case the processes still aren't quasistatic but will be closer to a quasistatic approximation that the single jump from cold to hot.

How about reversing the process? It still won't be quite reversible but it closer to being reversible than the big jump as the middle three reservoirs get brought back to exactly the same state and just the end two see a net change.

In the case of an infinite number of reservoirs with infinitesimal temperature differences the result would be that each individual step would be quasistatic and the whole process would be overall reversible.

So:

> If heat transfer takes place between two objects with an infinitesimally small temperature differences then the process is reversible.
>
> And a corollary of this is: an isothermal quasistatic process is also reversible.

7.2 The Carnot cycle

Consider a basic heat engine operating between a hot and cold reservoir as represented below:
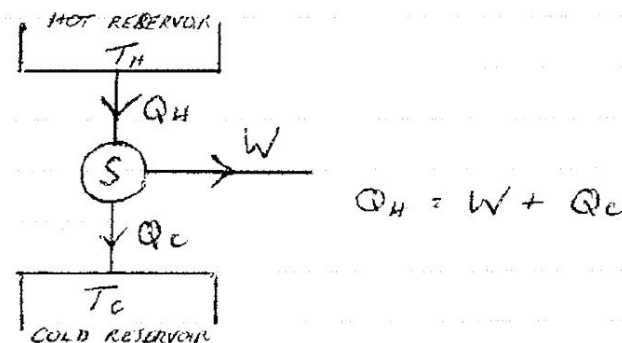
Figure 7.2 A heat engine operating between a hot and cold reservoir. The system, *S*, denotes a working substance which can be absolutely anything.

The second law tells us that the efficiency of the heat engine cannot be 100% - this is an empirically verified fact – so a natural question from pure physics point of view is to ask what maximum efficiency is possible from a heat engine. From a practical engineering point of view the clear questions that follow are how such a maximally efficient engine may be created and what sort of working substance might be used.

Undoubtedly many scientists and engineers would have been pondering these questions but it was Sadi Carnot's 1824 work "*Reflexions sur la Puissance Motrice du Feu*" ("Reflections of the Motive Power of Fire") that is generally credited with solving the pure physics part of the problem and going a long way to solving the engineering parts. Carnot's work continues to be a source of inspiration to physicists to this day.

Carnot recognised that to maximise efficiency processes would have to be frictionless and reversible. For reversible heat flow to occur, heat must be transferred from one object to another when they are at the same temperature.

Thus when the working substance draws heat from the hot reservoir, it needs to be at the same temperature as the hot reservoir for maximum efficiency.

And when the working substance expels heat to the cold reservoir, it needs to be at the same temperature as the cold reservoir for maximum efficiency.

This means two steps of a maximally efficient thermodynamic cycle are isotherms.

The isotherms must be connected to make a closed cycle. As the only heat transferred comes out of the hot reservoir along a hot isotherm and goes into the cold reservoir along a cold isotherm this means the transitions between the isotherms must be adiabats. There is no other thermodynamics process the connecting lines can be.

This logical thinking leads to the Carnot cycle: a cyclic set of processes that can be applied to absolutely any thermodynamic system. Consider that the working substance starts the cycle in thermal equilibrium with a cold reservoir at temperature T_C. Then:

---

1. A reversible adiabatic process is performed on the on the working substance such that its temperature is raised to exactly that of the hot reservoir at temperature T_H.
2. The working substance is held in thermal contact with the hot reservoir, thus maintaining thermal equilibrium with it while absorbing a quantity of heat, Q_H from it.
3. A reversible adiabatic process is performed on the working substance such that its temperature is lowered back to T_C.
4. The working substance is held in thermal contact with the cold reservoir, thus maintaining thermal equilibrium with it while transferring a quantity of heat, Q_C to it. The process is stopped when the working substance reaches exactly the same thermodynamic state it began the cycle with.

Any engine working according to these steps is called a Carnot engine. As all four processes are reversible the Carnot engine is a reversible engine. If the four steps do work in reverse then the system operates as a Carnot fridge.

Carnot cycle for a gas

For a gas (not necessarily ideal) the four steps correspond to:

1. An adiabatic compression
2. An isothermal expansion
3. An adiabatic expansion
4. An isothermal compression

The PV and TS diagram for the Carnot cycle for a gas are shown below:
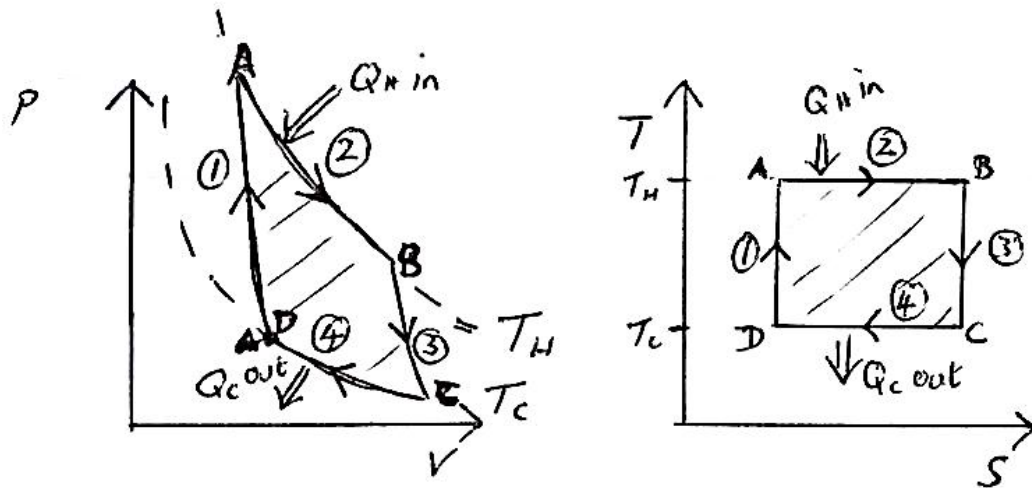
Figure 7.3 The Carnot cycle PV and TS diagrams for an ideal gas

These are the most important figures in this course. They hold just as well for a real gas as for an ideal gas but for most of the analysis that follows the ideal gas example will be used for calculations. As for any thermodynamic cycle operating in a clockwise direction the area enclosed gives the work done by the working substance over one cycle.

As these graphs are the most oft-used in developing the theory of the Carnot cycle the PV diagram in particular is often thought of as representing a general Carnot cycle. This isn't so. The Carnot cycle for two systems are provided (one below, one in this week's study handout) mainly to highlight that figure 7.3 only applies to a gas and is certainly not general.

Carnot cycle for a $1D$ elastic band

Many solid objects expand on heating and contract on cooling. Elastic bands are different – they contract when heated and expand when cooled. Forcing an elastic band to stretch quickly – an adiabatic extension – causes it to heat up.

Consider an elastic band held between two points at a low temperature in a certain state of tension. The Carnot cycle operates by:

1. An adiabatic (rapid) stretching
2. An isothermal contraction
3. An adiabatic contraction
4. An isothermal extension

A schematic generalised force-displacement graph for the elastic band's Carnot cycle has the schematic form:
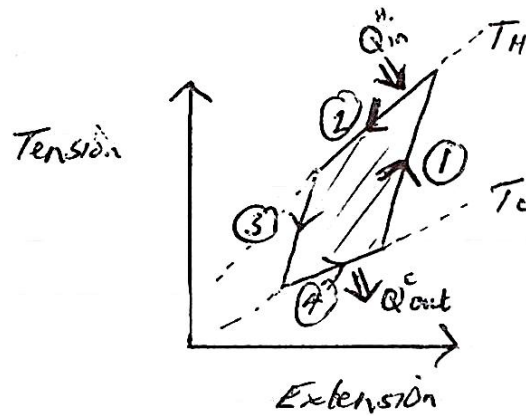
Figure 7.4 A schematic tension-extension graph for an elastic band in a Carnot cycle

7.3 The Carnot efficiency for an ideal gas

It is straightforward to compute the efficiency of a Carnot engine – the Carnot efficiency – for an ideal gas using the definition of efficiency, $\eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{Q_c}{Q_H}$ (equation 5.2b), work done as $Nk_BT \ln\frac{V_f}{V_i}$ for isothermal processes and $TV^{\gamma-1} = constant$ for an adiabatic process.

Going from the symbols on figure 7.3:

The positive amount of heat going into the system during step 2 can be written $Q_H = Nk_BT_H \ln\frac{V_B}{V_A}$.

And the positive amount of heat leaving the system during step 4 can be written $Q_C = Nk_BT_C \ln\frac{V_C}{V_D}$.

Thereby giving $\frac{Q_c}{Q_H} = \frac{T_C \ln\frac{V_C}{V_D}}{T_H \ln\frac{V_B}{V_A}}$.

For the adiabat along 3 we can write $T_H V_B^{\gamma-1} = T_C V_C^{\gamma-1}$

And for the adiabat along 1 we can write $T_H V_A^{\gamma-1} = T_C V_D^{\gamma-1}$.

Dividing these two gives $\frac{V_B^{\gamma-1}}{V_A^{\gamma-1}} = \frac{V_C^{\gamma-1}}{V_D^{\gamma-1}}$ and so $\frac{V_B}{V_A} = \frac{V_C}{V_D}$.

Thus rendering $\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$ for a Carnot engine[2] and the equation for the Carnot efficiency is:

$$\eta_{Carnot} = 1 - \frac{T_C}{T_H} \qquad \textbf{Equation 7.1}$$

This is a remarkable equation – it gives the maximum efficiency possible for a heat engine operating between two heat reservoirs. It is <u>impossible</u> to attain a greater efficiency than specified by the equation.

7.4 Carnot's theorem and the Carnot efficiency

Part 1

Thus far the explanation for the Carnot cycle being the most efficient cycle has been argued by some hand-waving logic but not proved rigorously. This can be done by using a similar argument to the one used for showing the equivalent of the Kelvin and Clausius statements of the second law.

A Carnot engine has efficiency η_{Carnot} and in one cycle takes heat Q_H from a hot reservoir and expels heat Q_C to a cold reservoir doing net work $W = \eta_{Carnot} Q_H$ in the process.

A Carnot engine is reversible and run in reverse is a Carnot fridge. In one cycle of a Carnot fridge Q_H is expelled to the hot reservoir, Q_C removed from the cold reservoir, and a net work W is put in.

Consider a heat engine – any heat engine, not a Carnot one – that is used to supply the work used to drive a Carnot fridge where both devices share the same hot and cold reservoirs:
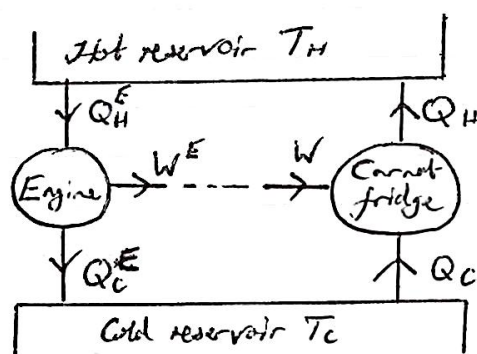
Figure 7.5 A heat engine running a Carnot fridge with shared hot and cold reservoirs

The engine has efficiency η^E and over the course of one cycle takes heat Q_H^E from the hot reservoir, does work W^E and expels heat Q_C^E to the cold reservoir.

If it is adjusted so it supplies just enough power to run the Carnot fridge so $W = W^E$ then the combined effect can be represented by:

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[2] This can be seen even more easily by looking at the TS diagram. Can you see how? The calculation from the PV diagram has been included for completeness' sake – nearly all textbooks use this approach.
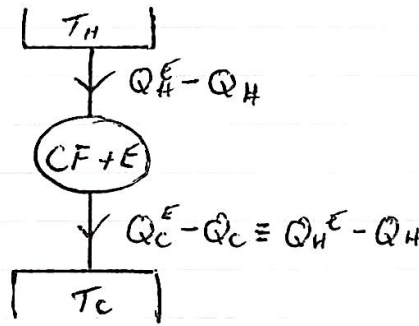
Figure 7.6 The combined effect of a Carnot fridge plus heat engine

The combined device transfers heat $Q_{net} = Q_H^E - Q_H$ from a hot reservoir to a cold one.

As $Q_H^E = \frac{W^E}{\eta^E} = \frac{W}{\eta^E} = \frac{\eta_{Carnot} Q_H}{\eta^E}$ this gives $Q_{net} = Q_H \left(\frac{\eta_{Carnot}}{\eta^E} - 1 \right)$.

Let's take this expression and decide how it works for various values of η^E.

1. If $\eta^E > \eta_{Carnot}$ i.e. if the heat engine is <u>more</u> efficient than a Carnot engine then $Q_{net} < 0$. This corresponds to the sole effect of the Carnot fridge plus heat engine being a transfer of heat from the cold reservoir to the hot one. This would violate the second law and thus this level of efficiency is impossible.

2. If $\eta^E = \eta_{Carnot}$ then the net heat transfer is zero and everything is transferred back to its initial state after one cycle implying with this efficiency the process is completely reversible.

3. If $\eta^E < \eta_{Carnot}$ then $Q_{net} > 0$ so the cycle involves a net transfer of heat from the hot reservoir to the cold one. This is of course fine but to restore the reservoirs to their original state would require a shifting of the heat back thus the process is irreversible.

The main message is that:

> No heat engine operating between two reservoirs can have a greater efficiency than a Carnot engine.

Part 2

Imagine that the engine used in the proof in part 1 was a Carnot engine after all. This would mean that the set up could work both ways with either the left hand engine powering the right hand fridge or vice versa. The only way this could be possible, bearing the analysis in point $1 - 3$ above, is if the efficiency of both the engines were equal. This gives the conclusion that:

> All Carnot engines operating between the same two reservoirs have the same efficiency.

8. Entropy and the Clausius inequality

We have seen entropy in some detail, and have developed an appreciation of the increase of entropy during thermodynamic processes but thus far we have not properly shown that entropy must increase as a consequence of the fundamental law. One way of stating the second law is simply to say that "entropy increases" and indeed that was one of the opening statements of this entire course but why does it do that? Really there is no fundamental proof – it is as much a law of nature as the conservation of energy – but we can show how it follows as a consequence of the physics we have met so far.

8.1 The multi-stage process approach

One way to demonstrate the principle is to consider an arbitrary system that undergoes a cyclic process consisting of N stages.

Stage 1 consists of placing the system in thermal contact with a reservoir at temperature T_1. The system takes in heat δQ_1 - which could be positive or negative - and does work δW_1 - which could also be positive or negative. It moves to a new state of equilibrium and moves to stage 2.

Stage 2 consists of placing the system in thermal contact with a reservoir at temperature T_2. The system takes in heat δQ_2 - which could be positive or negative - and does work δW_2 - which could also be positive or negative. It moves to a new state of equilibrium and moves to stage 3.

This same process occurs over all N stages. After the Nth cycle the system is returned to its initial state.

The main cycle could be represented schematically as:
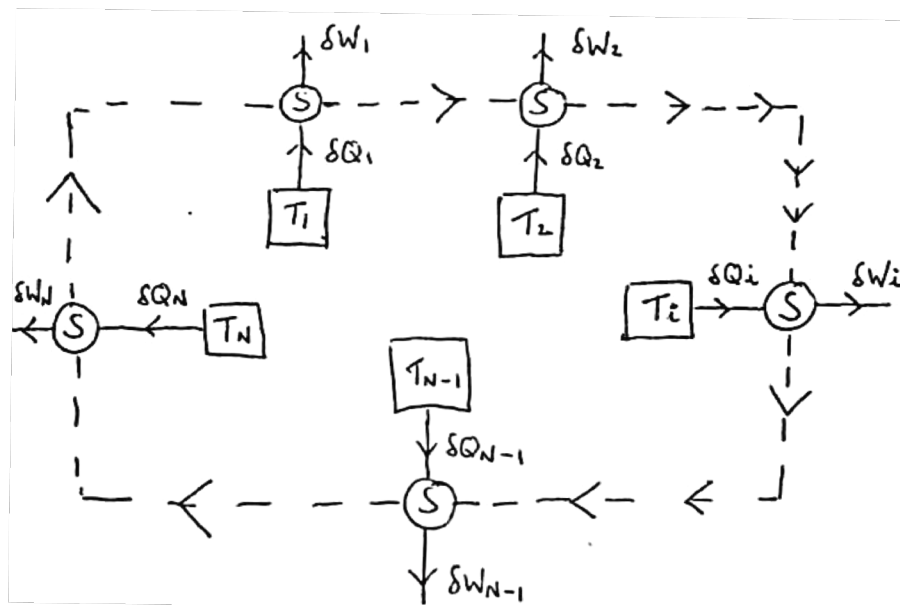
Figure 8.1 A schematic diagram of a multi-stage cyclic process performed on an arbitrary system

As the system has returned to its original state on completion of the cycle, using the first law we can state that $\Delta U_{system} = \sum_{i=1}^{N}(\delta Q_i - \delta W_i) = 0$.

This means the total work done by the system during the cycle is expressible by $W_{system} = \sum_{i=1}^{N} \delta W_i = \sum_{i=1}^{N} \delta Q_i$.

Of course all of the individual reservoirs will have been altered by the cycle so now consider that each of the reservoirs is "topped up" (or " brought down") to its original state by a single external reservoir.

Consider that this single external reservoir is set at a temperature T^* and is connected to a Carnot engine. It moves to each of the reservoirs in turn restoring them back to their original state by returning the amount of heat the transferred to the arbitrary system:
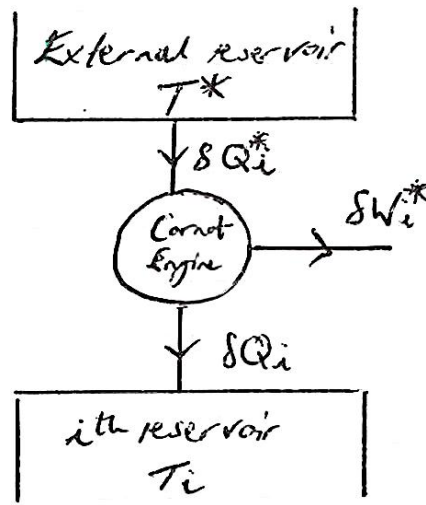
Figure 8.2 A Carnot engine restoring heat to the ith reservoir and doing some work in the process

The Carnot engine will either have to run forwards or in reverse depending on the sign of the heat transferred to the system.

For each stage the Carnot engine does some work given by $\delta W_i^* = \delta Q_i^* - \delta Q_i$.

So over the whole cycle after restoring each reservoir the Carnot engine has done total work $W_E = \sum_{i=1}^{N} \delta W_i^* = \sum_{i=1}^{N}(\delta Q_i^* - \delta Q_i)$.

We know that for each time the Carnot engine is used, $\frac{\delta Q_i}{\delta Q_i^*} = \frac{T_i}{T^*}$ so $\delta Q_i^* = T^* \frac{\delta Q_i}{T_i}$.

This gives the total work done over one cycle by the composite device (arbitrary system and Carnot engine) as $W_{total} = W_{system} + W_E = \sum_{i=1}^{N} \delta Q_i + \sum_{i=1}^{N}(\delta Q_i^* - \delta Q_i) = \sum_{i=1}^{N} \delta Q_i^* = T^* \sum_{i=1}^{N} \frac{\delta Q_i}{T_i}$.

Essentially the composite system has extracted heat from a single reservoir at temperature T^* and done an equivalent amount of work. If this amount of work is positive it is in direct contradiction of the second law.

It is, however possible, and not in contradiction of the law for the amount of work to be zero or negative – this merely corresponds to work being done <u>on</u> the system and an equal quantity of heat flowing <u>out</u>.

i.e. by use of the second law $W_{total} \leq 0$ so $\sum_{i=1}^{N} \frac{\delta Q_i}{T_i} \leq 0$.

If $\sum_{i=1}^{N} \frac{\delta Q_i}{T_i} = 0$ then $W_{total} = \sum_{i=1}^{N} \delta Q_i^* = 0$ meaning the external reservoir and everything else involved with the cycle has returned to its original state. This means the process was <u>reversible</u>.

If $\sum_{i=1}^{N} \frac{\delta Q_i}{T_i} < 0$ then $W_{total} = \sum_{i=1}^{N} \delta Q_i^* < 0$ meaning there has been a net into flow <u>into</u> the external reservoir. This means the process was <u>irreversible</u> and to get the composite system back to the original state we would need to extract heat back from the reservoir.

Consider now that the system were comprised of an infinite number of infinitesimally different reservoirs. In this case the sum tends to an integral and we end up with the <u>Clausius inequality</u>:

$$\oint \frac{\delta Q}{T} = \begin{cases} = 0 \ for \ a \ reversible \ cycle \\ < 0 \ for \ an \ irreversible \ cycle \end{cases} \qquad \textbf{Equation 8.1}$$

This statement is now close to the mathematical statement of the second law.

8.2 Entropy

Any cycle that is reversible satisfies $\oint \frac{\delta Q}{T} = 0$. Having derived his inequality Clausius then defined $\frac{\delta Q_R}{T}$ where the R implies the reversibility of the system as a new state variable – the entropy – and thus stated, for any reversible cycle, that

$$\oint_R dS = 0 \qquad \textbf{Equation 8.2}$$

Now consider an irreversible cycle consisting of an irreversible step from $A \rightarrow B$ followed by a reversible step from $B \rightarrow A$:
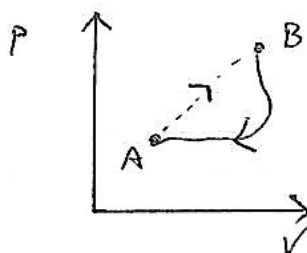
Figure 8.3 A cycle with an irreversible and a reversible stage

Using the Clausius inequality we can write $\oint_{A \to B \to A} \frac{\delta Q}{T} < 0$ which could also be written $\int_A^B \left(\frac{\delta Q}{T} \right)_{irrev} +$

$\int_B^A \left(\frac{\delta Q}{T} \right)_{rev} < 0.$

But $\int_B^A \left(\frac{\delta Q}{T} \right)_{rev} = \int_B^A dS = S_A - S_B$

And so $\int_A^B \left(\frac{\delta Q}{T} \right)_{irrev} < S_B - S_A.$

In the limit of a very small infinitesimal process this becomes $\frac{\delta Q}{T} < dS.$

What this means is that the Clausius inequality can be expressed as

$$dS = \begin{cases} = \frac{\delta Q}{T} \; for \; a \; reversible \; process \\ > \frac{\delta Q}{T} \; for \; an \; irreversible \; process \end{cases} \qquad \textbf{Equation 8.3}$$

which is the mathematical form of the second law as stated in section 6.

9. Thermodynamic potentials

The thermodynamic potentials build on something well known – potential energy – to look at thermodynamic systems in subtler and deeper ways than we have been able to do before.

9.1 Thermodynamic potentials

Some general physics

Energy is defined as the capacity to do work. The potential energy of a system is the capacity to do work as a result of its internal configuration. An essential feature of all forms of potential energy is that the energy stored can, in principle, be deduced simply by knowing the position of all the components of the system. Then with knowledge of the nature of the conservative force fields involved the amount of potential energy can be computed, giving the maximum theoretical amount of work that could be extracted from the system in rearranging all the components into a state of minimum potential energy.

The thermodynamic potential of a system is similar, but with one generalisation – it is the amount of work that can be extracted from a system plus the amount of heat that can be extracted from a system. We know by now that these are two very different types of energy, but as they are indeed both types of energy, the thermodynamic potential of a system can thus be defined by one single number of joules. To calculate the thermodynamic potential of a system one wouldn't just be able to look at the position of the system, one would also need the relative speed of everything inside the system as well – i.e. both the internal kinetic energy plus the potential energy of the system must be known.

Simply giving this number would be of limited use however as from a practical point of view if we want a system to do work then we need to know how much useful work can be extracted. The concept of useful work is important as well: if a system does work *en route* to thermodynamic equilibrium, is that work used to merely expand against the atmosphere or can it be used to actually move something else?

These distinctions are important and to properly appreciate them the forefathers of thermodynamics, most notably Josiah Willard Gibbs in the 1870s, essentially invented different types of thermodynamic potential for assisting in understanding the physics of different situations. We will meet four in this section and one more later in the course. The four here are:

1) Internal energy
2) Enthalpy
3) Helmholtz free energy
4) Gibbs free energy

As with potential energy the absolute value of any of the thermodynamic potentials is usually not a helpful quantity, rather the <u>change</u> in the thermodynamic potential as the result of a thermodynamic process is what we are interested in.

Some general mathematics

It is common in physics to use a mathematical operation to study nature from two different points of view.

A common two-way operation that you are familiar with is differentiating and integrating. When studying classical mechanics for example it is possible to study systems using forces, but also possible to use potentials. The force is literally derived from the potential. When using forces we thinking of masses as accelerating in response to a force, but using potentials we think of systems moving towards their state of lowest potential energy. Both ways of thinking about the problem are equally correct, and both will give the same result.

Another operation you have met this term is the Fourier transform – essentially a way of taking a data set in one domain and looking it in another domain (e.g. taking a time domain and switching it to a frequency domain).

These mathematical operations simply give an alternative viewpoint on the physics – doing the operation does not add or remove any information.

In looking at the thermodynamic potentials we make use of <u>Legendre differential transforms</u> which works as follows:

Consider a function of two variables $f(x, y)$ that satisfies

$$df = udx + vdy$$

If we want to change the description to one involving a new function $g(u, v)$ then the Legendre transform can be defined as

$$g = f - ux$$

which thus satisfies the equation

$$dg = -xdu + vdy$$

This process is used in the mathematical development of the new thermodynamic potentials in this section.

One result that we will use, is that if dG is an exact differential of the form

$$dG = Xdx + Ydy$$

then

$$\left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y$$

9.2 Internal energy

Internal energy doesn't require an introduction but the most important way of stating it in equation form is stated thus:

$$dU = TdS - PdV \qquad \text{Equation 9.1 (reproduction of equation 3.6)}$$

The internal energy of a system can be thought of as a system's ability to do work plus its capacity to release heat. It also has an easily interpreted microscopic definition viz. it is the sum of the kinetic energies and potential energies of all the particles in the system.

Internal energy is useful when considering a system that goes through changes in entropy and volume. We say that entropy is the thermal natural variable and volume is the mechanical natural variable for internal energy.

9.3 Enthalpy

The state function known as enthalpy, H, is defined by

$$H = U + PV \qquad \text{Equation 9.2}$$

which leads to $dH = dU + PdV + VdP$ and so using equation 9.1

$$dH = TdS + VdP \qquad \text{Equation 9.3}$$

The thermal natural variable of enthalpy is entropy and the mechanical natural variable is pressure. Enthalpy can thus be useful when considering processes involving changes in entropy and pressure.

Using and interpreting enthalpy

Unlike internal energy, enthalpy does not have a convenient microscopic definition but on a macroscopic scale it can be useful for certain types of thermodynamic process, most notably those which are isobaric and reversible. In fact, one way of describing enthalpy is to say that the change in enthalpy is the heat flow in an isobaric, reversible process. From equation 9.3 for such a process it is easily seen that $dH = \delta Q$ and this then gives expressions for constant pressure heat capacity of

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad \text{Equation 9.4}$$

In chemical reactions

Consider a chemical reaction inside a sealed cylinder with a frictionless, light piston under normal atmospheric pressure:
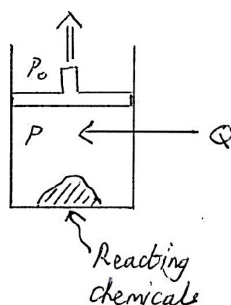
Figure 9.1 A chemical reaction causing a volume to increase

Imagine that the volume of chemicals changes during the reacting (e.g. expands as a gas is being liberated). This is the situation that normally exists in chemical reactions as the external pressure is constant (even when dealing with open systems).

The process need not be reversible, and in fact, for most chemical reactions will be far from it.

If the gas expands, then using the first law, $\Delta U = Q - P_0 \Delta V$ where Q is the heat supplied to the system. This can be written as $Q = \Delta U + P_0 \Delta V = \Delta U + \Delta(PV)$ which, following the definition of enthalpy, gives $Q = \Delta H$.

Notice that the internal pressure need not be equal to the external pressure during the reaction, it only needs to be the same at the start and the end.

What this means is that the change in enthalpy for a chemical reaction equals the heat supplied to the reactants for the reaction to progress. For exothermic reactions, the value is negative and for endothermic reactions the value is positive.

Enthalpy is thus an invaluable concept in chemistry and biology as it gives clearly quantifiable numbers for the energy transfer during any chemical reaction.

A further important property of enthalpy in adiabatic processes is discussed in section 11.

9.4 Helmholtz free energy

The state function known as Helmholtz free energy, F, is <u>defined</u> by

$$F = U - TS \qquad \textbf{Equation 9.5}$$

which leads to $dF = dU - TdS - SdT$ and so using equation 11.1

$$dF = -SdT - PdV \qquad \textbf{Equation 9.6}$$

The thermal natural variable of Helmholtz free energy is temperature and the mechanical natural variable is volume. Helmholtz free energy can thus be useful when considering processes involving changes in temperature and volume.

Using and interpreting Helmholtz free energy

As with enthalpy, Helmholtz free energy does not have a convenient microscopic definition but on a macroscopic scale it can be useful for certain types of thermodynamic process, most notably those which are isothermal and carried out in a closed system. One interpretation of it is that it is the change in Helmholtz free energy is the work available for use in a process that starts and ends at the same temperature. It is indeed the energy that is "free" for use (hence the symbol F; it is often also given the symbol A as well, from the German word *Arbeit* meaning "work").

There are three principal uses for Helmholtz free energy, of which one is outlined in detail here and the other two merely stated:

1) The work from a system with no temperature change

Consider a system in thermal contact with a reservoir on one side and otherwise thermally insulated from its environment on the other sides:
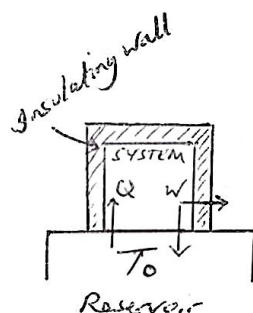
Figure 9.2 A system in thermal contact with a heat reservoir

Consider a process where heat Q passes from the reservoir to the system. This does not have to be done isothermally but imagine that at the start and the end of the process the temperature of the system is that of the reservoir, T_0.

The system can then do some work, either as expansion, as the walls do not have to be rigid, or in any other form. If ΔS is the change in entropy of the system and ΔS_0 is the change in entropy of the reservoir then the second law tells us that $\Delta S + \Delta S_0 \geq 0$.

As the temperature of the reservoir remains constant, $\Delta S_0 = -\frac{Q}{T_0}$ so $\Delta S - \frac{Q}{T_0} \geq 0$ which is essentially the same as the definition of entropy.

The first law states $\Delta U = Q - W$ so substituting in Q gives $\Delta U + W - T_0 \Delta S0 \leq 0$, or, $\Delta(U - TS) + W \leq 0$.

From the definition of Helmholtz free energy this gives $W \leq -\Delta F$. The amounts are equal for a reversible process.

What this means is that in any process that starts and ends at the same temperature, the <u>maximum</u> amount of work obtainable equals the <u>decrease</u> in the Helmholtz free energy. A profound result indeed.

<u>2) The equilibrium state for an isochoric process in contact with a reservoir</u>

Consider now that the walls are rigid in figure 9.2. In this case the resulting formula is the extremely simple $\Delta F \leq 0$ with the resulting argument being that in this case the equilibrium state is when the Helmoltz free energy has reached a minimum.

<u>3) Applications in statistical mechanics</u>

Helmholtz free energy is an integral part of discussing the variation of entropy with temperature in statistical mechanics with use of something called the <u>partition function</u>. This will be covered later this term.

9.5 Gibbs free energy

The state function known as Gibbs free energy, G, is <u>defined</u> by

$$G = H - TS \qquad \textbf{Equation 9.7}$$

which leads to $dG = dH - TdS - SdT = dU + PdV + VdP - TdS - SdT$ and so using equation 9.1

$$dG = -SdT + VdP \qquad \textbf{Equation 9.8}$$

The thermal natural variable of Gibbs free energy is temperature and the mechanical natural variable is pressure. Gibbs free energy can thus be useful when considering processes involving changes in temperature and presssure.

Using and interpreting Gibbs free energy

As with enthalpy and Helmholtz free energy, Gibbs free energy does not have a convenient microscopic definition but on a macroscopic scale it can be useful for certain types of thermodynamic process, most notably those which are connected to a heat and pressure reservoir. This essentially covers most naturally occurring chemical reactions and phase changes as the surrounding atmosphere essentially acts as both such reservoirs.

The central conclusion will be that in such conditions all systems move towards a state where the Gibbs free energy is a minimum and the initial Gibbs free energy thus gives the maximum amount of work available from the system.

Consider then the system below:
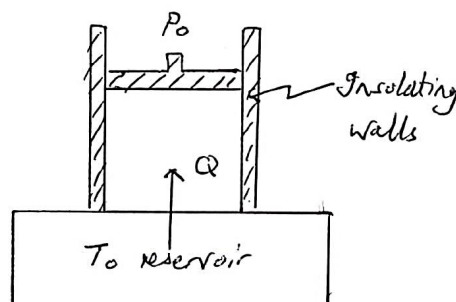
Figure 9.3 A system in thermal contact with a heat and pressure reservoir

From the second law, during a thermodynamic process, $Q - T_0\Delta S \leq 0$ where ΔS is the entropy change of the system, just as with the working following figure 9.2.

Using the first law, $\Delta U = Q - P_0\Delta V$ so substituting Q gives $\Delta U + P_0\Delta V - T_0\Delta S \leq 0$ which can be written $\Delta U + \Delta(PV) - \Delta(TS) \leq 0$.

This can be rewritten as $\Delta(U + PV - TS) \leq 0$ which, from the definition of Gibbs free energy, gives $\Delta G \leq 0$. For reversible processes $\Delta G = 0$.

This thus implies that any process tends to minimise Gibbs free energy, and while a process still runs, the Gibbs free energy keeps decreasing. It also implies that the amount of Gibbs free energy available at the start of a process is the maximum amount of work that can be obtained if the pressure and temperature at the start and end are the same.

We will meet use Gibbs free energy many times in this course, notably when studying phase changes and chemical potential.

9.6 Other thermodynamic potentials

There are other thermodynamic potentials available. One could even invent ones own if one felt that way inclined (though it would most likely not be very useful)! The four we have seen thus far are probably the most widely used and the most useful in physics. Their use can be summarised by this table:

	Constant volume	Constant pressure
Constant entropy	ΔU	ΔH
Constant temperature	ΔF	ΔG

Table 9.1 Summarising the use of the four thermodynamic potentials

The Gibbs free energy is the most oft used as so many things happen in contact with the ever present thermal and pressure reservoir that is the atmosphere.

In this course we will meet the chemical potential in section 12 – this can be thought of as the Gibbs free energy per particle.

In statistical physics you will use most of the five met here, plus the Landau potential (the "grand potential") which is useful for irreversible process for open systems with variable particle number and is therefore all-encompassing.

10. The Maxwell relations

The Maxwell relations are a set of differential equations that follow from the definitions of the thermodynamic potentials. They are useful in determining how one state variable varies with respect to another for different conditions.

10.1 Derivation of the Maxwell relations

The Maxwell relation that follows from internal energy

If internal energy is written as a function of its natural variables then

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad \textbf{Equation 10.1}$$

and by comparison with equation 9.1 we can see that $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $P = -\left(\frac{\partial U}{\partial V}\right)_S$. So if we know how the internal energy changes with respect to its natural variables then the temperature and pressure can be found. Furthermore, using the condition for exact differential we can see that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \textbf{Equation 10.2}$$

This is our first Maxwell relation. Notice that the natural variables appear outside the partial derivatives.

The Maxwell relation that follows from enthalpy

Following a similar procedure to that followed for internal energy we can write enthalpy as a function of its natural variables:

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \qquad \textbf{Equation 10.3}$$

and by comparison with equation 9.3, $T = \left(\frac{\partial H}{\partial S}\right)_P$ and $V = \left(\frac{\partial H}{\partial P}\right)_S$ so if enthalpy is known in terms of its natural variables then temperature and volume can be derived. Then using the condition for exact differential

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \textbf{Equation 10.4}$$

which is our second Maxwell relation with the natural variables appearing outside the partial derivatives again.

The Maxwell relation that follows from Helmholtz free energy

Following the same procedure as for internal energy and enthalpy we can write Helmholtz free energy as a function of its natural variables:

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \qquad \textbf{Equation 10.5}$$

and by comparison with equation 9.6, $S = -\left(\frac{\partial F}{\partial T}\right)_V$ and $P = -\left(\frac{\partial F}{\partial V}\right)_T$ so if Helmholtz free energy is known in terms of its natural variables then entropy and pressure can be derived. Then using the condition for exact differential

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \textbf{Equation 10.6}$$

which is our third Maxwell relation with the natural variables appearing outside the partial derivatives again.

The Maxwell relation that follows from Gibbs free energy

Following the same procedure as for the other three thermodynamic potentials we can write Gibbs free energy as a function of its natural variables:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \qquad \textbf{Equation 10.7}$$

and by comparison with equation 9.8, $S = -\left(\frac{\partial G}{\partial T}\right)_P$ and $V = \left(\frac{\partial G}{\partial P}\right)_T$ so if Gibbs free energy is known in terms of its natural variables then entropy and volume can be derived. Then using the condition for exact differential

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \textbf{Equation 10.8}$$

which is our fourth Maxwell relation with the natural variables appearing outside the partial derivatives again.

10.2 In summary

The Maxwell relations are repeated here, with a little extra on second derivatives included:

$$\frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \textbf{Equation 10.2}$$

$$\frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \textbf{Equation 10.4}$$

$$-\frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \textbf{Equation 10.6}$$

$$\frac{\partial^2 G}{\partial T \partial P} = -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \qquad \textbf{Equation 10.8}$$

They essentially are all equal to the second derivatives of their related potentials. They are important in that they are completely general and they allow us an insight into solving certain thermodynamic problems that might otherwise seem intractable.

10.3 Examples

Herewith two examples, with more in this week's study handout:

1) A block of copper of linear dimension $2.0\ \text{cm}$ is squashed reversibly and isothermally at temperature room temperature from zero pressure to a pressure of $150\ \text{GPa}$. How much heat flows out of the block? The thermal expansivity of copper is $51\ \mu\text{K}^{-1}$ and remains constant during the process.

Starting with the equation for reversible heat flow, $\delta Q_R = TdS$.

dS isn't going to be much use to us so we can get rid of it by realising that we want things in terms of temperature and pressure so we write $S = S(T,P)$ and thus $dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$ so $\qquad \delta Q_R = TdS = T\left(\frac{\partial S}{\partial P}\right)_T dP + T\left(\frac{\partial S}{\partial T}\right)_P dT$. This expression is completely general and applies to any process.

The second term is zero as the process is isothermal so $\delta Q_R = T\left(\frac{\partial S}{\partial P}\right)_T dP$. This simplified expression is now specific to an isothermal process.

Now using equation 10.8 gives $\delta Q_R = -T\left(\frac{\partial V}{\partial T}\right)_P dP$.

We recognise $\left(\frac{\partial V}{\partial T}\right)_P$ as βV where β is the thermal expansivity and so $\delta Q_R = -T\beta V dP$.

This gives $\Delta Q = -TV\beta \int_i^f dP \approx TV\beta(P_i - P_f)$ assuming only a small change in volume and the thermal expansivity remains constant.[3]

Plugging in values gives

$\Delta Q = 293 \text{ K} \times (2.0 \times 10^{-2} \text{ m})^3 \times 51 \times 10^{-6} \text{ K}^{-1} \times (0 - 150 \times 10^9 \text{ Pa}) = -17{,}931 \text{ J}.$

The minus sign implies that heat leaves the block, so the final answer is that approximately 18 kJ of heat flows out of the block during the process.

2) Another block of copper of the same dimensions is squashed rapidly 2.0 cm from zero pressure to a pressure of 150 GPa. If the block is initially at room temperature what temperature does it finish at? The constant pressure heat capacity of copper is $390 \text{ Jkg}^{-1}\text{K}^{-1}$ and remains constant during the process.

As the process is rapid, no heat has time to flow and thus starting again with the equation for reversible heat flow, $\delta Q_R = TdS$ we can write $TdS = 0$.

In this problem entropy is not a relevant variable, but pressure and temperature and pressure are so we can write $dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$ (as with the previous questions) and so $\left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT = 0$.

We can now make two substitutions to get rid of the entropy terms and replace them with quantities that are relevant.

Equation 9.4 gives us $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$ so $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$.

And Maxwell relation 10.8 gives us $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$.

Giving $-\left(\frac{\partial V}{\partial T}\right)_P dP + \frac{C_P}{T} dT = 0$.

From the definition of thermal expansivity this can be rearranged to give $\frac{dT}{T} = \frac{\beta V}{C_P} dP$.

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[3] The steps here can rightly cause some consternation. The process is defined as isothermal so how can we make use of a $\left(\frac{\partial V}{\partial T}\right)_P$ term on the way to the solution?

The key thing to recognise is that even though this particular process is isothermal, the block of copper under discussion does have a value of $\left(\frac{\partial V}{\partial T}\right)_P$ particular to it i.e. the block has a value of its rate of change of volume with temperature at constant pressure in m^3K^{-1} that could, in principal, be measured for it on a different experiment on a different day. This value is a property of the copper block.

In the mathematical development it is fine to use this value as it is just a value that is a property of the block and the fact that this particular process is isothermal is irrelevant.

This sort of step occurs frequently in the use of the Maxwell relations.

This can now be integrated as follows: $\int_{T_i}^{T_f} \frac{dT}{T} = \frac{\beta V}{C_P} \int_{P_i}^{P_f} dP$ so $T_f = T_i e^{\frac{\beta V \Delta P}{C_P}}$.

This is a relation to be wary of as it shows an exponential rise in temperature with pressure difference. If the cube can melt then the thermal characteristics change drastically and the answer won't be at all valid. If the exponent $\frac{\beta V \Delta P}{C_P}$ is greater than unity then the temperature will rise drastically and the copper will certainly melt.

But plugging numbers into the term in the exponent provides

$\frac{\beta V \Delta P}{C_P} = \frac{51 \times 10^{-6} \times (2.0 \times 10^{-2})^3 \times 150 \times 10^9}{390} = 0.1569$ which is not too high and we get $T_f = 1.169 T_i$. With a room temperature of 293 K this gives a final temperature of 342.8 K i.e. a relatively modest rise of about 50 K.

11. Adiabatic expansions

This section uses some of the material developed recently to study the expansion of real (i.e. non-ideal gases) under three circumstances. One is the regular adiabatic expansion seen in section 4.2.2.3, one is a free expansion into a vacuum and the other is forced expansion through a nozzle. Studying these phenomena reveal some interesting and subtle physics on the nature of gases. It also bring home a central message that "adiabatic" is not synonymous with "isentropic" i.e. process in which there is no supply of heat are not necessarily processes that see no entropy change.

11.1 The familiar version of adiabatic expansion

In the version of adiabatic expansions seen in the Structure of Matter course and in section 4.2.2.3 a gas expands against the environment with no input of heat:
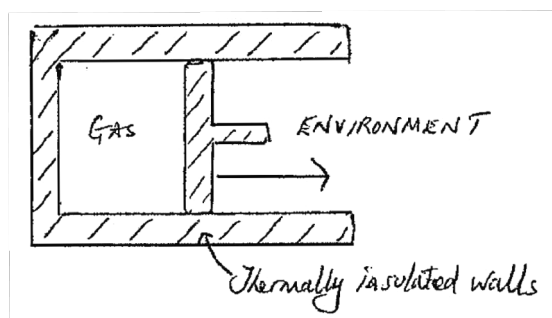

Figure 11.1 An adiabatic expansion of a gas in a piston

In addition to the familiar relations that apply to an adiabatic expansion seen in the aforementioned parts of the degree we can now derive another very general expression with some of our new knowledge of mathematics and physics. Let's say we want to find a value for the rate of change of temperature of the gas with volume during the expansion. We can be dealing with any closed system and thus cannot assume any properties of an ideal gas. As the process is done at constant entropy what we are looking for is an expression for $\left(\frac{\partial T}{\partial V}\right)_S$.

As we know there are two independent state variables and we want a process at constant entropy we can start by writing $S = S(V, T)$ and then setting $dS = 0$ as follows:

If $S = S(V, T)$ then $dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$ and so for a constant entropy process $\left(\frac{\partial S}{\partial V}\right)_T dV = -\left(\frac{\partial S}{\partial T}\right)_V dT$.

Now one of the Maxwell relations is $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and noting that $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ by definition gives $\left(\frac{\partial P}{\partial T}\right)_V dV = -\frac{C_V}{T} dT$ which rearranges to give

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V \qquad \textbf{Equation 11.1}$$

This expression is completely general – it applies to absolutely any closed system going through an adiabatic expansion or compression.

As temperature, heat capacity and $\left(\frac{\partial P}{\partial T}\right)_V$ are all positive quantities this means the right hand side of the expression is always negative and thus for expansion (dV positive) dT is negative i.e. temperature falls and for compressions temperature rises as one might expect both from intuition and from experience. Bear this in mind when considering the corresponding situations in sections 11.3 and 11.4.

It is left as an exercise for the student to find an expression for $\left(\frac{\partial T}{\partial V}\right)_S$ for an ideal gas and go on to show that this leads to the familiar relation $TV^{\gamma-1} = constant$.

11.2 Adiabatic free expansion

Now consider a gas in a thermally insulated container divided into two parts by a non-permeable wall. Initially one side is filled with gas while the other side is completely empty i.e. it contains a vacuum.
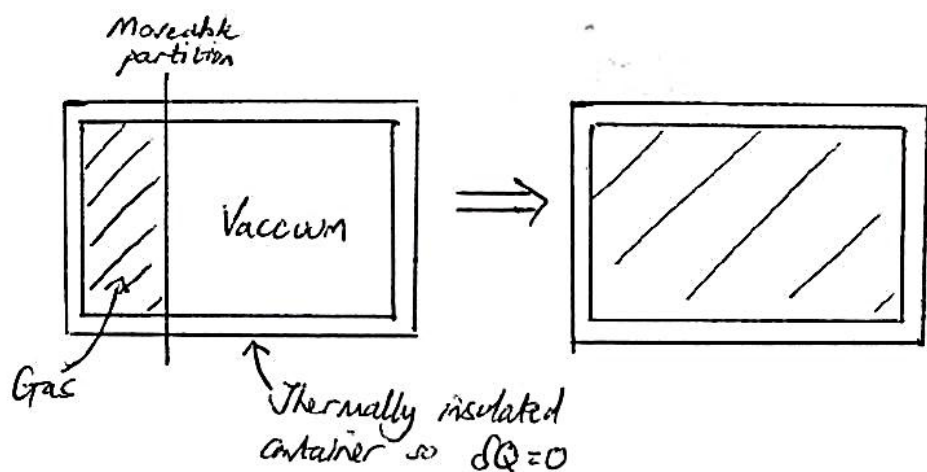
Figure 11.2 A free expansion into a vacuum

A partition is then moved so the gas expands to fill the space. In the situation described this will be rapid (with a time scale of order $\frac{L}{v}$ where L is the linear dimension of the container and v the root mean square speed of the particles) but certainly not instantaneous. It need not be as rapid; if the partition had a small hole of a few atoms' breadth the process could be slow and the same physics would apply.

This process is known as an adiabatic free expansion, or a Joule expansion.

Note that the between the start and end of the process the gas is not in thermal equilibrium and the process is neither quasistatic nor reversible.

The process is adiabatic by definition as no heat is supplied. So is the entropy change zero? The answer is an unequivocal "no"! The process is irreversible therefore $\Delta S > 0$.

The gas does no work as the expansion occurs into a vacuum.

So how can ΔS be calculated? Assuming the gas is ideal and that the removal of the partition has done no work on the gas the internal energy change of the gas must be zero and thus the temperature stays constant. This makes sense when one thinks of the speed of the particles – nothing has been done to speed them up or slow them down so the temperature can't have altered.

As the initial and final states have the same temperature the entropy change is simply the same as for an isothermal reversible expansion and is given by $Nk_B \ln\frac{V_f}{V_i}$.

Temperature changes for non-ideal gases

It can be useful in looking at such problems to define a quantity as the temperature per unit volume change for the gas i.e.

$$\eta = \frac{dT}{dV} \qquad \textbf{Equation 11.2}$$

where η is a scalar with unit of Km^{-3} and is sometimes referred to as the **Joule coefficient.** To avoid confusion it might be better to define the quantity as $\eta = \left(\frac{dT}{dV}\right)_U$ to distinguish it from the quantity $\left(\frac{dT}{dV}\right)_S$ is section 11.1 but as we are not going to mix the two examples and that when dealing with the Joule coefficient in physics it is implicit and essential that internal energy is constant while entropy changes it means 11.2 is entirely correct and there is no need for partial derivatives with subscripts.

The Joule coefficient for an adiabatic expansion is a property of a gas. A positive Joule coefficient means a gas heats on expansion and negative means it cools on expansion. The Joule coefficient of an ideal gas is exactly zero.

Let us examine the Joule coefficient further.

By writing the internal energy of the gas as a function of temperature and volume i.e. $U = U(V, T)$ gives $dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$.

Now recalling that heat capacity at constant volume is $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ (equation 4.5) and recognising that $dU = 0$ as no heat is supplied in the process means for the Joule expansion $0 = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V dT$ and thus we get a general expression for the Joule coefficient of $\frac{dT}{dV} = \eta = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{C_V}$.

The numerator of this expression is given, in general, by $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ (see Study Handout 4) and so we get a new, general, expression for the Joule coefficient:

$$\eta = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] \qquad \textbf{Equation 11.3}$$

This is similar to the expression for the adiabatic expansion in a piston but with greater by an absolute amount $\frac{P}{C_V}$.

By taking the equation of state for an ideal gas we can quickly see that $\eta_{Ideal\ gas} = 0$ as previously surmised.

To see how this might be different for a non-ideal gas take the equation of state for a van der Waals gas (equation 3.8): $\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_BT$ leads to $\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk_B}{V-Nb}$.

This gives $\eta_{vdW} = -\frac{1}{C_V}\left[\frac{Nk_BT}{V-Nb} - P\right] = -\frac{1}{C_V}\left[P + \frac{aN^2}{V^2} - P\right] = -\frac{aN^2}{C_VV^2}$.

So for conditions under which a gas behaves according to the van der Waals equation of state the Joule coefficient is negative and the gas cools on adiabatic free expansion. Why might this be? In fact this cooling of the gas is true for most real gases though the effect is small. Further detail on the problem is provided in this week's study handout.

11.3 Throttling

Now consider a different situation where a gas is forced through a valve by a constant pressure on a piston P_1 on the left side of a valve and P_2 on the right side of a valve with $P_1 > P_2$.
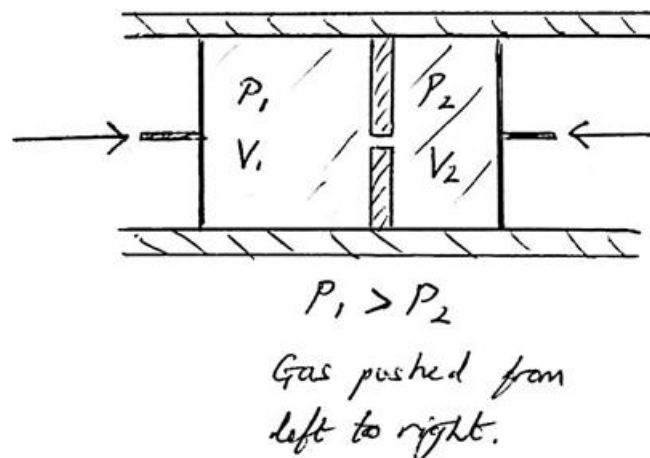

Figure 11.3 A gas forced through a valve by a pressure differential

The walls of the chamber are well insulated so no heat can flow in or out. The process is known as a **Joule-Thomson expansion**, a **Joule-Kelvin[4] expansion** or **throttling**. As no heat is supplied the process is, by definition, also adiabatic.

The physics is more complicated than the Joule expansion as the gas does work on the right hand side. It is convenient to define as the temperature change per unit pressure difference experienced by the gas as it moves through the valve:

$$\mu = \frac{dT}{dP} \qquad \text{Equation 11.4}$$

where μ is a scalar with unit of KPa^{-1} and is sometimes referred to as the **Joule-Thomson coefficient.**

As with the Joule coefficient, the Joule-Thomson coefficient is a property of a gas.

Throttling is isenthalpic

We can prove that a throttling process is one of constant enthalpy. Recall that enthalpy is useful quantity when considering processes with changing pressure and entropy.

The work done on the gas on the left hand side of the valve is P_1V_1 and the work done on the gas on the right hand side is $-P_2V_2$. As the process is adiabatic, using the first law, $\Delta U = U_2 - U_1 = P_1V_1 - P_2V_2$.

This gives $U_2 + P_2V_2 = U_1 + P_1V_1$ which, from the definition of enthalpy, $H = U + PV$ (equation 11.2) shows the process is isenthalpic. For this reason the more general mathematical way of defining the Joule-Kelvin coefficient is $\mu = \left(\frac{dT}{dP}\right)_H$ though as with the Joule coefficient the full derivative variant is completely correct and unlikely to bring about confusion as the processes are never mixed.

Let's look at the entropy change for the process. Writing entropy as a function of temperature and pressure i.e. $S = S(T, P)$ gives $dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$.

This can be transformed using three previously seen relations:

From equation 9.4 we know $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$ so $dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \frac{C_P}{T} dT$.

From equation 10.8 (a Maxwell relation) we know $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ so $dS = -\left(\frac{\partial V}{\partial T}\right)_P dP + \frac{C_P}{T} dT$

And thermal expansivity is given by $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ so

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[4] Note that William Thomson and Lord Kelvin are the same person.

$$dS = -\beta V dP + \frac{C_P}{T} dT \qquad \textbf{Equation 11.5}$$

This is a general expression for any gas in a Joule-Thomson expansion.

We can go further by recognising the process is isenthalpic so going from $dH = TdS + VdP$ (equation 9.3) we can write $VdP = -TdS$ and so equation 11.5 becomes $-\frac{V}{T}dP = -\beta V dP + \frac{C_P}{T}dT$ which rearranges to $\frac{dT}{dP} = \frac{V}{C_P}(\beta T - 1)$ i.e. for any gas

$$\mu = \frac{dT}{dP} = \frac{V}{C_P}(\beta T - 1) \qquad \textbf{Equation 11.6}$$

Let us consider what this equation means by looking at the signs of the terms on both sides of the equation. Volume and heat capacity are always positive quantities and so the right hand side of the equation has a sign determined by the sign of $(\beta T - 1)$. The term $\frac{dT}{dP}$ is the rate of change of temperature with respect to pressure during the throttling process. As the gas is pushed from high pressure to low pressure the dP part is negative and therefore:

- If $\beta T > 1$ then dT is negative i.e. the gas cools on throttling.

- If $\beta T = 1$ a gas goes through no temperature change on throttling

- If $\beta T < 1$ then dT is positive and the gas heats on throttling.

So in principle, whether the gas heats, cools or stays the same temperature during throttling depends on the gas type, and, as thermal expansivity is a function of temperature, it depends on the temperature of the gas as well.

Broadly speaking this happens because when gases are highly compressed the particles tend to have a net repulsive force between then so an expansion into a larger space causes then to spring apart and have more kinetic energy and thus a higher temperature; when rarefied the particles have a net attraction so permitting them to be further apart lowers increases their mutual potential energy and lowers the kinetic and so the temperature falls.

Isenthalps and inversion curves

Any substance that expands goes through a Joule-Kelvin expansion expands at constant enthalpy. Lines of constant enthalpy can be drawn on a temperature-pressure diagram to inspect the process. For an ideal gas the isenthalps always have zero gradient but for real fluids the insenthalps tend to have the form shown schematically below:
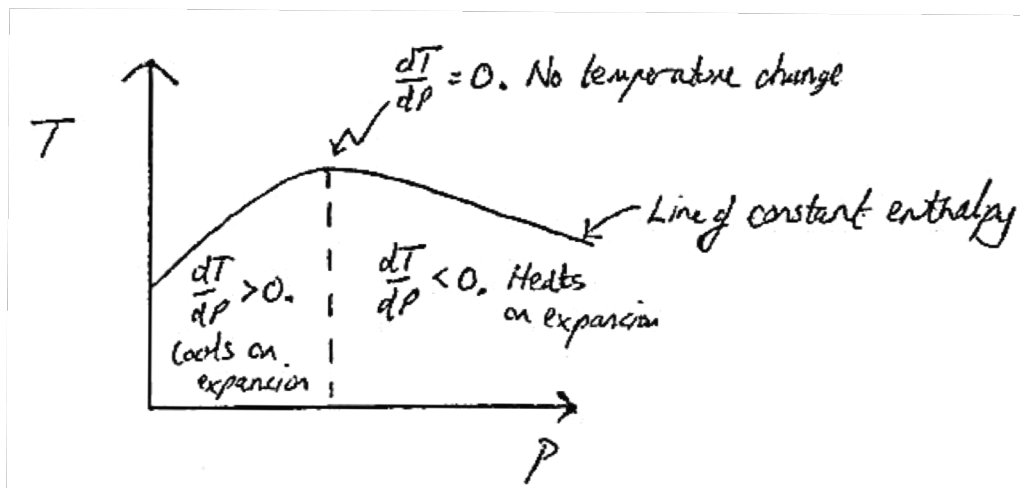
Figure 11.4 Schematic line of constant enthalpy for a real fluid on a temperature pressure diagram

It is, in principal, possible to use equations of state to calculate information about exact shape of the isenthalps for fluids but in general the mathematics is unrewarding and doesn't provide functions that lend themselves to simple analysis. Plus, more importantly, for real fluids the journey along an isenthalp often leads to a the properties of the fluid changing so significantly that no one equation of state will suffice, with a common extreme being for phase changes. Unless the equation of state in question is sophisticated enough to incorporate the changing properties the results will only be useful for a small portion of the curve. So instead we will merely inspect empirical results.

One can see on the generic TP isenthalp that at low initial pressure the gradient $\frac{dT}{dP}$ is positive meaning the gas will cool on expansion, at some some critical pressure the gradient levels off so no temperature change occurs and for higher pressures the gradient is negative so the gas heats on expansion.

Although isenthalps all have the same generic shape the position and of the isenthalp and the critical pressure for the switch from positive to negative gradient varies with temperature. For all gases there is a certain critical temperature above which the gas will only heat on expansion – the particles move rapidly enough so they, in general, experience mutual repulsion no matter how rarefied and any expansion causes them to spring apart even faster. This is known as the **inversion temperature** of the gas. A schematic diagram of the isenthalps for a generic fluid with several features annotated is shown below.
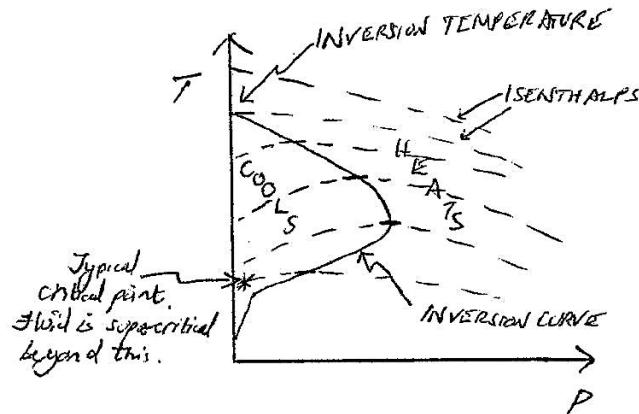
Figure 11.5 Schematic inversion curve for a typical fluid.

Producing experimental inversion curves for any given fluid is a non-trivial experimental endeavour however empirically it has been shown that most gases tend to share the characteristics shown in the figure. The inversion temperature is a property of the gas alone; for the abundant gases in air it is several hundred Kelvin so air cools on throttling, but helium has $T_{inversion} \approx 50$ K and hydrogen ~ 200 K so they warm up on throttling at room temperature.

The throttling process is often used in engineering systems for cooling fluids. In fridges and heat pumps the refrigerant is cooled by pushing it through a valve before it flows over the food (fridge) or ground) heat pump to remove heat from them.

11.4 Summary of the three adiabatic expansions

To summarise here is a comparison of the three adiabatic expansions in table form:

Type of adiabatic expansion	Constant quantity	Relevant equation to inspect the temperature change	Do fluids cool or heat on expansion?
Expansion against environment in a piston or similar arrangement	Entropy, $dS = 0$	$\left(\dfrac{\partial T}{\partial V}\right)_S = -\dfrac{T}{C_V}\left(\dfrac{\partial P}{\partial T}\right)_V$	Always cool
Adiabatic free expansion into a vacuum	Internal energy, $dU = 0$	$\left(\dfrac{\partial T}{\partial V}\right)_U = -\dfrac{1}{C_V}\left[T\left(\dfrac{\partial P}{\partial T}\right)_V - P\right]$	Usually cool
Throttling through a nozzle from high to low pressure	Enthalpy, $dH = 0$	$\left(\dfrac{\partial T}{\partial P}\right)_H = \dfrac{V}{C_P}(\beta T - 1)$	May cool or heat depending on the gas type and initial conditions

12. Chemical potential

This section looks at our fifth thermodynamic potential – the chemical potential - and uses it to investigate the nature of Gibbs free energy and phase transitions in more detail than permissible before.

12.1 Defining and understanding chemical potential

There are several ways of interpreting this new quantity as follows:

12.1.1 The need for chemical potential when considering open systems

In our development of the principles of thermodynamics we have usually considered closed systems i.e. systems where the number of particles is constant. Of course this is a simplification for most systems as particles numbers are usually variable. An open system doesn't just have to be a system where matter can be scooped out or added like a bucket of water where a person could remove some or rain could fall in. Other examples are:

- Melting ice in water: the ice loses particles and the water gains them; considering either phase as a single system means the phase change renders the systems open
- Any chemical reaction by definition causes a change in the number of types of particle within a system

Such variable particle number systems require a modification to the central equation of thermodynamics, $dU = TdS - PdV$, as now N, the number of atoms in the system, is an independent state variable along with temperature and pressure.

Considering a system with one type of particle only, the central equation of thermodynamics can be chosen to be written

$$dU = TdS - PdV + \mu dN \qquad \textbf{Equation 12.1}$$

where μ is called the chemical potential of the system and, following the equation, can thus be defined as the internal energy change per particle added under conditions of constant entropy and volume i.e.

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \qquad \textbf{Equation 12.2}$$

Chemical potential is a scalar quantity with SI units of joules. It is an intensive variable as the value is a property of the system at a particular pressure and entropy with the number of particles being its extensive conjugate (see section 13).

If a system contains a mixture of i different types of particle equation 12.1 is easily modified to give what known as the fundamental equation of thermodynamics

$$dU = TdS - PdV + \sum_i \mu_i dN_i \qquad \textbf{Equation 12.3}$$

where μ_i is the chemical potential of the ith particle type with a generalised definition of $\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j} i \neq j.$

12.1.2 Defining chemical potential by considering phase equilibria

Consider a one-component system in two distinct phases held in isolation (so the whole system is closed):
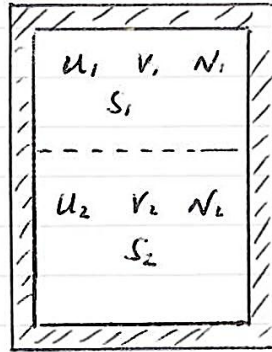

Figure 12.1 Two phases of a one-component system in isolation

This could be something as simple as ice in water for example.

Consider that the system is not in thermodynamic equilibrium and what must happen to it as it moves towards equilibrium. The four extensive variables for the whole system – internal energy, entropy, volume and number of particles – can all be the written as the sum of the variables for the two phases i.e.

$$U = U_1 + U_2$$

$$S = S_1 + S_2$$

$$V = V_1 + V_2$$

$$N = N_1 + N_2$$

As no work is done on the system, nor heat supplied the total internal energy of the system must be constant, as is the volume and the total number of particles. This means $dU_1 = -dU_2$, $dV_1 = -dV_2$ and $dN_1 = -dN_2$.

A similar thing cannot be said for the entropy: now consider the entropy <u>change</u> of the system which must occur when the system moves towards thermodynamic equilibrium. It can be written:

$$dS = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} dU_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2} dU_2$$

$$+ \left(\frac{\partial S_1}{\partial V_1}\right)_{U_1,N_1} dV_1 + \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2,N_2} dV_2$$

$$+ \left(\frac{\partial S_1}{\partial N_1}\right)_{V_1,U_1} dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right)_{V_2,U_2} dN_2$$

This has six independent variables, but these can be reduced to three by recognising that the drop in one gives the rise in the other so:

$$dS = \left[\left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2}\right] dU_1$$

$$+ \left[\left(\frac{\partial S_1}{\partial V_1}\right)_{U_1,N_1} - \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2,N_2}\right] dV_1$$

$$+ \left[\left(\frac{\partial S_1}{\partial N_1}\right)_{V_1,U_1} - \left(\frac{\partial S_2}{\partial N_2}\right)_{V_2,U_2}\right] dN_1$$

The second law tells us that entropy rises until a system reaches thermodynamic equilibrium, and when it has reached thermodynamic equilibrium the entropy is a maximum and it will remain in that state. i.e. at equilibrium, $dS = 0$.

So when the system under consideration is in equilibrium each of the parenthesised parts of the above expression must each be zero because internal energy, volume and particle number are independently variable.

The condition $\left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} = \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2}$ essentially means the two components are not exchanging any heat between each other i.e. they are in thermal equilibrium, or more simply phrased are at the same temperature. With fixed volume and particle number entropy changes mean temperature changes.

The condition $\left(\frac{\partial S_1}{\partial V_1}\right)_{U_1,N_1} = \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2,N_2}$ means the two components are not doing work on each other and thereby trading volumes i.e. they are in mechanical equilibrium, or simply phrased, the pressures are equal.

So this leaves the condition that $\left(\frac{\partial S_1}{\partial N_1}\right)_{V_1,U_1} = \left(\frac{\partial S_2}{\partial N_2}\right)_{V_2,U_2}$ which is that there is no trading of particles between the two phases. If the <u>chemical potential for each phase</u>, μ_i, is now <u>defined</u> by

$$\mu_i = -T_i \left(\frac{\partial S_i}{\partial N_i}\right)_{V_i,U_i} \qquad \textbf{Equation 12.4}$$

Then the condition for equilibrium becomes $\mu_1 = \mu_2$ which says that <u>in equilibrium the chemical potential of two phases is the same</u>.

Equivalence of the two definitions

The two ways of defining chemical potential are rather different but can quickly be shown to be equivalent mathematically. The change in entropy of the whole system under consideration can be written

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{V,U} dN$$

$$= \frac{1}{T} dU + \frac{1}{T} PdV - \frac{1}{T} \mu dN$$

which can be rearranged to give $dU = TdS - PdV + \mu dN$ which equation 12.1 as before.

12.1.3 Chemical potential and the free energies

Chemical potential has an important relationship with the Helmholtz and Gibbs free energies:

Helmholtz free energy

This is defined as $F = U - TS$ so $dF = dU - TdS - SdT$ which can now be more generally written $dF = -SdT - PdV + \mu dN$ which leads to the important

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} \qquad \textbf{Equation 12.5}$$

This gives a different interpretation of chemical potential as being the increase in Helmholtz free energy of a system when one particle is added at constant volume and temperature. Remember that Helmholtz free energy is a measure of how much work a system can do in a process that begins and ends at the same temperature. Some sources define chemical potential using equation 12.5.

Gibbs free energy

A similar procedure, and indeed a similar relation can be determined with use of Gibbs free energy, which is defined by $G = H - TS$ which leads to $dG = dU + PdV + VdP - TdS - SdT$ now has the general form $dG = -SdT + VdP + \mu dN$ which leads to

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} \qquad \textbf{Equation 12.6}$$

which provides another interpretation for chemical potential, along with a link between the free energies given by

$$\left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{P,T} \qquad \textbf{Equation 12.7}$$

Following equation 12.6, chemical potential can be thought of as the Gibbs free energy per particle. In fact this is the most oft-used form for chemical potential. Gibbs free energy per particle is given the symbol $\hat{g}$ and thus

$$\mu = \hat{g}(T, P) \qquad \textbf{Equation 12.8}$$

This formula is only true for a single component system, though the condition that two phases require $\mu_1 = \mu_2$ for equilibrium can now be written $\widehat{g_1}(T, P) = \widehat{g_2}(T, P)$.

This provides another way on interpreting the Gibbs free energy – it is a measure of the relative stability of a phase at constant temperature and pressure.

Specific Gibbs function

The Gibbs function is an extensive variable, but $\hat{g}$ is intensive with units of joules. Some texts deal with the quantity as per amount rather than per particle giving the quantity in units of joules per mole, or per mass in units of joules per kilogram. These, unfortunately, always tend to use only minor variants on the same symbol, g, so when using the quantity it should be clearly stated which version is being used. The saving grace is that the general physics remains the same no matter which version is used.

In the section 14 we will use the specific Gibbs function which is defined as the Gibbs function per unit mass, along with specific entropy, $s = \frac{S}{m}$ and specific volume, $v = \frac{V}{m}$ which is of course the reciprocal of density.

As, from section 10.1 $S = -\left(\frac{\partial G}{\partial T}\right)_P$ and $V = \left(\frac{\partial G}{\partial P}\right)_T$ these specific variables are related by $s = -\left(\frac{\partial g}{\partial T}\right)_P$ and $v = \left(\frac{\partial g}{\partial P}\right)_T$.

13. Generalised variables

This short section examines some general themes that arise from thermodynamics related to the work done and heat transferred in thermodynamic processes.

13.1 Generalised force and displacement

By definition, work done equals force multiplied by displacement. If an unbalanced force acts on a system then it causes a displacement to the system – the force "drives" the displacement and work is thus done on the system. The amount of work done is given by $\delta W = \boldsymbol{F}.d\boldsymbol{x}$ or for large displacements but the area under an force-displacement plot.

In this case, force is an intensive variable and displacement is an extensive variable.

Whatever is happening the system can be considered as a thermodynamics system that is striving to find some sort of mechanical equilibrium.

The generic concept can be applied to several systems we already know and beyond.

13.1.1 Mechanical system examples in one, two three dimensions

In $1D$: the stretched wire

In this case, using the symbols provided in this course, a tension causes a change in length of a wire and the amount of work done is given by $\delta W = J.dL$ for small displacements and the area under a tension-length graph for large amounts. Tension is the intensive variable and length is an extensive variable.

In $2D$: surface tension

The surface of a liquid essentially forms a $2D$ system. Whether the surface is simply to top of a liquid, or whether it is like a soap film stretched across a wire framework, the surface acts like an elastic membrane in a two-dimensional tension (often called a "surface pressure"). There are lots of fun experiments that can be done with surface tension, like "breaking" the membrane on the surface of water by adding a surfactant (basically this quickly reduces the surface tension) or noticing that soap films always minimise their potential energy by naturally finding the minimum surface area possible (hence soap bubbles are perfectly spherical).

Anyway, the magnitude of a liquid's surface tension, γ, is the force per unit length it exerts on the boundary it touches. Surface tensions act to pull boundaries together. When boundaries are free, the surface tension thus causes a change in area, and the work done is given by $\delta W = \gamma.dA$ for small area sweeps and the area

under surface tension-area graph for large amounts. Surface tension is the intensive variable and are is an extensive variable.

In $3D$: the gas in a cylinder

This doesn't really need reiterating other than to say the work done is $\delta W = -P.dV$ where the pressure drives the volume change, with pressure being the intensive variable and volume the extensive variable.

13.1.2 Non-mechanical system examples

The electrochemical cell

A simplified way of describing the energy pushed around a DC circuit is to say the cell provides an EMF which drives a charge around a circuit. The work done by the cell is given by $\delta W = \mathcal{E}.dQ$ or the area under an EMF-charge graph with the EMF being the intensive variable and charge the extensive variable.

Chemical reactions

This is essentially the subject of section 12. In a chemical reaction the chemical potential, μ, available, causes some amount of substance, N, to undergo a chemical change to another substance. The work done is given by $\delta W = \mu.dN$ with chemical potential as the intensive variable and the amount of substance as the extensive variable.

13.1.3 Heat transferred

This is, of course, given by $\delta Q = TdS$ and can be though of in the same way: the temperature difference drives the entropy change with temperature as an intensive variable and entropy the extensive variable.

μdN is an energy term with μ the generalised force which drives the change in N which is the generalised displacement. This energy term is distinct from TdS (heat flow) and PdV (mechanical work) and is sometimes called the reversible chemical work.

Temperature differences drive a flow of heat.

Pressure differences lead to mechanical work.

Chemical potential differences drive a flow of matter.

13.1.4 The generalised coordinates and conjugate variables

In all of these cases we say that the intensive variable is the <u>generalised force</u> and the extensive variable is the <u>generalised displacement</u>. Multiplying them together gives another extensive variable – the amount of work done on the system. And in every case the generalised forces drives the generalised displacement – something is unbalanced – i.e. not in thermodynamic equilibrium – and pushes in a direction so as to try and attain thermodynamic equilibrium.

Sometimes the two variables are referred to as <u>conjugate variables</u>. Note that this is a little different from the more general usage in physics (where two conjugate variables would usually be Fourier transforms of one another – this is not quite the case here).

14. Phase transitions

This section defines phases of matter and phase transitions in general before looking at the importance of the specific Gibbs function in development of the topic.

14.1 Phases of matter

A phase of matter is any distinct volume of space where the chemical and physical properties of the material within that volume are relatively uniform.

For the chemical properties of the material to be uniform the chemical composition of the material and the assembly of the atoms therein must also be uniform. Chemical uniformity doesn't imply uniform structure. The material could be a perfectly uniform crystal like quartz, or something amorphous and non-repeating like glass (both examples being essentially the same chemical – silicon dioxide – with the atoms ordered differently).
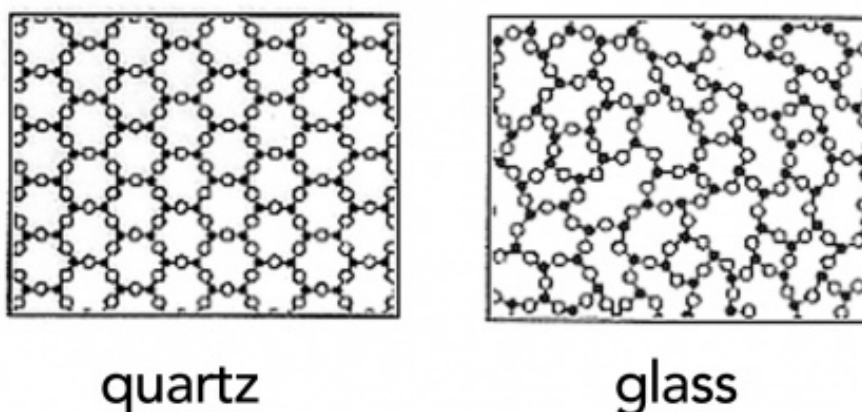
Figure 14.1 The crystal structures of quartz and glass as examples of regular and amorphous arrangements (image from http://www.cmog.org/article/what-is-glass)

The physical properties of the material refer to all the intrinsic physical properties the material can have. The list of these is endless but consider that these don't just include thermodynamic properties (like density, specific heat capacity, thermal conductivity and compressibility) but also properties than normally see their place in other branches of physics (like resistivity, refractive index, magnetic permeability and electric permittivity) and even properties that may not normally be associated with accurate measurements or rigorous definitions (like colour, smell or taste).

States of matter

The four well-known states of matter are, of course, solid, liquid, gas and plasma with the first three being the most abundant on Earth. The definitions of these states of matter are as they pretty much have always been: solids have a fixed volume and shape, liquids have a fixed volume but alter shape to fit the force field they're in, gases expand to fill a container and plasmas are essentially ionised gases.

There are many other exotic states of matter that exist under extreme conditions; you will meet many of these during your degree with Bose-Einstein condensates and Fermionic condensates featuring in Statistical Physics.

Notice that the definition of <u>phases</u> of matter is more general than the definition of <u>states</u> of matter. In fact states of matter are a subset of phases of matter. A system with distinct phases of matter would not necessarily have distinct states of matter. An example is a mixture of oil and water - the two are simply immiscible and separate into different phases.

Miscible materials and length scales

If two substances are miscible then they can form one phase even though on a small scale they will be discontinuous. Cold milk for example is a mixture of water with fat, proteins and vitamins that isn't a solution - the particles of these nutrients aren't dissolved - but a colloid where the particles remain in suspension indefinitely. These particles are typically a few microns (μm) in size - much larger than what we consider microscopic. Most rocks are single phase objects comprised of a large number of minerals (crystals that have a chemical formula of their own) thoroughly mixed and also separable on a micron scale.

Figure 14.2 A photograph of thin section of granite taken through a microscope. The scale is approximately 10:1. The picture shows differentiable crystals of minerals in the material. (Image from http://www.cas.usf.edu/~jryan/rocks.html)

The scales could be much larger still depending on the size of the system we are interested in. For example sections of the Earth's mantle can be considered to be of one phase despite having chunks of different

materials of several kilometres cubed spread throughout; on an astronomical scale one could even define galaxy clusters as being distinct phases.

Phase boundaries (one definition)

In any system where there exists more than one phase of matter there will be a phase boundary where one phase touches another. These tend to be sharp boundaries.

A gradual change from one point to another in a material would not count as a phase boundary. For example, consider a long iron bar with one end held at $100\ °C$ and the other at $0\ °C$. If people measured the physical properties of one end of the bar they would be a little different from the other end of the bar. This would be simply considered a gradual phase transition rather than a phase boundary.

14.2 Phase transitions

A phase transition is the transfer of any phase of matter to another without the introduction or removal of any material from the matter. The phase transitions is <u>always</u> accompanied by the transfer of heat (either into or out of the material) and <u>may</u> also see either work being done on the material or the material doing work on the surroundings.

Phase changes are always accompanied by a change in entropy and are isothermal process – even though the whole thermodynamic process may involve a net change in temperature of the material during the phase change process its temperature remains constant. The entropy change corresponds to a reordering of the atoms in the material – making them less ordered requires an input of heat and a making them less ordered involves an output of heat. As the temperature is constant during the transition process the entropy change is simple to calculate as $dS = \frac{\delta Q}{T}$.

By definition, when a material goes through a phase transition, its chemical properties and some of its physical properties must change.

The most well-known phase transitions are between solids, liquids and gases. These are the ones we will use for most of our development of thermodynamic ideas though they are nearly always general to all phase changes.

14.2.1 Latent heat of fusion

Imagine heating a solid with a constant surrounding external pressure. When heat is transferred into a solid the temperature rises according to the rate at which heat is supplied and the heat capacity of the solid. Eventually the solid reaches its melting point. Heat continues to be transferred to the melting solid but its temperature doesn't rise during the process. Because the temperature doesn't rise the heat added during

this time is known as <u>latent heat</u> (from the Latin for "hidden"). One the solid has fully melted, the resulting liquid's temperature rises once more if heat continues to be transferred (at a different rate as the heat capacity has altered).

The latent heat of fusion of a solid object is the amount of heat required to fully transfer it from the solid phase to the liquid phase when at its melting point.

The <u>specific latent heat of fusion</u> of a material is an intensive variable and it defined and the latent heat of fusion per unit mass of the material:

$$L_f = \frac{\delta Q_{melting}}{m} \qquad \text{Equation 14.1}$$

Values of specific latent heats of fusion are typically of the order of tens or hundreds of $kJkg^{-1}$ with water having a particularly high latent heat of fusion at atmospheric pressure of ~ 330 $kJkg^{-1}$.

It is useful to also define a specific entropy of fusion which is the entropy released during melting per unit mass and is thus given by

$$s_f = \frac{L_f}{T} \qquad \text{Equation 14.2}$$

where T is the melting point of the material. Water has a specific entropy of fusion of ~ 1.2 $kJkg^{-1}K^{-1}$.

It should be pointed out that molar version of equations 14.1 and 14.2 of course exist and in fact are the most widely used forms.

14.2.2 Latent heat of condensation

Continue heating the liquid and it will eventually reach its boiling point. A similar process occurs during the phase change when heat is transferred and no change in temperature occurs until the liquid has completely reached the gas phase.

By extension of the definition for the melting process the latent heat of vaporisation of a liquid is the heat required to turn it from the liquid phase to the gas phase when at its boiling point. Note that this will usually be larger than the amount of heat supplied for the melting process: in the transfer from solid to liquid the atoms' mean separation has only increased a little, but in the liquid to gas transfer the separation has increased many times more. This requires a greater input of energy to fully break the bonds between the atoms.

Specific latent heat of vaporisation is latent heat of vaporisation per unit mass

$$L_v = \frac{\delta Q_{boiling}}{m} \qquad \text{Equation 14.3}$$

Values of specific latent heats of vaporisation are typically of the order of hundreds or thousands of $kJkg^{-1}$ with water again having a particularly high value at atmospheric pressure of ~ 2.2 $MJkg^{-1}$.

Again, it is useful to also define a specific entropy of vaporisation which is the entropy released during vaporisation per unit mass and is thus given by

$$s_v = \frac{L_v}{T} \qquad \textbf{Equation 14.4}$$

where T is the boiling point of the material. Water has a specific entropy of vaporisation of ~ 5.9 $kJkg^{-1}K^{-1}$.

Trouton's rule

One interesting empirical rule of thumb is that when using the molar version of the quantity they are roughly the same for most liquids (but not water which is really an extremely unusual liquid). The value is approximately 90 $kJmol^{-1}K^{-1}$.

14.3 Phase diagrams

A phase diagram, or PT diagram, is a pressure vs. temperature chart for a substance showing which phases can exist at equilibrium. They are essential tools when considering how a material behaves when heat and work are applied to a system containing the material.

The basic $2D$ phase diagram

A "normal" material has a phase diagram of this form:
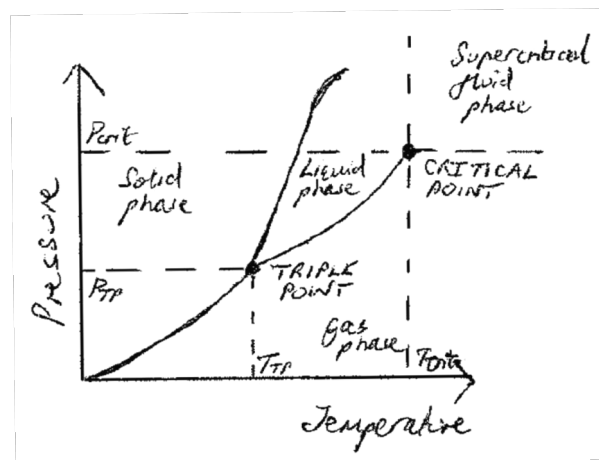

Figure 14.3 A generic phase diagram for a typical material

This simplified picture shows the <u>equilibrium lines</u> or <u>phase boundaries</u> (the other definition – notice it is quite different!). If the material were subjected to a certain external pressure and temperature the corresponding point on the phase diagram specifies the phase of matter it would be in when in thermodynamic equilibrium. If the pressure and temperature lie on one of the phase boundaries then both phases will coexist in thermodynamic equilibrium. If a material is subject to a process which makes it pass through a phase change then it is always accompanied by a transfer of heat and an entropy change.

14.4 PT diagrams

To fully understand the nature of the phase change(s) of a material it is actually better to consider a <u>PVT surface</u> for a material. Such diagrams can then be used to look at PV, TV and PT diagrams for a phase change. A PVT surface and the related PVT diagrams for a generic material that always expands on heating are shown below. All these figures are taken from <u>http://sounak4u.weebly.com/properties-of-pure-substance.html</u>.
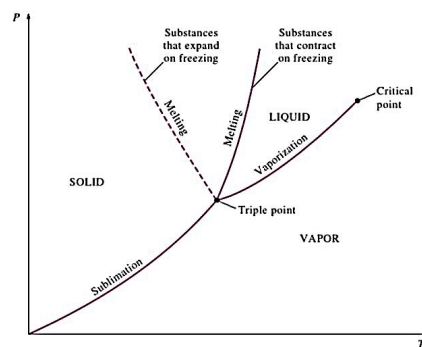

Figure 14.4a A general PT diagram showing the curves for substance that both contract and expand on freezing
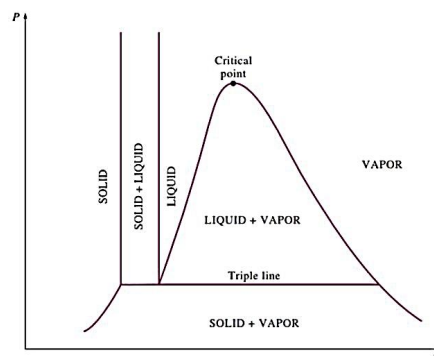

Figure 14.4b A general PV diagram for a pure substance. The PV diagrams that we have previously used for gases still apply provided the isotherms remain beyond the top right section of the figure for a given material.
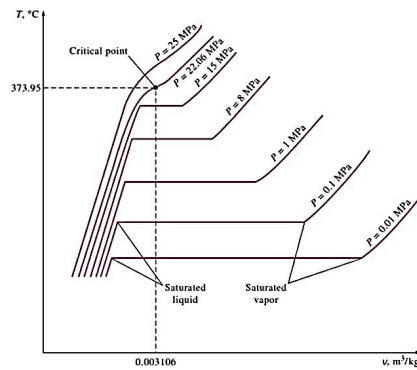
Figure 14.4c A general TV diagram for a pure substance showing various isobars
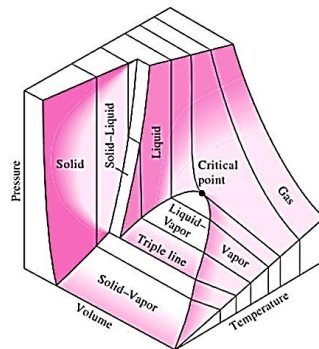

Figure 14.4d The PVT surface for a given substance is a complicated figure but does, in principal, allow all information from the other three plots to be obtained

A reversible phase transition is one which stays on the PVT surface and most everyday phase transitions do this.

Consider an idealised phase transition from gas to liquid by reducing temperature at fixed pressure (e.g. what would happen to water vapour at $1\,\text{atm}$ when the temperature is lowered from above to below $100\,°\text{C}$.) To do this reversibly the gas is cooled very gradually and remains on the PVT surface. The projection of the path is as shown on the simplified figures below:
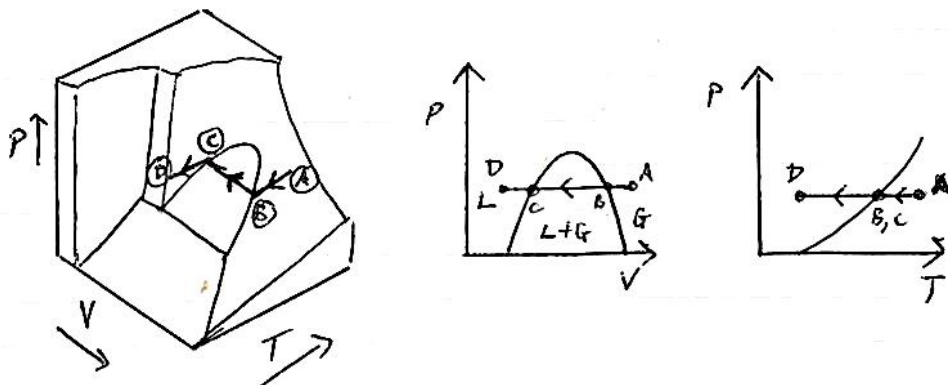

Figure 14.5 A gas to liquid phase transition at constant pressure

The steps are as follows:

From $A \rightarrow B$ the system is in a single gaseous phase and heat moves from out of the system to the outside world. $\delta Q = C_P dT$ with a fall in both temperature and volume.

From $B \rightarrow C$ to phases can coexist in equilibrium. Heat flows out of the system but $\delta Q = L dm$. The volume falls as gas condenses to liquid but the temperature stays constant.

From $C \rightarrow D$ the system is in a single liquid phase and heat moves from out of the system to the outside world. $\delta Q = C_P dT$ with a fall in both temperature and volume again.

14.4.1 First order phase changes

During a phase transition heat flows in or out and changes the relative proportions of the two phases. The constant pressure specific heat during the change is effectively infinity as the heat supplied causes no temperature change.

And during a phase change the specific volumes of specific entropies of the two phases differ but the specific Gibbs functions are the same by definition i.e. during any phase change from a state $1 \rightarrow 2$:

- $v_1 \neq v_2$
- $s_1 \neq s_2$
- $g_1 = g_2$

We also know that $s = -\left(\frac{\partial g}{\partial T}\right)_P$ and $v = \left(\frac{\partial g}{\partial P}\right)_T$ and these are therefore discontinuous functions during a phase change.

The behaviour of materials when going through liquid/gas, solid/liquid and solid/gas transitions can be represented by the following figures:
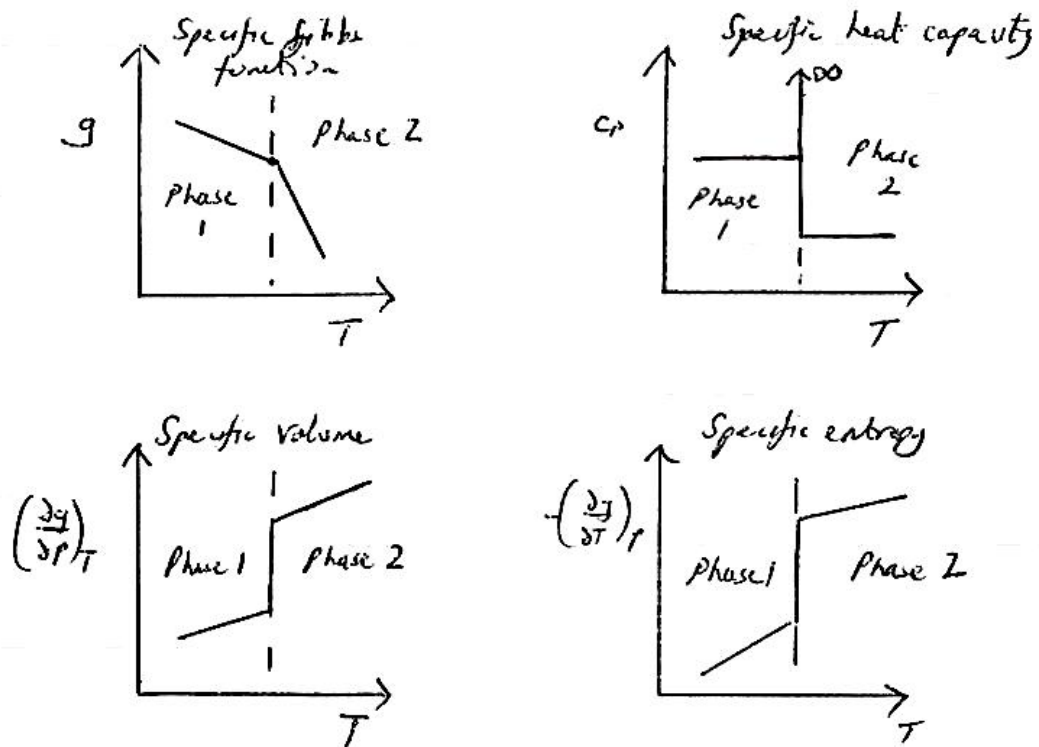
Figure 14.6 Generic plots for various variables in a first order phase transition

There are also such things as second order phase transitions. These involve continuous first derivatives of g but discontinuous second derivatives. Such phase changes occur at the onset of superconductivity for example. These will be covered in the Advanced Statistical Physics option in year 3.

15. The Clausius-Clapeyron relation

The Clausius-Clapeyron relation is a way of studying the relation between two different phases of matter by referral to their PT diagram.

15.1 The Clausius-Clapeyron relation

The Clausius-Clapeyron relation describes the slope of a PT diagram along a phase boundary. Consider a small section of this boundary:
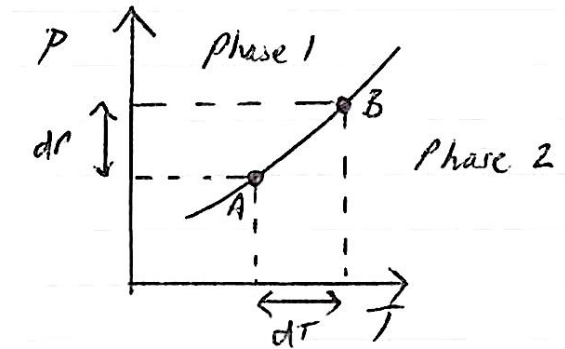
Figure 15.1 A small section of a generic PT phase boundary

If A and B are two points on the phase boundary and $g_{1 \, or \, 2}^{A \, or \, B}$ is the specific Gibbs function corresponding to the relevant phase and point then by writing $g = g(T, P)$ and using the normal procedure $dg = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP = -sdT + vdP$.

This gives

$$dg_1 = g_1^B - g_1^A = -s_1 dT + v_1 dP$$

and

$$dg_2 = g_2^B - g_2^A = -s_2 dT + v_2 dP.$$

And so

$$g_1^B = g_1^A - s_1 dT + v_1 dP$$

and

$$g_2^B = g_2^A - s_2 dT + v_2 dP.$$

Subtracting these two equations gives $\left(g_2^B - g_1^B\right) = \left(g_2^A - g_1^A\right) - (s_2 - s_1)dT + (v_2 - v_1)dP$.

But by definition $g_2^B = g_1^B$ and $g_2^A = g_1^A$ which gives the Clausius-Clapeyron equation in one of its forms:

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} \qquad \textbf{Equation 15.1}$$

and as specific entropy is also specific latent heat per unit temperature (equation 5.2) this can also be written

$$\frac{dP}{dT} = \frac{L}{T\Delta v} \qquad \textbf{Equation 15.2}$$

These are well-used equations for any phase change process.

15.2 Applications and examples

Examples

1. Pressure dependence of melting point

   If we want to consider this for ice for example then we need the latent heat of fusion of water, which is 3.35×10^5 Jkg^{-1} and the specific volumes of water in the solid and the liquid phase. These can be looked up (as the reciprocal of the density) as $v_{solid} = 1.09070$ cm^{3}g^{-1} and $v_{liquid} = 1.00013$ cm^{3}g^{-1}. This gives $\Delta v = -0.0906 \times 10^{-3}$ m^{3}kg^{-1} and thus $\frac{dP}{dT} = \frac{3.35 \times 10^5}{273 \times -0.0906 \times 10^{-3}} = -1.35 \times 10^7$ PaK$^{-1} \cong -134$ atmK^{-1}.

   This means a pressure increase on ice of -134 atm lowers the melting point by one degree. Such a value is well verified by experiment. This goes some way to explaining the movement of glaciers and ice skating.

2. Pressure dependence of boiling point

   In this case the latent heat of vaporisation is needed, 2.257×10^6 Jkg^{-1}, and the specific volumes at the boiling point are $v_{liquid} = 1.043$ cm^{3}g^{-1} and $v_{gas} = 1{,}673$ cm^{3}g^{-1}. The Clausius-Clapeyron equation gives $\frac{dP}{dT} = \frac{2.257 \times 10^6}{373 \times 1.672} = 3{,}620$ PaK$^{-1} \cong 0.036$ atmK^{-1}.

   This means a pressure drop from normal atmospheric pressure to 0.36 atm (approximately that on the top of Mount Everest) causes a fall in boiling point of $\frac{\Delta P}{0.036} = \frac{1-0.36}{0.36} = 18$ K so water boils at about $82\,°C$ and, as rumoured, you would not be able to make a proper cup of tea.

16. The third law of thermodynamics

The third law is different from the first three for three principal reasons. Firstly, it does not introduce a new and fundamental state variable. Secondly, arguably as a direct result of the first point, it is a lot less helpful in our development of general understanding of thermodynamic systems. And thirdly it becomes inherently a quantum problem which can only be investigated in real detail with the use of quantum mechanics and statistical physics. That said, there is a place for the law in a course that deals almost exclusively with macroscopic thermodynamics and inclusion of the topic in the segue to statistical physics is appropriate.

16.1 Various statements of the third law

The most basic two statements are:

> It is impossible to reach absolute zero in a finite number of steps.

which can be thought of as a simple macroscopic version of the law, and

> The entropy of a perfect crystal is zero at absolute zero.

which can be thought of as a simple microscopic version of the law; sometimes it is phrased by saying the entropy tends to zero as the temperature tends to zero. This is sometimes known as the Planck statement of the third law.

Planck's statement followed from a statement by Nernst which is similar but more complicated:

> The entropy change in a process between two equilibrium states associated with a change in external parameters tends to zero as the temperature approaches absolute zero.

Sometimes the Nernst statement is given as the most fundamental way of stating the third law but really Planck's statement is more powerful and general - the Nernst statement can be derived from it but not vice versa.

There is also a subtle, less well-known, and, now, old-fashioned, way of expressing the third law developed by Simon (and usually bears his name). Simon refers to certain parts of a system as "aspects" where aspects are things like the electron orbital states, the states of energy of the nucleus and the various types of kinetic energy (rotational, translational, vibrational) of a system. His work on low temperature physics hinted that at low temperatures the aspects of a system became uncoupled i.e. they all operate independently. This is even more strongly believed to be the case today. The Simon statement is

> The contribution to the entropy of a system from each aspect when in thermodynamic equilibrium disappears for each aspect at absolute zero

and is useful when analysing a system in terms of its various aspects at low temperatures.

Regardless of the statement the third law is a well-verified law of physics and no repeated experiment has ever been conducted that refutes it.

16.2 The meaning of absolute zero

All statements of the third law focus around the absolute zero of temperature so it is worth including a few words on it. Of course it is a lower bound of the temperature achievable of a system with $0\,\text{K} \equiv -273.15\,°\text{C}$ and this is well verified by experiment; temperatures of just a fraction of a kelvin are now possible in laboratories but it gets progressively more difficult to get to ever lower temperatures.

The understanding of absolute zero is inherently quantum. This can be seen by considering the entropy of an ideal gas: going from $dU = TdS - PdV$ so $dS = \frac{1}{T}(dU + PdV)$ with $dU = \frac{n_d}{2}Nk_B dT$ leads to the entropy for an ideal gas as $S = S_0 + \frac{n_d}{2}Nk_B \ln T + Nk_B \ln V$. This equation suggests as $T \to 0$ then $S \to -\infty$ which is inconsistent with experiment.

Isotherms on PV and TS diagrams would also be unusual and impossible features at absolute zero with the PV isotherms going along the axes and the TS adiabat simply being the horizontal line at $T = 0$.

We have also mentioned absolute zero in the context of the Carnot cycle as being the temperature of the cold reservoir that could give a theoretical maximum efficiency of unity; this involves the cold isotherm-adiabat stage of the cycle hugging the axes as mentioned above.

Quantum mechanics is essential to understand the behaviour of materials at low temperatures and this will be broached in many core and optional lecture courses at Imperial. We won't say much more about this now other than to comment that (as have met in quantum mechanics) that even at absolute zero the atoms of a material still possess quantum mechanical zero point energy i.e. the kinetic energy at this point is <u>not</u> zero.

It is also worth remembering that properties of materials either become exactly zero at absolute zero (e.g. heat capacity) or become independent of temperature at absolute zero (e.g. density).

16.3 The unattainability of absolute zero

We can show that the macroscopic version of the third law is consistent with the microscopic version by means of a thought experiment. Consider any state variable of a closed system other than temperature or entropy. Let's say the state variable has symbol λ (chosen simply because it is not similar to any others we have seen in the course - it could be any of the ones we have met or any new one that we haven't) and we have closed system in a state denoted by T_A, S_A, λ_A. Now consider cooling the substance in way which keeps the state variable λ constant. As the temperature drops the entropy also drops and, eventually, provided

the contents of the system form perfect crystals the iso-line for the state variable will meet the origin according to the third law.

Now let's say the system starts in different initial state T_B, S_B, λ_B and is again cooled under conditions of constant λ. Once again the iso-line sees both temperature and entropy falling until it meets the origin.

A completely general picture of the lines of constant λ is shown below:
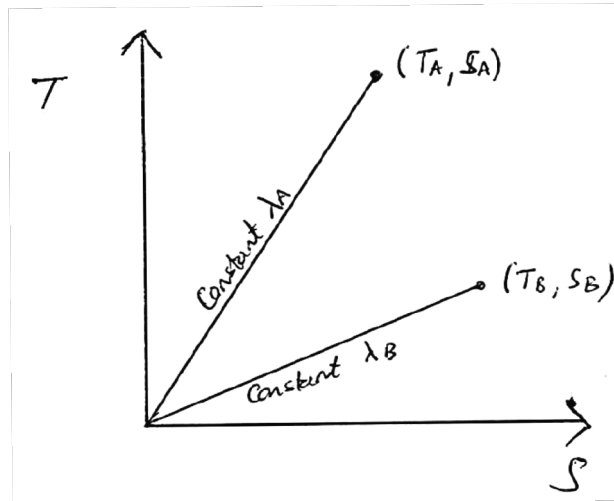

Figure 16.1 Lines of constant generic state variable for a cooling process for two different starting values of the state variable. In the absence of further information the iso-lines are drawn as straight lines for simplicity; in general they will be monotonically increasing curves of some kind.

The third law tell us that regardless of the value of the state variable λ all lines of constant λ must converge and meet uniquely at the origin - the point of zero entropy and an absolute zero of temperature.

The next point to recognise is that no state variable can touch the T or S axis: for substances that form crystals no state variable has a meaningful value at $(T > 0, S = 0)$ or $(T = 0, S > 0)$. What this means is that, using the simplified straight line examples, the gradient of the upper line can never be infinite and the gradient of the lower one can never be zero.

Now to the practicalities of cooling. By the second law is a substance if ever colder than its surroundings then heat flow from outside will warm the system. A direct cooling step that avoids this is the adiabatic expansion. If we start from point A an adiabatic expansion eventually reaches a value of the state variable λ_B.

As the substance will always have a defined value for the state variable, which cannot be defined at $T = 0$, the expansion can simply get to absolute zero and must finish at some new value of λ which we can call λ_B. The substance can be cooled again, by going through another adiabatic expansion, but to do so needs to achieve a state where it can be compressed back to λ_B. It should do this without gaining temperature so needs to go through an isothermal compression:
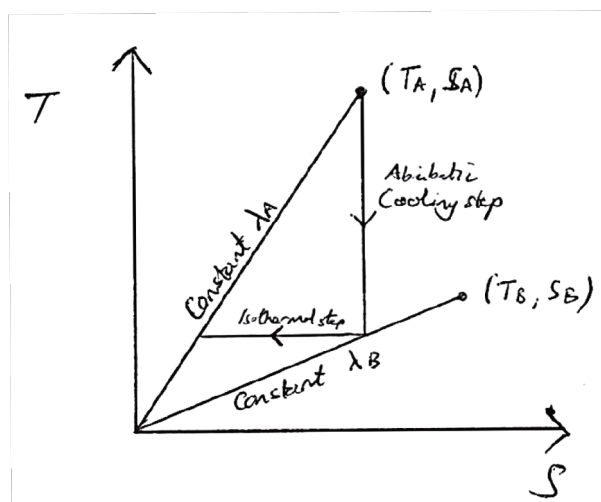
Figure 18.2 An isothermal step to bring the substance back to its original state variable value.

The substance can then go through an adiabatic expansion again, followed by an isothermal compression, and then again, and then again:
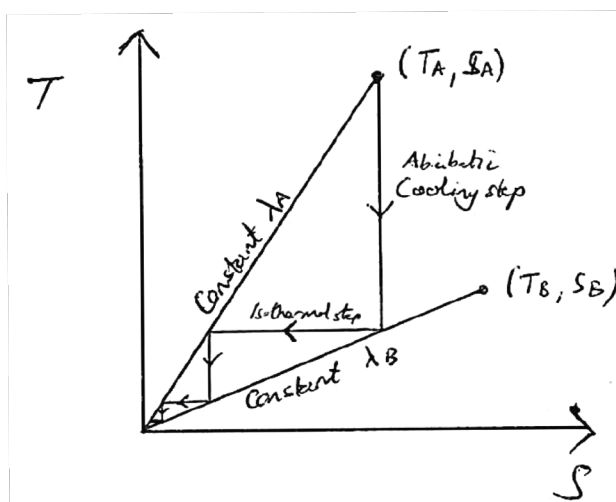

Figure 18.3 A series of adiabatic and isothermal steps to get closer to absolute zero.

In principle we merely need to carry on this process many times do get to absolute zero.

The central point of the macroscopic version of the third law is that "many times" is actually infinity - regardless of the shapes of the curves that define the lines of constant λ a series of adiabats and isotherms would get closer and closer to the origin but never quite reach there.

If the substance were does form perfect crystal but instead formed an amorphous solid (like glass) with no atomic repeat unit then absolute zero does not correspond to zero entropy but the same argument still applies except the meeting point of the isolines is at some value $(T = 0, S = S_0)$ i.e. offset along the entropy axis. The infinite steps idea still applies provided the iso-lines do not have gradients of zero or infinity and meet at a single point at zero kelvin.

16.4 The Nernst heat theorem

Enthalpy is defined as $H = U + PV$ from which $dH = TdS + VdP$ follows and it provides a measure of the amount of heat that is liberated <u>overall</u> in a process. (It does not say whether a reaction will occur spontaneously so, for example, when a match burns the enthalpy change is highly negative i.e. energy is liberated which is useful to know but enthalpy alone doesn't inform anyone that an initial push is needed.)

Gibbs free energy is defined as $G = H - TS$ from which $dG = -SdT + VdP$ follows and it provides a measure of whether a process will run spontaneously. We can also write $dG = dH - TdS - SdT$.

The chemist Walter Nernst, working in the early 20th century, noticed that the difference between dG and dH decreased for decreasing temperature and hypothesised that the two quantities approached each other asymptotically as the temperature approached absolute zero:
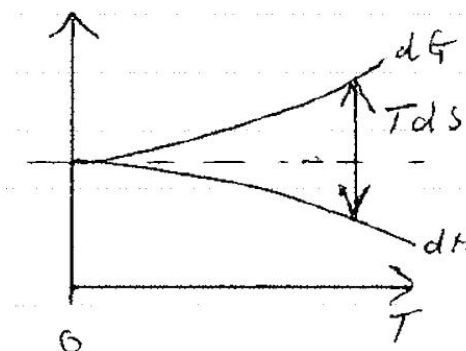

Figure 16.4 $dG - dH$ as temperature approaches absolute zero as follows Nernst's hypothesis

For a constant temperature transition, $dG - dH = TdS$ so in the limit that $T \to 0$, $dG \to dH$ as was Nernst's assertion.

Nernst's hypothesis was well verified by experiment and for a while was known as the definitive version of the third law.

Furthermore, we know $S = -\left(\frac{\partial G}{\partial T}\right)_P$ (section 10.1) and can therefore write an expression for the small <u>change</u> in entropy as $dS = -\left(\frac{\partial (dG)}{\partial T}\right)_P$ (which might look a bit odd; most texts use a capital Δ which looks nicer but we stick with d for the small change for consistency). The negative of the slope of the curve is the entropy change and as the slope becomes zero, the entropy change becomes zero at absolute zero as well.

This means chemical reactions at absolute zero take place with no change in entropy.

16.5 Some consequences of the third law

Heat capacity at absolute zero

The heat capacity of objects becomes zero at absolute zero. This follows from the end of the previous section; $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ and as the enthalpy curve is shown empirically to tend to zero so must the heat capacity.

Also consider that $\Delta S = \int_0^T \frac{C_V}{T} dT$. For the left hand side of the equation to remain finite down to absolute zero the heat capacity itself must also tend to zero to avoid a singularity.

Expansion coefficients

Take the Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$. As $S \to 0$ when $T \to 0$ the left hand side of the equation becomes zero for all values of pressure and thus $\lim_{T \to 0} \left(\frac{\partial V}{\partial T}\right)_P = 0$. This effectively means the coefficient of thermal expansion is zero at absolute zero for all substances.

The Clapeyron curve

Equation 15.1 tells us the slope of the Clapeyron curve for a first order phase transition is $\frac{dP}{dT} = \frac{\Delta s}{\Delta v}$ which implies the slope becomes zero at absolute zero i.e. the temperature of the phase transition never changes much for a substance until it is clearly above absolute zero.

17. The arrow of time

This section looks at how entropy change and the direction of progression of time are linked by the second law of thermodynamics.

17.1 Degradation of energy

Consider an ideal gas of initial volume V_i and temperature T that goes through an expansion process whereby it finishes with volume V_f and the same temperature. There are infinite ways in which this process can happen as the gas need only start and finish with the same uniform temperature. Consider the two thermodynamic extremes: an isothermal expansion and an adiabatic free expansion.

An isothermal expansion involves the gas being in contact with a reservoir at temperature T and is reversible. All the heat that is put in to the gas is used to expand against the environment. The heat supplied equals the work done and is equal to $Nk_BT \ln\frac{V_f}{V_i}$. The entropy change of the reservoir is $\Delta S_{reservoir} = -Nk_B \ln\frac{V_f}{V_i}$, the entropy change of the gas is $\Delta S_{gas} = +Nk_B \ln\frac{V_f}{V_i}$ and the total entropy change of the universe is zero i.e. $\Delta S_{total} = 0$. The work done by the gas could be put to any kind of use (like generating electricity or moving a vehicle).

The adiabatic free expansion involves the gas expanding into a vacuum – it does no work at all. In this case the entropy change of the gas is still $\Delta S_{gas} = +Nk_B \ln\frac{V_f}{V_i}$ but now there is no corresponding drop in entropy of another object so $\Delta S_{total} = +Nk_B \ln\frac{V_f}{V_i} > 0$.

In going from $V_i \rightarrow V_f$ we had the opportunity to extract a useful amount of work from the system. In the reversible process we did so, but in the irreversible process we wasted the opportunity forever.

This illustrates a general point – in an irreversible process energy is conserved but it is also <u>degraded</u> i.e. there is less energy available for useful work. The total entropy change in a process gives the extent of the degradation.

17.2 Heat death of the Universe

As all real processes are irreversible, entropy always increases and the amount of energy available for useful work is irretrievably reduced. This is universally true, and, as far as we know, always has been and as best we can guess always will be.

In the 19th century Lord Kelvin posited the notion of the heat death of the Universe which can essentially be phrased in several different ways that all ultimately mean the same thing:

The total entropy of the Universe is always increasing and will continue to do so until it reaches a maximum value.

The Universe is continually moving towards a state of thermodynamic equilibrium and will continue to do so until thermodynamic equilibrium is completely attained.

The thermodynamic free energy available from the Universe to do useful work is decreasing and will continue to do so until it is reduced to zero.

Note that heat death doesn't actually imply a very cold temperature, or, indeed, any temperature at all.

A rather grim prospect! But as with all of thermodynamics the time scale for the heat death is not specified and really we have nothing to worry about for now. One estimate for the time until certain heat death is of the order of 10^{100} **years**. Furthermore, *en route* to thermodynamic equilibrium ordered structures are often created as by products, life itself being one such by-product.

It is also worth pointing out that though Kelvin's hypothesis is correct, as far as we can ascertain, the Universe is much more interesting than Kelvin could have known. He would not have known anything about the Big Bang, inflation, black holes and general relativity and thus his understanding of cosmology would have been extremely naïve compared to today's scientists'. Modern cosmology is, in fact, one of the most interesting areas of research into thermodynamics today with the nature of black holes being one particularly exciting topic. Of course to make proper headway into the investigation of such structures a good understanding of general relativity is necessary.

What our current level of thermodynamics does tell us though is that if there is such a thing as a Big Crunch, the Universe will look a lot different as it heads towards collapse than it did when expanding – the Universe started in a state of low entropy and high order and will end in a state of high entropy and low order. This essentially means material will be clumped together more and more with time in black holes with the final crunch essentially being one black hole singularity (according to some theories).

17.3 The arrow of time

Temperature is difficult to define but we all have an intuitive idea of what it is. The same also applies to entropy: watch any video of an irreversible process run backwards and it is always clear that the video is running backwards. They always look odd and may be funny or eerie. The only law of physics that is broken during the backwards-run video is the second law of thermodynamics – when we see entropy decreasing in a process we know it isn't right.

So the change in entropy of a system tells us which direction time is going in. The second law of thermodynamics is almost unique in that, apart from certain rare subatomic particle interactions involving the weak nuclear force, it is the only law we know of in physics that isn't time reversible. Newton's laws,

Maxwell's equations, energy conservation, relativistic problems and the Schrodinger equations all work just as well with $-t$ as $+t$ in the equations.

An ideal clock would be a frictionless oscillator with a perfectly regular period of oscillation – this would only be ideal for time going forwards however, if one wanted a clock that also measured the direction time were progressing as well some friction would have to be deliberately introduced into the system! An entropy clock is a device that simply measures the direction of time progression; the British astrophysicist Sir Arthur Eddington actually suggested that human brains have a built in entropy clock.

Of course the law is a statistical law in the sense that for example, when we stir milk in our coffee there is a possibility that the all the molecules could rearrange themselves back into the unstirred state but these probabilities are so low that the time one would have to wait to see such spontaneous processes occurring is way beyond anything that humankind could ever observe so the law is as valid as any other within the discipline. As always the acid test of the theory is experiment and it is absolute fact that no-one has ever performed an experiment that contradicts the second law of thermodynamics.

So rather than say entropy increases with time we could say that time moves in the direction of increasing entropy. As to which is the more fundamental quantity is one of the greatest unsolved questions in the whole of physics.

Modern quantum mechanics does suggest that the phenomenon of quantum entanglement and wave function collapse are the root causes of the arrow of time as on a quantum level all processes lead to greater correlations within systems and the wave function collapse itself is a time irreversible process that results from the observation of a system.

17.4 Maxwell's demon

There are many thought experiments that attempt to explain how the second law could be broken and we finish this section by looking at the most famous, with a quantitative explanation of its resolution.

Consider a box with a moveable partition with equal amounts of an ideal gas on each side of the partition, with the gas at some initial temperature, T, throughout. Now imagine a clever homunculus – Maxwell's demon - standing on the box with control over the partition. They are able to observe the molecules of the gas and open the partition when the want a molecule to pass and close it when the want a molecule to stay where it is.
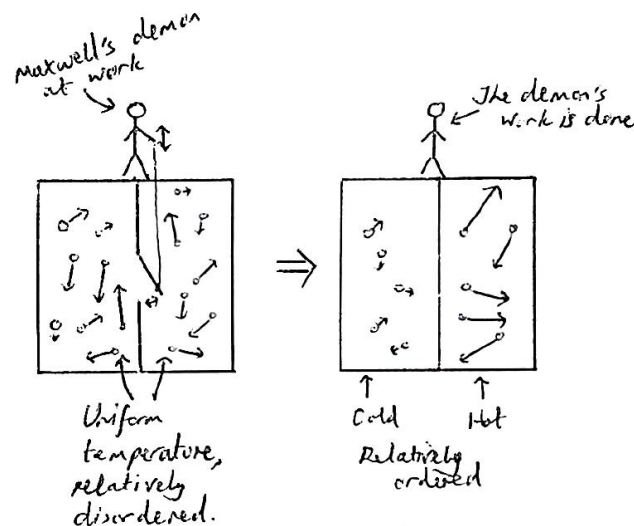
Figure 17.1 Maxwell's demon in action

Imagine the demon only permits slow moving molecules pass from right to left and only lets fast moving molecules move from left to right. Eventually the demon will render the left hand side a full of cold, slow molecules and the right hand side full of fast, hot molecules and will have increased the order of the system i.e. decreased its entropy.

There is nothing wrong with this thought experiment – it could happen, in principle, (with some kind of machine that measured molecules' speeds rather than a creature of course) and this would indeed decrease the entropy of the gas. This is put forward as an argument that the second law of thermodynamics can be violated.

The resolution to the problem is simple – the entropy of the demon needs to be considered. The whole system includes the demon and it is the entropy of the whole system that needs to be discussed. Essentially to make any action that takes a step towards decreasing entropy involves (a) a measurement of some kind by the demon (molecule speed and direction) and (b) an action (raising and lowering the partition) and both of these irreversible actions cause the demon's entropy to rise more than the corresponding decrease of the gas's entropy.

Of course this is qualitative answer – to begin to make it quantitative one would need exact details on how the demon operates the system and then calculation may be permissible.

In reality the resolution is rather straightforward and doesn't add much to our understanding of physics but asides from being a historically interesting "paradox" it does give another insight into another type of entropy that you may want to investigate – information entropy. One way of looking at the problem discusses the idea that the demon receives and uses information and the entropy of this information increases with time.

18. More on entropy and moving on

This section provides a final look at entropy, closing off some potential loose ends and deliberately introducing some others. It also provides a few comments (mainly contained within the lecture itself) on exam technique.

18.1 Answering a classic question

In the 2016 exam one 5 mark question read:

"The Sun causes icebergs to melt thereby increasing their entropy but causes plants to grows thereby decreasing their entropy. Write short notes to help resolve this apparent contradiction."

The questions was poorly answered. Many candidates only wrote about the entropy change when a plant grows (which is the most difficult part) and didn't mention the iceberg at all. One in five candidates stated that the entropy of the whole system increased because the entropy increase of the iceberg more than offset the entropy decrease of the plant! And one in 20 candidates said that while the entropy of the plant decreased now, when it later died and decomposed this would all be offset so entropy increased after all. Ugh!

This is one of those questions that any physicist should be able to answer. Not because it is more or less important than some other questions but it is the kind of question that one gets asked in the pub by naysayers that like to pick flaws in the discipline. It is always fun to have arguments about such things but it is good to be clear on those answers which are unequivocal.

Hopefully you can see the issues in the non-local argument that the iceberg's entropy change offsets the plant's and the non-causal argument that the plant's entropy rockets when it dies.

18.2 Entropy and life

Having said all that the nature of entropy and life is a big topic and is fascinating. I can strongly recommend Erwin Schrödinger's short book "What is Life" which contains deep musings on the nature of life, order, disorder, crystalline structures, the nature of DNA (before the discovery of the double helix), entropy, free will and consciousness.

Life is remarkable in that it is does reduce internal entropy at the expense of its surroundings. While not explicitly stated as one of the seven characteristics of life at school several of them do incorporate this fact. Indeed it has been pointed out that in the search for extraterrestrial life we should perhaps look for examples of localised reductions of entropy in the Universe.

Schrodinger even went as far as to propose that living organisms decrease their entropy by feeding on negative entropy. He later rescinded the idea in an updated version of the text but the idea of negative entropy in connection with living organisms and in some other non-physics applications still sees some use.

18.3 Entropy and thermodynamic beta

This will be covered in the Statistical Mechanics course but one equation that arises when considering temperature and entropy from a microscopic point of view is $\beta = \frac{1}{k_B T} = \frac{1}{k_B}\left(\frac{\partial S}{\partial U}\right)_{V,N}$. The equation directly relates temperature, entropy and energy in a way which we have not seen before now. Essentially it defines temperature in terms of energy and entropy going beyond Definition 4 of section 2.1.1. One interesting property of temperature that arises from this definition is that certain system can have a negative temperature on the Kelvin scale if the rate of change of entropy with energy of the system is negative.

18.4 Entropic forces

Temperature differences drive a change in entropy but it is also a law of nature that entropy always increases as time progresses. One way of thinking about systems is to posit that the entropy is the driving force and the development of system follow as a result of the entropy increase.

18.5 How far we've come

We have a covered a huge amount really. All three (or four if you include the zeroth) laws of thermodynamics have been covered in some detail. The first law has been covered in more depth than ever before by use of the concept of entropy which was not formally met before these lectures. This should also have assisted in bolstering understanding in the nature of forces, work and energy. The limits of the amount of useful energy that can be extracted from systems has been clarified and from this classifications in the types of energies systems can have has been seen with the thermodynamic potentials. The Maxwell relations have empowered us with the ability to analyse systems and solve classes of problems that we have not seen before. Discussion of the third law has even seen our perception of the fundamental and universal quantity of time be viewed from a different perspective.

But this is really just a beginning of sorts. Your knowledge and understanding of the topic can and will continue to develop during this degree and beyond.

18.6 Development of thermodynamics in the core degree course

The big one that follows on from this is in Statistical Physics which provides a microscopic view of the world and suggests how the laws of thermodynamics follow from a statistical understanding of the components of matter.

Later in the second year the Nuclear part of Nuclear and Particle Physics looks at energy release in nuclear process and moves towards an understanding of the thermodynamics of stars. And Solid State essentially provides the framework for how solid material behave as a result of their constituent atoms including regards for energy transformation and thermal properties.

The third year goes further by bringing in the nature of how electromagnetic radiation reacts with materials and with itself in the Light and Matter course. The Physics of the Universe course provides a small amount of material on the thermodynamics of the Universe as a whole.

18.7 Development on thermodynamics in degree course options

Many of the optional course will develop concepts in thermodynamics, mainly in applied settings but occasionally giving some extra depth to the subjects. Applications are covered in Environmental Physics and Suns, Stars & Planets in year 2, then Astrophysics, Plasma Physics, Principles of Instrumentation in year 3 and Advanced Hydrodynamics, Atmospheric and Space Physics in year 4.

Courses that will go beyond mere applications are year 3 Statistical Mechanics, the General Relativity, Advanced Hydrodynamics, Cosmology and possibly Unification and Quantum Field Theory.

18.8 Some interesting areas of the discipline that won't be covered

Or rather, probably won't be covered; some lecture courses could easily include segues into any of these topics and you may well work on a final year project that has some of these topics as minor or major part.

One omission that really belongs beyond undergraduate degree course is in non-equilibrium thermodynamics. This deals with non-homogenous system, transport of material, flow of fluids and turbulence. The idea of entropy as a force is often a central feature. This is very much a developing field.

I don't believe there is much on quantum thermodynamics featured within the undergraduate degree course though some courses may include parts. This is very much still a current area of research in quantum mechanics.

The use of entropy in information theory is something that some of you may well go on to study beyond your undergraduate course. In communications, entropy is given a parallel definition to that in physics to do with how unpredictable the information provided in communication is. The basic rule is the same in that the entropy always increases.