

The second law of thermodynamics

‘Official’ statements (i.e. textbook standards):

“No process is possible whose only effect is to transfer heat from a colder to a hotter body” *Clausius*

“No process is possible whose only effect is the complete conversion of heat into work” *Kelvin*

**(i.e.: “Heat flows from hot to cold unless you do work to push it back”
The Rough Guide)**

More generally:

“The state variables of a multiparticle system can develop irreversibly with time”

Or:

“The direction of an irreversible process is a function of the states of the system”

Or more simply:

“Irreversible means irreversible”

71

Chapter 2

2nd Law and Entropy

2.1 One Way Processes

2.2 The Second Law

2.3 Heat engines and the Carnot Cycle

2.4 Thermodynamic Temperature Scale

2.5 Equivalence of Clausius and Kelvin Formulations

2.6 Real heat engines

2.7 Clausius’ Theorem and Entropy

2.8 Entropy and the 1st Law

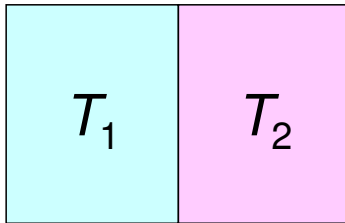
2.9–2.12 Applications of Entropy

2.13 Entropy and the degradation of energy

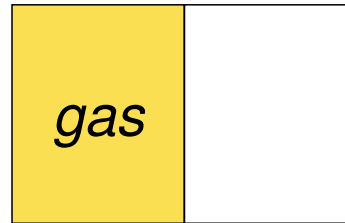
72

2.1 One way processes

- The 1st Law states **conservation of energy**.
- Empirically**: not all processes permitted by the 1st law actually occur - *e.g. consider two classic irreversible processes*:



If $T_2 > T_1$, heat flows from $2 \rightarrow 1$, but not the other way



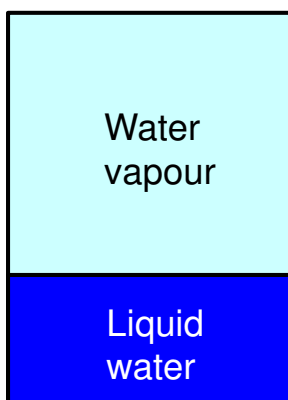
Remove partition – gas spontaneously expands to fill the entire box, but 'never' goes back.

- Any process where any form of 'result' or macroscopic scale change is achieved has to be an irreversible one** – if its not, the internal motion/fluctuations that enacted the change can just cause the system to diffuse back to where it came from.

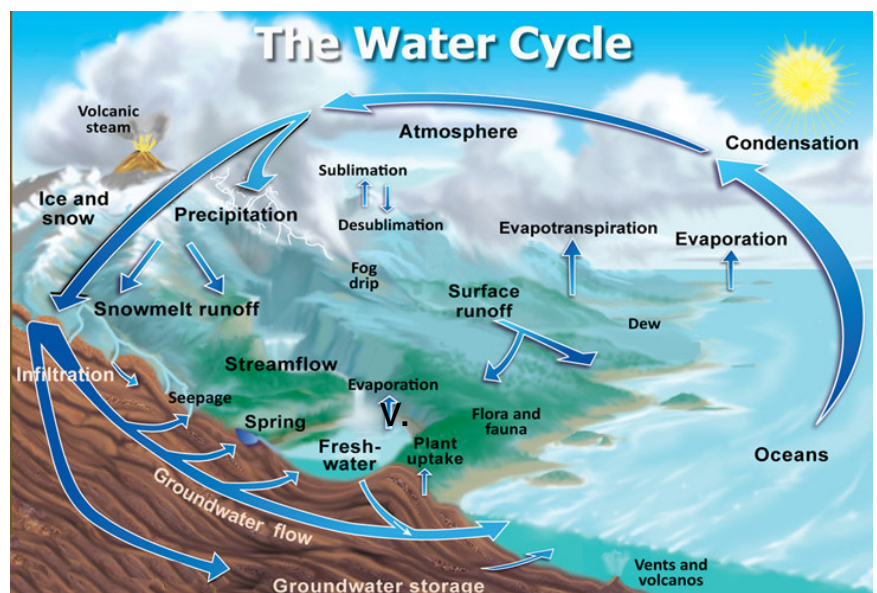
73

Irreversibility and change: eg the water cycle

- Reversible processes themselves are relatively boring – we want to consider things that change!
- Compare the equilibrium between liquid water and its vapour in a closed container with the 'water cycle' – a large number of steps, each of which is irreversible.



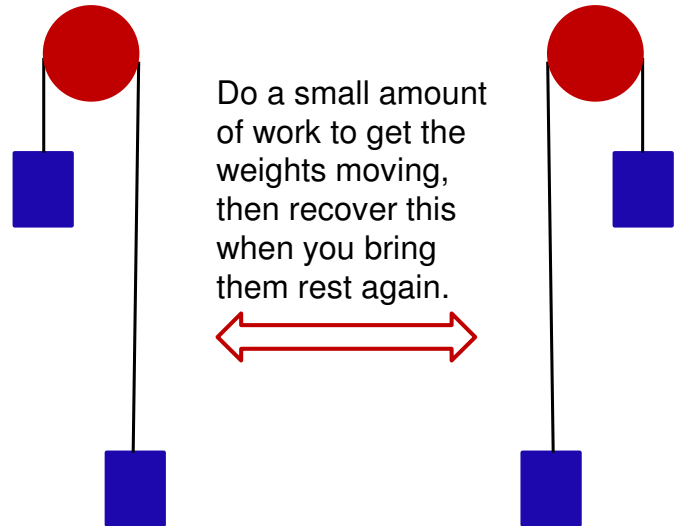
v.



- Can we make general statements/principles about these irreversible changes – in particular what can, and cannot actually happen and how may they be harnessed and controlled?

Pulleys and switches: pulleys

- Consider two equal weights connected by a string that passing over a pulley that runs without friction. **It looks like you can change the state of the system reversibly.**
- BUT air molecules (or radiation if in vacuum) buffet the weights, which perform Brownian motion.



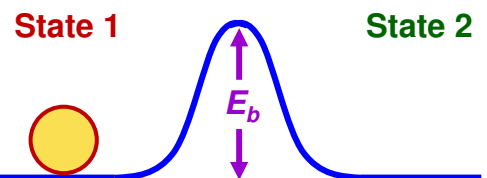
(Brownian motion is thermally induced motion of a macroscopic object – named after botanist Robert Brown who first observed the random motion of grains of pollen in water in 1827)

- If you put the weights to a new position, they will not stay there, they can do a Brownian motion random walk to any other position: you have not achieved a definite final state.
- If you wish to keep the result you have achieved, you need to apply a brake to the pulleys, and to control the brake you need a switch of some sort to change the on/off state of the brake.

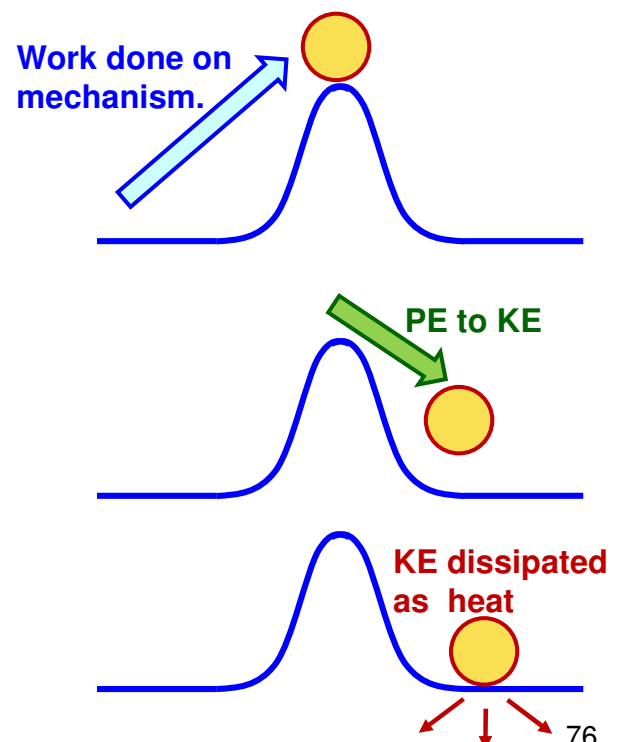
75

Pulleys and switches: switches

- **A switch has to have an energy barrier** between states in order to keep it located one way or another. (Otherwise it will drift from one state to the other and back by Brownian motion.)



- To change the state of the switch:
 - **Work is done against the switch mechanism to push it to the top of the barrier.**
 - Once just over the barrier, this energy stored in the switch mechanism is converted to kinetic energy, which is then dissipated as heat when the switch hits state 2
 - **The work has ended up in the as-good-as-random motion of the molecules** of the switch. The switch has no mechanism for keeping track of where this energy is: it has 'lost information' – the energy could be in any one of many microstates - and cannot direct the molecules to all bring the energy back at the same time so as to throw the switch back to state 1, so we have an irreversible change.



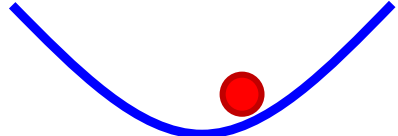
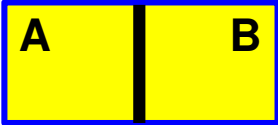
76

Macroscopic irreversibility v. microscopic reversibility

- The laws of physics allow you, conceptually at least, to reverse all velocities (classical mechanics) / reverse the propagation of the whole system wavefunction (QM) and run a system backwards to where it came from – so how can a macroscopic system be irreversible (**Loschmidt's paradox**)? (There are rare processes involving the weak nuclear force that break time reversal symmetry, but the jury is out on what is going on: eg if you are in a rotating frame of reference if you forget to reverse the direction of rotation of the frame, time reversal symmetry is apparently broken.)
- **Macroscopic irreversibility arises because we only reverse the external conditions** (move the piston the other way) – but don't at the same time reverse all the velocities of all the atoms. **The system 'in internal flux' continues to propagate 'forwards'** – i.e. simply responds to the new conditions imposed on it.
- **If we make a half way decent attempt at reversing the velocities** – e.g. the action of a lens – **the system does indeed pretty much reverse** (the photons converge back to a tolerable image).
- Given that we are not even trying to reverse the microscopic motions **it would seem inconceivable that one could ever have a reversible macroscopic process**. **BUT, if we move by small steps from one equilibrium to another we can use the fact that a fluctuating system will come to equilibrium** – i.e. it will find equilibrium itself and we do not have to 'tell the constituents where to go' in order to achieve this.

77

Reversible processes and equilibrium

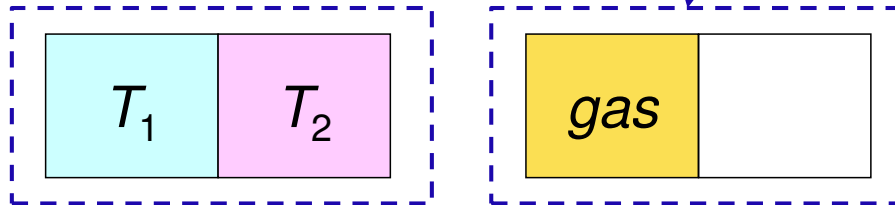
- For a system to be in stable equilibrium there must be a 'restoring' action to return it to its equilibrium point if it is perturbed.
- Consider volumes, A and B separated by a moving wall

If by random fluctuation a small amount of **heat flows** from A to B, the **temperature of B rises**, which causes heat to flow back

If by random fluctuation the no of molecules hitting the A side of the wall is larger than average – the wall will move towards B, **volume is effectively transferred** from B to A, **increasing the pressure** in B, which causes the wall to move back.
If there is an aperture in this wall and by random fluctuation an **excess of particles diffuse** into B, then **the number density** in B increases, which causes a net flow of molecules back through the hole.
- If you disturb a system in equilibrium by an amount \leq the random fluctuations, in many ways the system cannot 'know' that this change is not just another random fluctuation – and so it can 'take care' of a correction to restore equilibrium: hence Le Chatelier's principle: 'systems in equilibrium react so as to oppose changes in external constraints'.
- A series of very small changes do, of course, not just change the 'static boundaries' of the system, but the dynamics as well - molecules bouncing off a moving piston wall have their velocities changed – so the nature of the equilibrium is indeed changed as a result.

78

Irreversibility: what's in 'the box'??

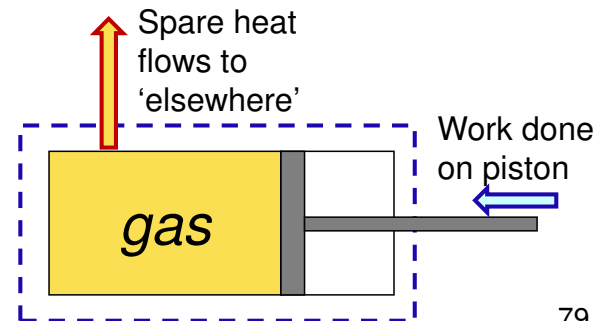
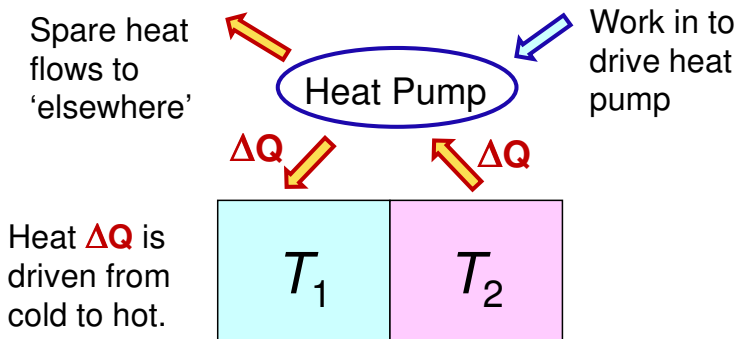
- **The concept of irreversibility applies to an isolated 'setup'** -i.e. the whole thing is contained in a notional box, the contents of which have no communication/interaction with anything outside.
- ***e.g. consider the two classic irreversible processes:***

If $T_2 > T_1$,
heat flows
from $2 \rightarrow 1$,
but not the
other way



Remove partition –
gas spontaneously
expands to fill the
entire box, but
'never' goes back.

- Both processes can be reversed by intervention from outside the box. Note, in both cases you have to do work on the system, and the equivalent heat flows out to 'elsewhere'.

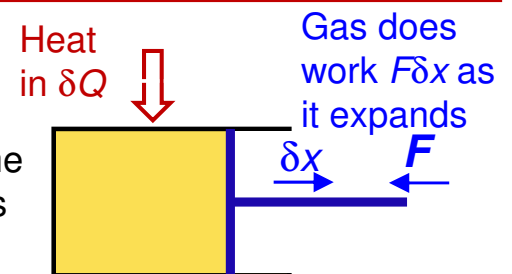


79

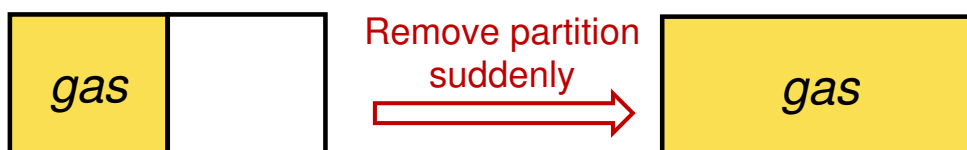
Reversible/irreversible change – a classic example

Reversible isothermal expansion

- infinitesimal reduction in F
 - the gas expands infinitesimally, does work $F\delta x$ against the piston, cools infinitesimally, heat δQ flows in from the walls to restore the gas temperature.
 - The whole process is done so slowly that the temperature of the gas remains equal to that of the wall, and the pressure/temperature of the gas are uniform throughout its bulk.
 - The process can be precisely reversed by an infinitesimal increase in force F .
-



Sudden (Joule) expansion: irreversible



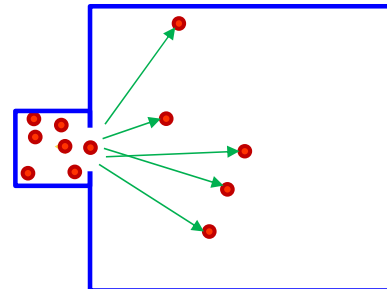
- No heat flows into gas, and gas does no work as it expands.
- For an ideal gas (U all KE): final T and P same for both paths.
- Putting the partition back does not make the gas move back!
- If you try compressing the gas its volume goes back, but it heats up...
- Whilst work may reverse the change for the system – it cannot reverse everything globally – the work has gone into heating up the surroundings outside the system.

Comments on 'Rev. Isothermal v. Joule Expansion'

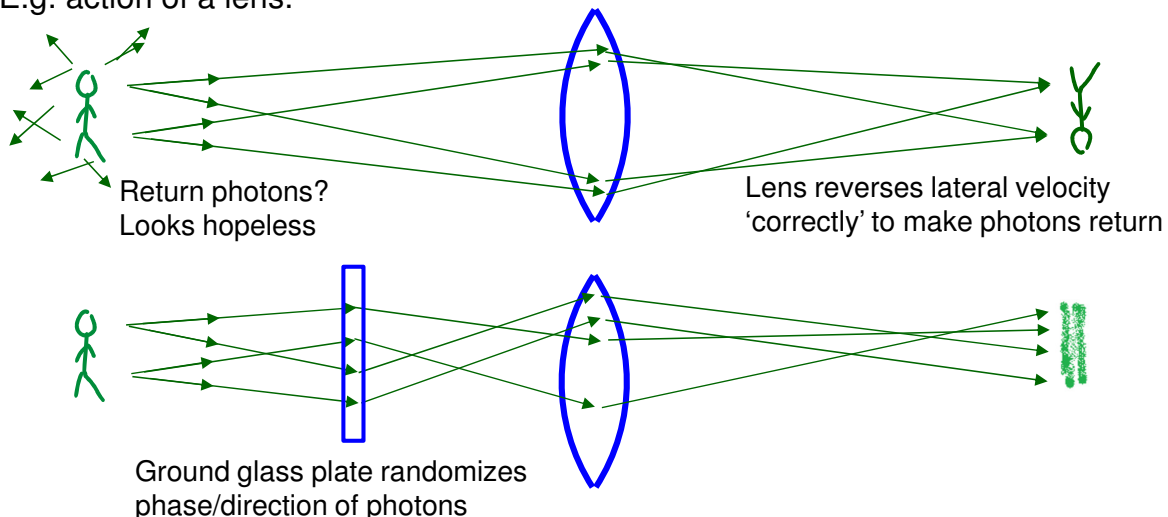
- An ideal gas does not change its temperature during Joule expansion – its energy is stored purely as K.E. and is unaffected by the distance between the molecules – *i.e.* U is a function of N and T only.
- The comparison between reversible isothermal expansion and sudden, (irreversible) Joule expansion illustrates that **there can be different paths that lead to the same destination** – in this case if the gas is ideal the final state functions, T , P , N , and U are the same in both cases, but the **work done** and the **heat transferred** are different (**they are path dependent**)
- **During the reversible isothermal expansion** of any gas (indeed of anything – solid, liquid or gas) **heat is converted smoothly to work**, and **if the process is reversed, work is converted back to heat**, and at the end of a closed cycle of isothermal expansion/contractions everything is back where it was at the start, it was all reversible.
- **Comparing the two expansions illustrates the fact that when you replace an irreversible process with a reversible one, the 'driving force' in the irreversible change can be harnessed to produce useful work.** This work must come from heat – there is nowhere else to get it from: this apparent 'driving force' is not derived from a potential energy – so extra heat must flow into the system.
- 'Thermodynamics potentials' (such as the Gibbs and Helmholtz free energies) can be constructed with derivatives that give this driving force under certain circumstances – and include both the effects of this 'tendency to spread out/dissipate' and actually energy effects to give what work can be extracted. 81

Irreversible processes and 'information loss'

- After removing a partition, before the molecules hit the walls, they still have encoded in their trajectories where they came from – so if you can think of a way of reversing all the motions – the molecules would all return, together, to the small box.



- E.g. action of a lens.

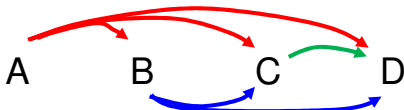


- Once the molecules have hit the wall, or the phonons gone through the ground glass plate the connection between the particles' current and initial trajectories has been effectively lost – and the change has become irreversible by macro scale actions. 82

Reversing trajectories and 'information'

- When we, or nature, 'manipulate' a multiparticle system at the macro scale level it is done via 'constraints' – actions that are not specific to the motion of each particle but work on all trajectories. E.g. a gas expands against a piston, every molecule that hits the piston is slowed down, but you don't actively track each molecule and work separately on them in a targeted way on it. When the gas is compressed again, every molecule is speeded up by the piston and we can return to where we were.
- If you let a system go 'out of equilibrium' – eg photons leave an object and fly off into space – encoded in the trajectories is where the system came from – time reversibility applies straightforwardly to the trajectories - and you can still reverse the situation if you have a way of reversing the trajectories. A mirror or lens suitably configured can do a reasonable job.
- The irreversibility occurs at the point you 'loose track' – *i.e.* no longer have the means or intent to reverse the individual particles motions by some action applied to all the trajectories. This is sometimes referred to as 'loosing information'. This way of talking can be confusing as we never did know what the trajectories were in the first place. Perhaps talking about increased uncertainty is better. We were uncertain where the particles were when they were in a small box, but when they move into a bigger one, we become more uncertain..
- Thermodynamics uses modelling constructions/methods that enable us to describe and manipulate multiparticle systems on the macro scale. If what we can do changes, we need to change the model. *E.g.* if suddenly you are able to tell the difference experimentally (*i.e.* by some process) between isotopes of a gas, then we need to change the description (*i.e.* the state variables) to allow for the fact that our gas is now a mixture of two distinguishable species that can be separated, whereas before it was a one component system.

A state variable to quantify 'irreversible progress'?



- If we have a system with a series of macro states that are not equilibrium variants of each other – A, B, C,... then we have a chain of possible one way processes:

- E.g. imagine a container with walls kept at $\approx 300\text{K}$ by immersing it in a large amount of water (2000m³ will do here to keep temperature changes down to 1K) so that its temperature barely changes when heat is transferred to/from it. Then hypothetical states A to E could be specified as having the inner box containing:

The 'Box' – contents isolated from 'Outside'

Massive tank of water: a 'thermal reservoir'

'Sub-system' = A-E
or some mixture thereof.

- A: 10 mmol electrons, 10 mmol protons 8 mmol neutrons
 B: 10 mmol electrons, 2 mmol protons 1 mmol oxygen nuclei
 C: 2 mmol H atoms, 1 mmol oxygen atoms
 D: 1 mmol H₂ molecules, 0.5 mmol O₂ molecules
 E: 1- ϵ mmol H₂O as liquid 0.5, ϵ mmol H₂O as gas

Each state can change irreversibly to a state with a later letter.

- Each system has the same total energy, volume and particle number, but we can rank these systems according to their state as to 'how far they are done the irreversible path'. It is reasonable to look for a new state function that quantifies this, which will have contributions from both the H/O system and the 'reservoir' of water that keeps absorbs heat from the H/O system to keep the temperature constant.
- The question the arises as to how this new state variable:
 - relates to the work that can be harvested form an irreversible process.
 - Can be used to 'quantify' equilibrium between phases – eg the liquid and gas in E.

Towards the second law

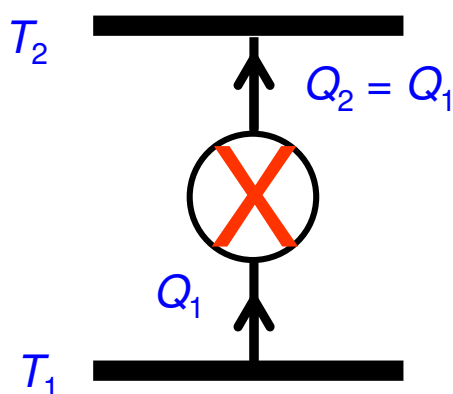
- We started with the realisation that ‘there are irreversible processes’ – and the whole discussion so far has been derived from this. This is actually a good general statement of the second law of thermodynamics. The law states that there really is no way back for an irreversible process of an isolated system which means the direction of an irreversible change is determined not by details of the processes, but by the states themselves, and thus could in principle be characterised by a state variable – just as temperature was.
- We have been quick to accept this result – but that is because we understand that matter is made of particles so have understanding that backs up this notion. As yet, however, this notion is based really on the scantiest of ‘evidence’ – heat and particle flow in very simple circumstances – but is this really true?? Ultimately to have confidence in the 2nd law we would need to see some other principle on which is based of which we are (more, at least) certain. Certainty can only be based on other certainty, or it needs to be qualified (explained not to be really certain). At least it helps to know what ‘certainties’ we are actually basing science on because then we know where to look to see if they are certain, or if we have missed something.
- One has to remember that ultimately the whole of science goes back to observation – science codifies what we observe to happen. You cannot derive science with pen, paper and logic - it is fundamentally experimental. We may be the astronomers, the observers, which is a truly remarkable position to have in the Universe, but at the end of the day we are creatures and not the Creator, and do not have creator rights and understanding.
- We shall see that the second law is based on time reversal symmetry, and the more experimental evidence we have for either of these concepts, the more confidence we have in the other.

85

2.2 Second law

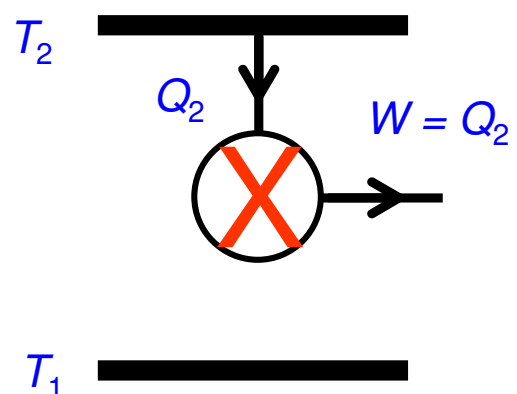
Two (equivalent) traditional statements

Clausius’ formulation



“No process is possible whose only effect is to transfer heat from a colder to a hotter body”

Kelvin’s formulation



“No process is possible whose only effect is the complete conversion of heat into work”

These statements were based on empirical observation

Just for the record (not examinable: NE)

- Kelvin's statement of the second law, as per the previous overhead, is what is attributed to him by many thermodynamics textbooks and is the definition that you are expected to know that takes Kelvin's name.
- **Kelvin**'s actual statement of the second law was: *'It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects'*. If you think (hard) about this you will realise that it amounts to pretty much the same thing.
- **Max Planck** made the following proposition: *'It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and cooling of a heat reservoir'* which is actually pretty close to the traditional 'Kelvin' statement – so some call this statement the 'Kelvin-Planck' statement of the second law.

87

Clausius's and Kelvin's 2nd law statements

Clausius' formulation

"No process is possible whose only effect is to transfer heat from a colder to a hotter body"

Kelvin's formulation

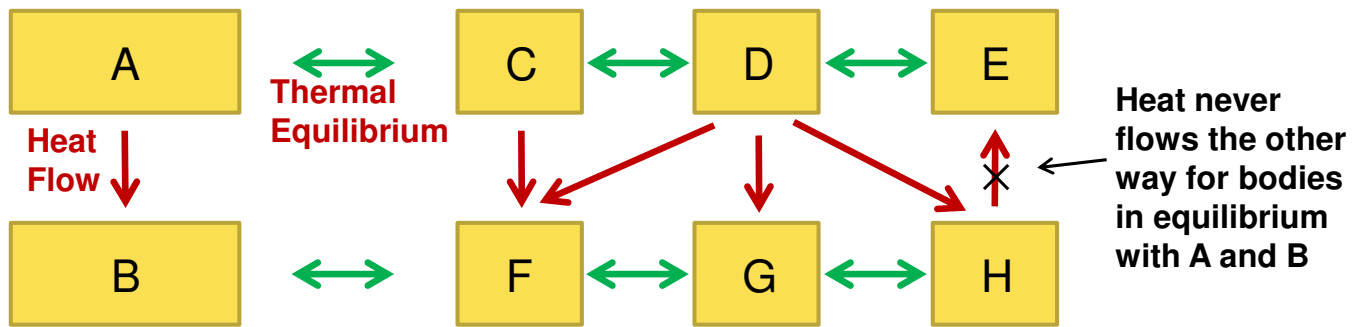
"No process is possible whose only effect is the complete conversion of heat into work"

- We will show shortly that the two statements are equivalent.
- The most important requirement for the statement of a law of physics is that it done in way that makes a very clear statement that is easy to use – which is why these two statements of the 2nd law are generally quoted.
- An added bonus is if they can be stated in a way that makes it very obvious why they are true – and Clausius's statement is clearly trying to do this. If you think about it, **all Clausius's statement is saying is that heat flows from hot to cold, unless you do something to push it back**, – but it is presented the other way round, I think, because it is easier to make a water-tight logical statement in that way: heat can flow in quite complicated ways (central heating systems, fridges) – but the rule 'heat flows from hot to cold' only applies if nothing else happens (fridges consume electrical power).

88

What is the 2nd law actually saying?

- The second law is based on the observation that once you have decided which of two bodies is hotter (A) than the other (B) (by looking at which direction heat flows) then heat will always flow from any body at the same temperature as A to any body at the same temperature as B. *i.e.* it boils down to saying that the direction of net heat flow is a unique function of the difference in temperature between two bodies (unless you have some process where work is expended pushing it back).



Observe first which way heat flows between A and B, and then you can deduce how heat will flow between bodies in thermal equilibrium with A and B

89

Is the 2nd law a tautology?

- Does this law say anything more than heat flows from hot to cold?** Why do we need it? What is actually going on? Is it not just a tautology? – after all we don't we define hot and cold by the direction of heat flow?
- The first point is that heat can flow from A to B by many means – not just direct thermal contact, (fridges, central heating systems *etc*) so the fact that **whatever you do, and for ANY process the net effect is that heat flows from hot to cold** (unless you do something that amounts to more than just letting heat flow – *i.e.* you expend work), is worthy of a law.
- More fundamentally, this result is so well known to us that we subconsciously added it to the 0th law**. The 0th law says there is a function of state that determines if two bodies are in thermal equilibrium. **IT DOES NOT SAY ANYTHING ABOUT HOW HEAT FLOWS IF THEY ARE NOT!** It is actually a separate experimental observation that once you have determined the direction of heat flow for two bodies – heat will flow in the same direction between all other bodies at these two temperatures.
- Just as Newton's first law is a special case of his second – **the 0th law of thermodynamics is a special case of the 2nd**, and we will see that temperature is actually the derivative of entropy as a function of reversible heat transfer – it is not quite such a new variable as it seemed.

90

‘Allowed’ processes and functions of state

- Fundamentally the second law is saying that for multiparticle systems in a state of internal flux, whether a state **I** can transform into state **II** ‘by itself’ – *i.e.* not by being pushed by something outside the system (e.g. no work expended on it) is not just determined by conservation laws, but by something extra to do with the nature of the states e.g. once you know the temperature of A and B the direction of heat flow (*i.e.* a process) is determined. So a more general statement of the 2nd law would be that **‘the direction of an irreversible process is a function of the states of the system.’**
- **An alternative, fundamental, definition of the second law could be ‘multiparticle systems in a state of internal flux show irreversible behaviour if left to themselves’:** if the change really is irreversible, then however it has happened, or can happen, it cannot go back – so the direction of the change is not determined by how it happens, but by the nature of the start and end states.
- The 2nd law lays the foundation for a new state function that will determine which processes can actually happen, over and above the requirement that conservation laws be obeyed.
- The need for this extra function of state in thermodynamics (as compared to classical or quantum mechanics) arises because we are dealing with the behaviour of a system of many particles about which we have rather limited knowledge – but **its most probable action** (heat flows hot to cold, gas expands into a vacuum) **is clear**, and we need a state function that encodes the relative probability of states. 91

2.3 Heat, and heat engines.

- Historically the **nature of heat** was a real scientific puzzle, but of real technological importance – early steam engines were very inefficient – **the need to improve efficiency** was a key motivation for the development of thermodynamics.

(Thomas Newcomen’s engine, c1710, was about 0.5% efficient. Eventually James Watt improved this ~5x (first engines installed in 1776) , but it was not till 1870’s with higher boiler pressures and triple expansion (‘compound’) engines that long distance cargo ships could carry more freight than coal, but to design such engines successfully you need to understand the ‘rules’ that govern the conversion of heat to work.)

- We are today, perhaps, surprised at their ignorance – what did they think heat was then?? But they were working before it was generally realised/accepted matter was made of particles – and if you have a 0.5% efficient steam engine the chance of noticing heat has been lost and converted to work is slim.
- Thermodynamics became the subject that described how heat and mechanical systems can be coupled, and a central issue is to what extent heat and work can be interconverted.

Heat engines and the Carnot Cycle

- Historically, the key issue was 'how do you make a better steam engine'
- Underlying this is the question 'is there a limit to how efficient a heat engine can be and if so what determines it'.
- Carnot showed that (mentally at least) you could construct a perfectly reversible heat engine (the 'Carnot Cycle') and then used his version of the 2nd law of thermodynamics (you only get work from a cyclic engine when heat flows from hot to cold) to showed that **all reversible (= working steps are reversible) heat engines have the same efficiency** and that irreversible heat engines are less efficient.

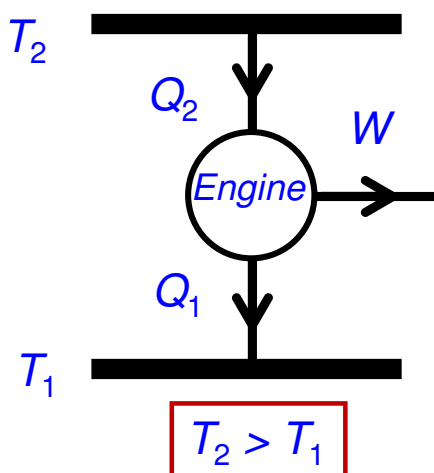
(You may ask 'but if it is reversible, what makes it go forwards': well..., precisely.. It will only go in a determined direction, and definitely convert heat to work if it is at least slightly irreversible, for example if the furnace is slightly warmer than the boiler so heat flows into the boiler and not out of it.)

- Subsequently, Clausius showed that there was a **new function of state that lay behind Carnot's observation**, which he called **entropy**, and that **for any reversible process entropy remains the same, but rises for irreversible processes.** (*Entropy actually codifies probability: processes where the entropy of the universe decreases are 'not allowed' = are monumentally unlikely*)

93

Cyclic heat engines

- We will consider idealised heat engines which are 'cyclic' – composed of a series of steps with the engine returning periodically to its initial state so that the stuff of which the engine is composed does not, of itself, act as a source or sink of energy.



- Conceptually the simplest sort of heat engine operates between two 'reservoirs' which are so large that their temperature is not changed when heat is transferred in and out of them. Heat Q_2 , is transferred to the heat engine from the high temperature reservoir, the engine does work W , and rejects heat $Q_1 = Q_2 - W$ in the colder reservoir.

- The question is 'what is the (or is there a) maximum W that can be obtained for a given Q_2 other than the value $W=Q_2$ allowed by conservation of energy?'

94

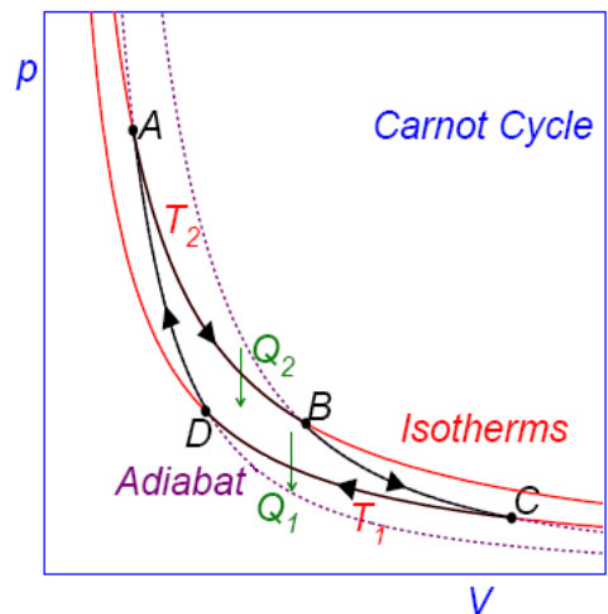
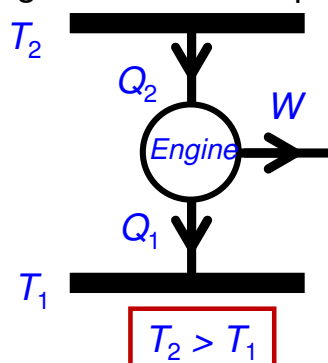
Carnot's reasoning

- By considering the heat engines he knew about (steam engines) **Carnot came to the conclusion that work could only be generated if heat flowed from a hot to a cold reservoir**. (A perfectly good statement of the second law of thermodynamics.)
- Carnot realised that the **greater the temperature difference the more work you could get out of the engine**. (He thought of heat flowing through a heat engine like water driving a water wheel giving out energy as it lost height: his father designed and built water mills).
- He then realised that **irreversible processes do not give as much work as reversible ones**. He argued that if, for example, boiling water is at a lower temperature than the wall of its container, it might as well be connected to a heat reservoir at lower temperature and the engine will give correspondingly less work – for a particular reservoir temperature the most work is obtained if the water is at the same temperature as the reservoir.
- Carnot noted that many substances – gases, liquids, solids - expand when heated, and if allowed to expand adiabatically, will cool, and any one of these could be used to make a heat engine. So **he proposed an idealised heat engine - i.e. a cycle of steps - for which he did not need to specify what 'expansion' medium was to be used – the 'Carnot cycle'**.

95

Carnot Cycle

- Working substance used cyclically and **reversibly**.
- Two isotherms, T_1 , T_2 ; ($T_2 > T_1$) connected by adiabats (B to C and D to A).
- Heat Q_2 absorbed during isothermal expansion at T_2 ; heat Q_1 deposited during isothermal compression at T_1 .

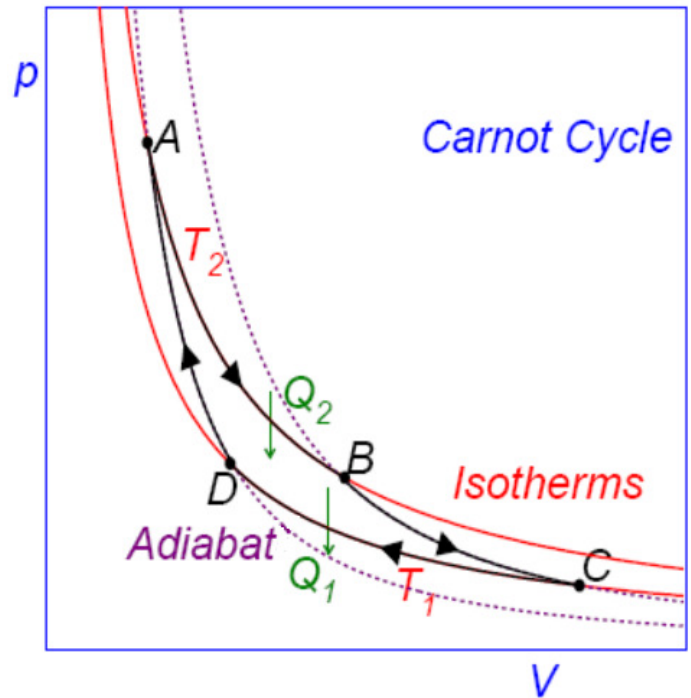


- Work done $W = Q_2 - Q_1$ is equal to area of cycle: $= \oint p dV$
- Working medium, and hence relation between p and V , unspecified.
- Given Carnot was going to do thought experiments with reversible engines working between fixed temperature reservoirs, he had to know that in principle such a thing existed.

96

Carnot Cycle in Detail

- **A → B:** Isothermal expansion at T_2 ; heat absorbed from high temperature reservoir Q_2 ; work is done on surroundings.
- **B → C:** Adiabatic expansion; $\Delta Q = 0$; work is done on surroundings, medium cools to T_1 .
- **C → D:** Isothermal compression at T_1 ; heat given out to cold reservoir Q_1 ; work is done by surroundings.
- **D → A:** Adiabatic compression; $\Delta Q = 0$; work is done by surroundings, medium warms to T_2

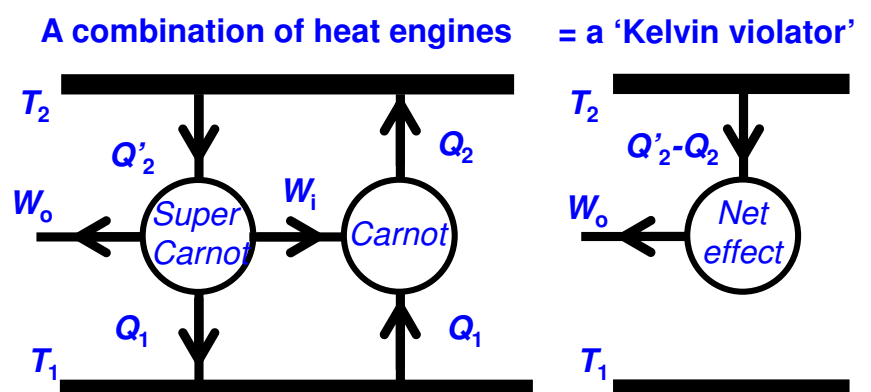


97

Carnot's Theorem: No engine operating between two reservoirs can be more efficient than a Carnot engine.

- **Carnot's (perfectly correct) proof:** Suppose there was a 'super-Carnot' heat engine (need not be reversible) that is more efficient than a Carnot engine then we could syphon off some of the work from the super-Carnot engine and use it to run the Carnot engine backwards (as a fridge, or heat pump) to pump the heat rejected to the cold reservoir by the super-Carnot engine back up to the hot reservoir. Between them they would be generating work without net heat flow from the hot to the cold reservoir – in violation of **Carnot's version of the second law of thermodynamics (work can only be produced when heat flows from a hot to a cold reservoir)** – so the super-Carnot engine cannot be more efficient.

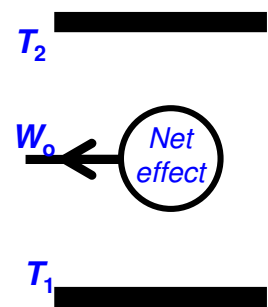
Modern argument: if the super-Carnot is more efficient – for the same heat transfer to/from the cold reservoir the super-Carnot produces more work – so after running the Carnot backwards (work W_i) there is work left over to output (W_o). Conservation of energy means that Q'_2 must be $> Q_2$ so the net effect of the combination would violate Kelvin's statement of the second law.



An aside for interest: so what did Carnot not know?

- **Carnot did not know about conservation of energy (the 1st law came later than Carnot's work) and he thought heat was a conserved fluid.** This means that he thought that all the heat that came out of the hot reservoir was rejected to the cold one *i.e.* $Q_1 = Q_2 = Q'_2$ and therefore he was left with a combined engine that took no heat out of the top reservoir as well as rejecting no heat to the cold one – and simply produced work:

Carnot's idea of the combined heat engine



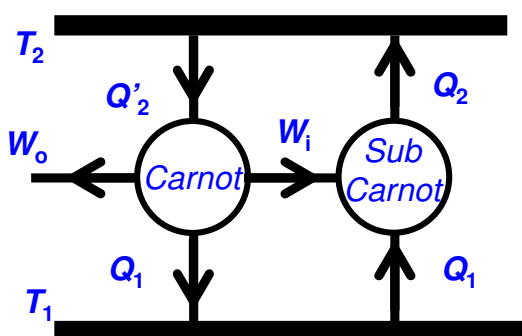
- **He objected to this not just because it violated his basic principle (work only produced when heat flows from hot to cold) but because limitless amounts of work would be produced from nothing** – ‘not even by consuming heat’. In this almost throwaway statement he is reflecting perhaps the start of a realisation that heat was not the conserved fluid of the caloric theory and he was effectively stating “Kelvin's” version of the second law – ‘there is no process whose sole function is the transfer of heat to work’. One wonders how far he would have got if he had had a chance to discuss his work with Count Rumford.

99

Carnot's Theorem continued

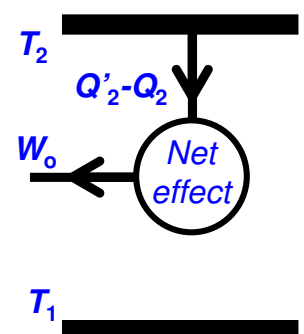
Carnot's theorem has the corollary that **all reversible engines operating between two temperatures have the same efficiency as a Carnot engine.**

- **Proof:** as for the proof of Carnot's theorem – but swap the forward running ‘super-Carnot’ for a Carnot, and the backward running Carnot for a sub-Carnot that is running backwards (we can run the sub-Carnot backwards with the same efficiency as forwards because we have specified it is reversible) .



If the Sub-Carnot is less efficient:

For the same heat transfer to/from the cold reservoir the Carnot produces more work – so after giving enough work (work W_i) to drive the sub-Carnot backwards and pump the heat reject to the cold reservoir (Q_1) back up to the hot reservoir, there is work left over to output (W_o). Conservation of energy means that Q'_2 must be $> Q_2$ so the net effect of the combination would violate Kelvin's statement of the second law:



100

Carnot's Work: Summary

- Carnot realised that the most efficient heat engines must be reversible.
- To see what he could deduce about the efficiency of reversible heat engines he constructed a 'thought engine' – an idealised, cyclic heat engine that took heat in from a hot reservoir and rejected heat to the cold one, and produced work in the process. (A 'Carnot' engine)
- He noticed that for a closed cycle engine to produce work, heat had to flow from the hot to cold reservoir (effectively his statement of the second law) and used this to prove that:
 - No engine (reversible or irreversible) can be more efficient than one of these 'Carnot' engines.
 - No reversible engine can be less efficient – *i.e.* all reversible heat engines have the same efficiency.
 - (and hence that his original insight – reversible engines are the most efficient - was correct)
- Carnot managed to argue all this correctly without knowing that heat was internal energy – but he did have a wrong picture in his mind of the details of how the heat moved around. 101

A historical aside: so what happened next?

- Carnot published his work in 1824 'Reflections on the motive power of heat' (for an English translation see: http://en.wikisource.org/wiki/Reflections_on_the_Motive_Power_of_Heat/Chapter_3) but tragically died of cholera in 1832 and his work was went unnoticed until 1834 when French mining engineer Émile Clapeyron put it on a graphical footing in his *Memoir on the Motive Power of Heat*..
- James Prescott Joule discovered the first law of thermodynamics in the early 1840's and it slowly began to be accepted.
- In the early 1850's the German engineer/inventor/physicist Rudolf Clausius and Lord Kelvin rediscovered Carnot's work at roughly the same time (Clausius via Clapeyron's work), and in the light of Joule's work on the first law (which Kelvin accepted rather slowly) reworked Carnot's arguments, giving their separate statements of the second law.
- Clausius developed the concept of entropy (he coined the term, making it deliberately similar to 'energy') from the second law.
- Kelvin (as theorist) and Joule (as experimentalist) worked together (mainly by correspondence) on further thermodynamics issues.

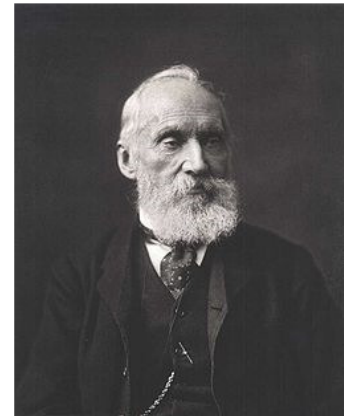
Originators of the 2nd law



Nicolas Sadi Carnot
(1796 – 1832)



Rudolf Clausius
(1822 – 1888)



William Thomson
(Lord Kelvin)
(1824 - 1907)

103

Efficiency of a Carnot Cycle

- So far we have shown all Carnot cycles and hence all reversible heat engines have the same efficiency – but we have not worked it out. To do so consider a Carnot cycle that uses an ideal gas as its ‘working medium’.

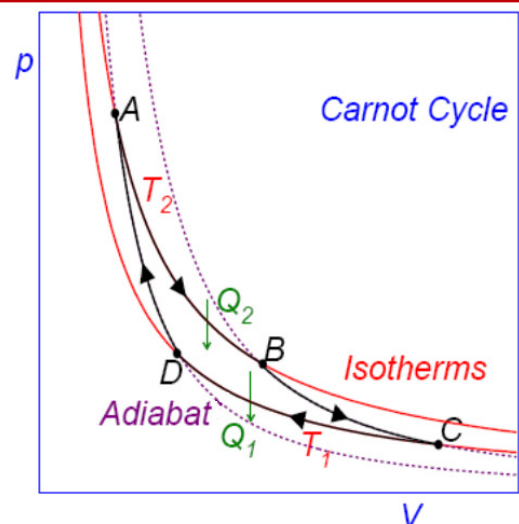
- Efficiency η defined by:

$$\eta \equiv \frac{\text{Work done by system}}{\text{Heat absorbed}} = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}$$

- For 1 mole of an ideal gas, $pV = RT$, the change of heat along an isotherm is:

$$Q_2 = \int_{V_A}^{V_B} p dV = \int_{V_A}^{V_B} \frac{RT_2}{V} dV = RT_2 \ln \left(\frac{V_B}{V_A} \right)$$

- Likewise: $Q_1 = RT_1 \ln \left(\frac{V_C}{V_D} \right)$



104

Efficiency of a Carnot Cycle

- Using the adiabatic expansion equation

$$TV^{\gamma-1} = \text{const.}$$

$$T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1} \quad \text{and}$$

$$T_2 V_A^{\gamma-1} = T_1 V_D^{\gamma-1}$$

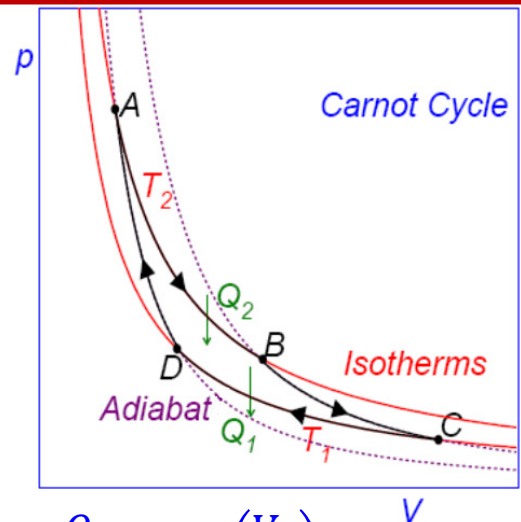
$$\Rightarrow \frac{V_B}{V_C} = \frac{V_A}{V_D} \Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

From previous slide: $\frac{Q_1}{RT_1} = \ln\left(\frac{V_C}{V_D}\right)$ and $\frac{Q_2}{RT_2} = \ln\left(\frac{V_B}{V_A}\right)$

Therefore: $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ and $\eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$

- Carnot's theorem means this result is true for **all reversible heat engines**; not just for those involving an ideal gas.

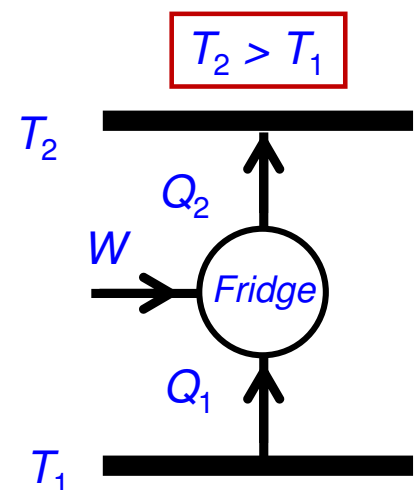
- n.b. $T_2 > T_1$, so $0 < \eta < 1$.



105

Refrigerator

- An ideal refrigerator is a Carnot cycle run in reverse.
- By doing work W , we can extract heat Q_1 from the reservoir at T_1 . We want to dump heat $Q_2 > Q_1$ at some higher temperature T_2 (hence the radiator at the back of a fridge).



- Efficiency = (heat extracted)/(work done)

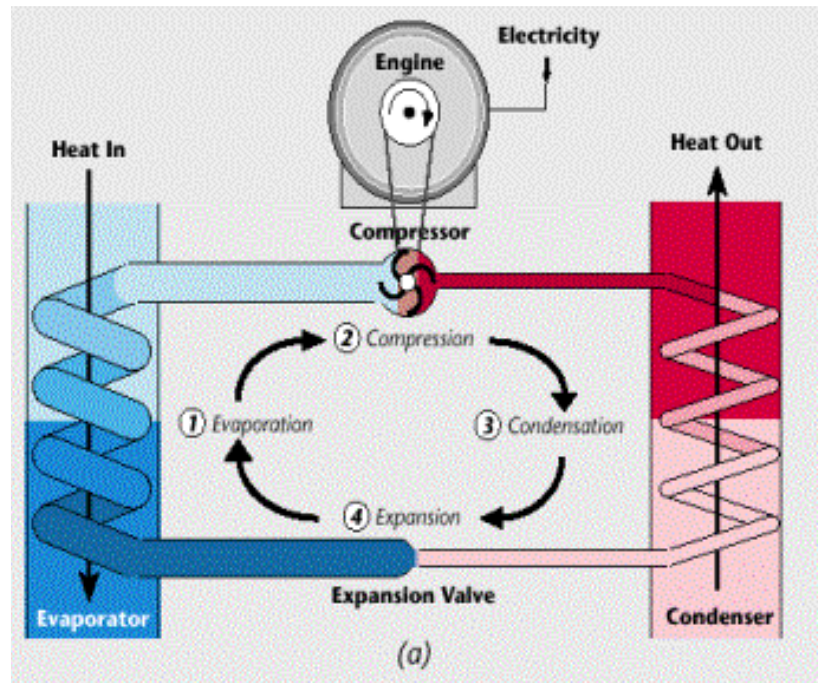
$$\eta \equiv \frac{Q_1}{W} = \frac{Q_1}{Q_2 - Q_1} = \frac{T_1}{T_2 - T_1}$$

Can be highly efficient: $\eta \gg 1$ if $T_1 \approx T_2$

106

Heat Pump

Typically a heat pump will use the fact that a liquid boils at a higher pressure at higher temperatures



http://www.esru.strath.ac.uk/EandE/Web_sites/01-02/heat_pump/background.html 107

Heat Pump

- Like the refrigerator, but use Q_2 to heat a building by pumping heat from the outside air or the ground.
- The efficiency or “*coefficient of performance*” is

$$\eta \equiv \frac{Q_2}{W} = \frac{Q_2}{Q_2 - Q_1} = \frac{T_2}{T_2 - T_1} > 1$$

⇒ much more efficient than heating a house directly, especially if temperature difference between inside and outside is not too large.

A word about efficiencies

- **Trying to remember definitions of efficiency for all these separate situations is near impossible – so you need to be able to work them out.** If you need to know the efficiency of, for example, a fridge, think ‘what is the fridge supposed to do (pump heat out of a cold space) – so the efficiency will be how much heat you pump out of a cold reservoir divided by the work you have to expend doing it. A heat pump, however, is designed to pump heat into a building, so its efficiency would be the heat transfer into the hot reservoir divided by the work expended.
- One the needs to remember that the most efficient process is a reversible one – so, once you are happy with the concept of entropy ($dS = dQ_{rev}/T$), one can use the fact that the entropy changes of the hot and cold reservoirs must be the same, so the heat transfers for a reversible cycle are proportional to the temperatures – i.e.:

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

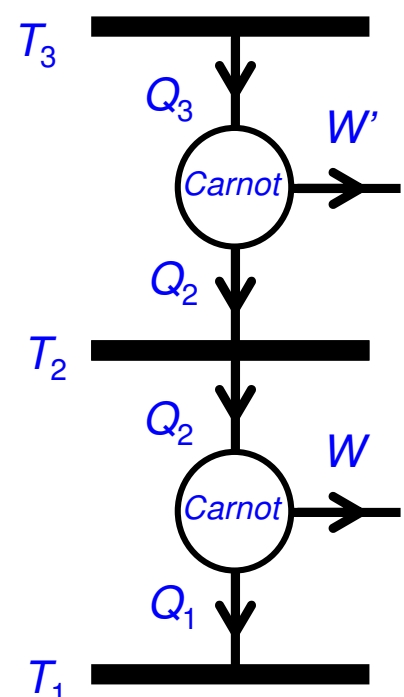
and the work is given by the difference between Q_1 and Q_2 .

109

2.4 Thermodynamic Temperature Scale

- Carnot’s Theorem means that the ratio of the heat transfers into and out of the hot and cold reservoirs is a function of the temperature of the reservoirs only.
- This allows us to define a temperature scale: introduce ‘empirical temperatures’ θ_1 and θ_2 such that $Q_2/Q_1 = f(\theta_1, \theta_2)$
- Consider two Carnot engines: with $Q_3/Q_2 = f(\theta_2, \theta_3)$

⇒ equivalent to a single reversible engine operating between θ_3 and θ_1 .



$$\frac{Q_3}{Q_1} = f(\theta_1, \theta_3) = \frac{Q_2}{Q_1} \cdot \frac{Q_3}{Q_2} = f(\theta_1, \theta_2) f(\theta_2, \theta_3) \quad \forall \theta_1, \theta_2, \theta_3$$

110

Thermodynamic Temperature Scale

$$\frac{Q_3}{Q_1} = f(\theta_1, \theta_3) = f(\theta_1, \theta_2)f(\theta_2, \theta_3) \quad \forall \quad \theta_1, \theta_2, \theta_3$$

 independent of θ_2

- Hence $f(\theta_1, \theta_2)$ must be of the form

$$\frac{Q_2}{Q_1} = f(\theta_1, \theta_2) = \frac{g(\theta_2)}{g(\theta_1)} = \frac{\Theta_2}{\Theta_1}$$

i.e. why not just take these $g(\theta)$ functions, i.e. the reversible heat transfer, as defining the thermodynamic temperature.

- Carnot's Theorem plus a knowledge of the efficiency of one Carnot engine (ideal gas one) means we know that Q_2/Q_1 always = T_2/T_1 , so we have:

thermodynamic temp. = ideal gas temp. (up to some multiplicative factor)

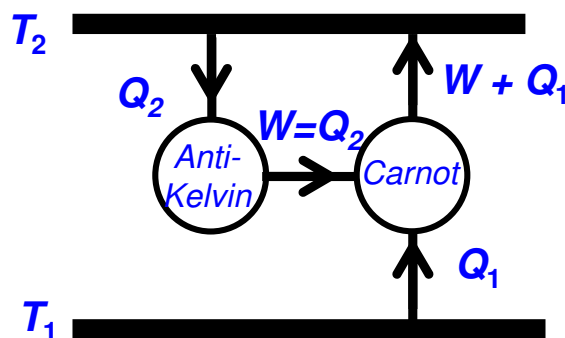
$$\Theta \equiv T$$

This is why ideal gas temp. is the natural choice in Thermodynamics.

2.5 Clausius & Kelvin Formulations

- Suppose we have an engine that violates Kelvin's formulation.

Use its work to drive a Carnot engine as a heat pump:

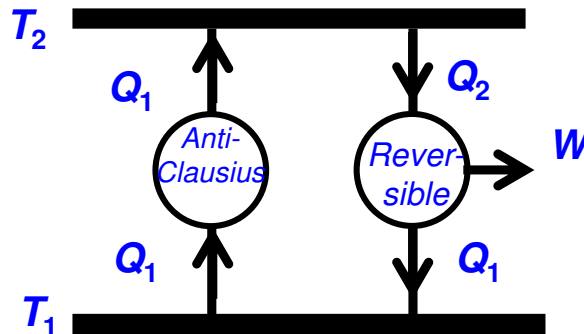


- Net effect is to transfer heat from T_1 to T_2 .

 violates Clausius' formulation.

Clausius & Kelvin Formulations

- Suppose we have an engine that violates Clausius' formulation.
Run it in tandem with a Carnot engine thus:



- Net effect is the complete conversion of heat to work.

➡ violates Kelvin's formulation

➡ **Both formulations are equivalent.**

113

2.6 Real Heat Engines

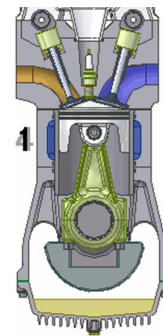
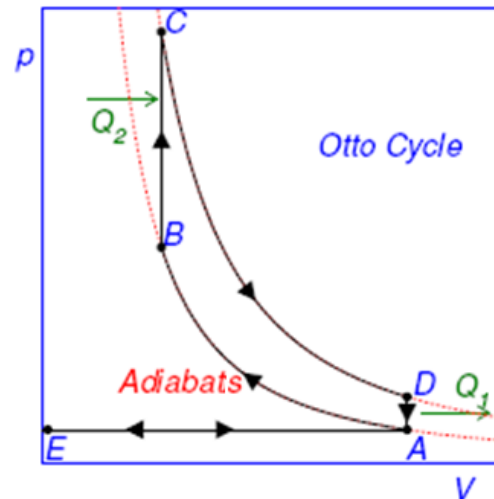
- **Real** heat engines are **not reversible**, e.g.
 - ✱ Losses of heat through thermal conduction.
 - ✱ Friction, turbulence are irreversible processes.
 - ✱ Changes are usually fast, requiring significant temperature and pressure gradients.
- **Real heat engines can have 'design flaws'**. A piston steam engine has the serious flaw that the walls of the piston take up some average temperature, colder than the steam when it enters (and so heat flows irreversibly to them from the steam) and then warmer than the steam once the steam has expanded, again producing irreversible heat flows. A compound steam engine gives a greater, multistage expansion and has less steam cooling and smaller temperature differences on each stage. In a steam turbine each set of blades remains at the same temperature, each one cooler than the last, as the expanding steam flows past them, enabling much higher efficiencies.
- Real engines often don't involve pure substances; e.g. car engine contains mix of fuel vapour, air, exhaust gases, which changes through the cycle.
- They may not operate between fixed temperatures.
- Often approximated by using 'Air standard' cycles: air is taken as working substance; assume ideal gas & reversibility.

114

Air Standard Otto Cycle

Approximates the internal combustion engine.

- **E → A** Intake stroke: fuel + air drawn in to cylinder
- **A → B** Compression stroke: assumed adiabatic
- **B → C** Ignition: heat generated by combustion of fuel.
- **C → D** Power stroke: adiabatic gas expansion
- **D → A** Open exhaust valve
- **A → E** Expel remaining gas



115

Otto Cycle Efficiency

$$Q_2 = C_V (T_C - T_B)$$

$$Q_1 = C_V (T_D - T_A)$$

$$\eta = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{T_D - T_A}{T_C - T_B}$$

- Adiabatics:

$$T_D V_A^{\gamma-1} = T_C V_B^{\gamma-1} \Rightarrow T_D = T_C r^{1-\gamma}$$

with the compression ratio $r = V_A/V_B$

- Likewise: $T_A = T_B r^{1-\gamma}$ hence, $\eta = 1 - r^{1-\gamma}$

116

Otto Cycle Comments

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

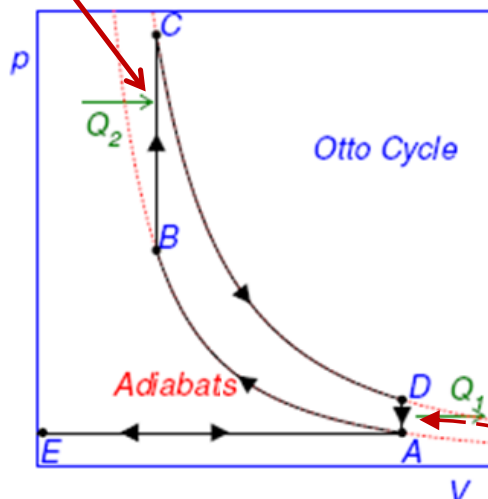
- The efficiency is determined by compression ratio V_A/V_B . Typically limited to about 8-10, otherwise 'pinking' or 'knocking' occurs: the high temperatures generated during compression ignite the mixture before compression is complete- *shock waves* generated - hence sound/engine damage – as well as much reduced efficiency and power output because the gas is being compressed after it has started to burn and so it is hotter.
- For $\gamma = 1.4$, $r = 10$, $\eta \sim 0.6$. Efficiency of real engines likely to be only half of this.
- Diesel engine can use a higher compression ratio (between roughly 15:1 and 21:1 depending on cylinder head design)- as fuel is injected after the compression stroke there is no need to worry about premature ignition. The fuel is injected 'slowly' which keeps the pressure and temperature roughly constant as the gas expands during the combustion phase.

117

Comparison Otto/Diesel Cycles

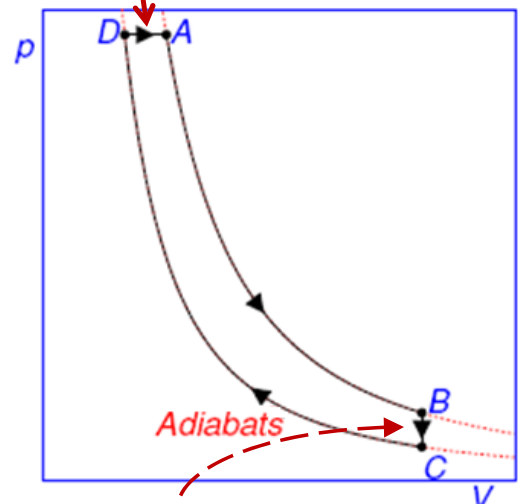
Otto cycle

Gas heated by 'instantaneous' explosion



Diesel cycle

Gas heated by relatively 'slow burn' as fuel is injected



Hot exhaust gas swapped for cold air (+fuel for Otto)

118

Stirling Engine – External Combustion Engine

- Stirling engines are 'external combustion' engines, (cf steam engine)-work by allowing compressed gas to expand in a hot (or hot part of a) cylinder and then moving it to a cold (or cold part) cylinder where it is compressed.
- Relatively small Stirling engines can be very efficient (50%) compared to massive steam turbines (45%: critical temperature for water is 647K – hard to run a 'supercritical' steam turbine). Overall steam turbine power station efficiency about 35-40% max – more efficient if you burn gas first in a gas turbine, then use the waste gas to run a steam turbine (55%).

- Can use any source of heat – for example solar:
Image is of a point focus parabolic mirror with Stirling engine at its centre and its solar tracker at Plataforma Solar de Almería in Spain



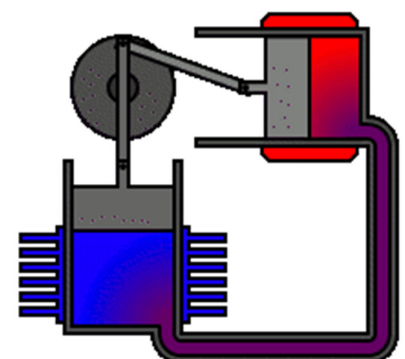
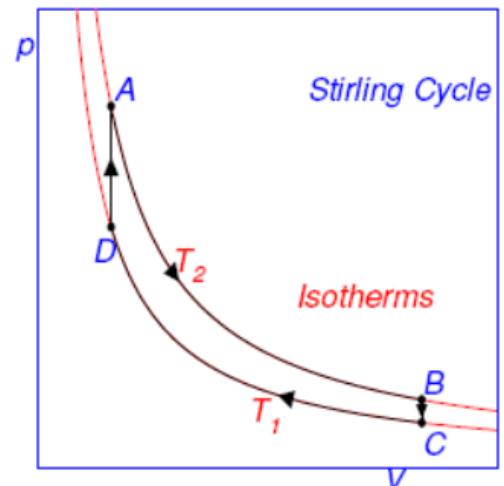
By Psacemat - Own work, CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=31704574> 119

Stirling Engine – Idealised v. Real Cycle

- Ideally a Stirling engine allows compressed gas to expand in a hot cylinder (**A→B**) and then moves it to a cold cylinder (**B→C**) where it is compressed (**C→D**) and then transferred back to the hot cylinder (**D→A**).
- More complex to realise – various ways, eg:

Imagine 2 cylinders 180° out of phase and at the same temperature – if they are connected gas will just flow to and fro between them, no work is done.

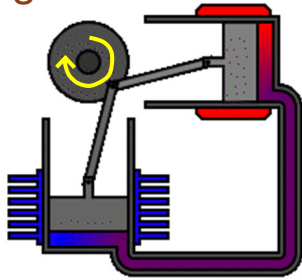
If they are 90° out of phase, at some parts of the cycle the total volume will be small (the gas is compressed) and at others it will be large. The direction of rotation is such that when the gas is getting compressed it is in, or moving to, the cold cylinder so the pressure is kept low and relatively little work is required, whereas as it is expanding it is in, or moving to, the hot cylinder so the pressure is kept high and relatively more work is done. Because the cylinders are in quadrature, at any one time one tends to be moving and the other stationary so you can make sure that as the volume varies the gas is basically in the 'right' temperature cylinder.



https://en.wikipedia.org/wiki/Stirling_engine

Stirling Engine – External Combustion Engine

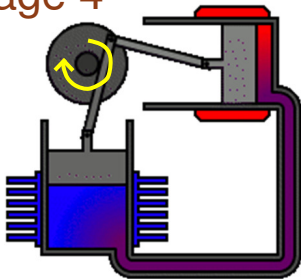
Stage 1



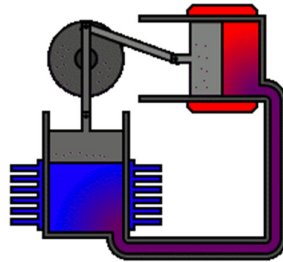
Gas in cold cylinder compressed



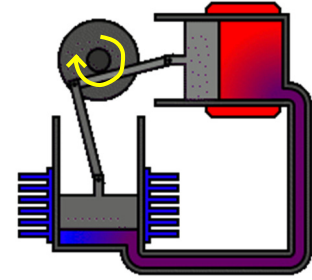
Stage 4



Gas expanding in hot cylinder



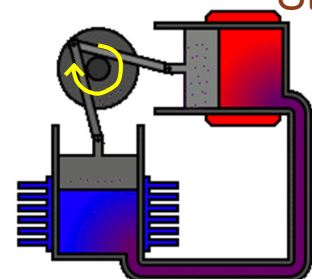
Stage 2



Gas transfer to cold cylinder, gas in cold cylinder expands



Stage 3



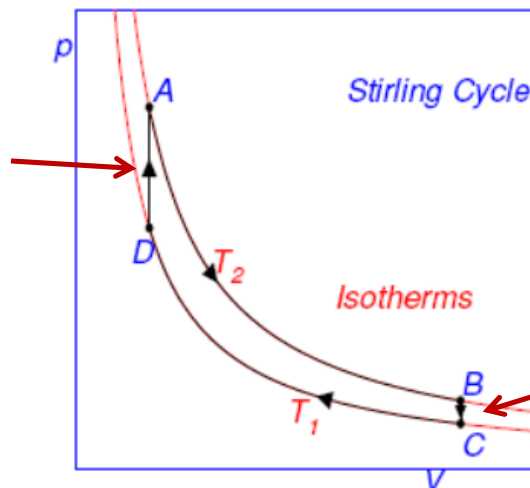
Remainder of gas transferred to cold cylinder and compressed at cold temperature



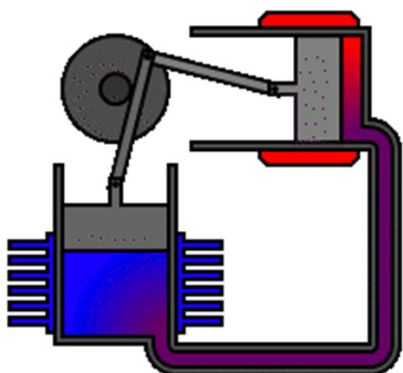
121

Stirling Engine – the Regenerator

Gas must be heated



Gas must be cooled



Connecting pipe may be filled with fine wire to act as a 'regenerator'.

Hot gases entering the pipe are cooled by contact with the pipe/wire, which stores heat

When cold gas goes the other way, it is heated by the wire/pipe

Pipe/wire temperature always close to that of the gas –so heat transfer not too irreversible

122

2.7 Clausius' Theorem and Entropy

- For a Carnot cycle: $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$ i.e. $\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$
- But as far as heat transfer **TO** the engine goes Q_2 and Q_1 have different signs - if one is heat transfer into the engine, the other is heat out. Suppose we have the engine running forwards taking in heat from high temperature T_2 and rejection it at T_1 we could define a reversible heat transfer to the system with $Q_{rev,2} = Q_2$ and $Q_{rev,1} = -Q_1$. We then have:

$$\frac{Q_{rev,2}}{T_2} = -\frac{Q_{rev,1}}{T_1} \text{ i.e. } \frac{Q_{rev,2}}{T_2} + \frac{Q_{rev,1}}{T_1} = 0 \text{ or as an integral } \oint \frac{dQ_{rev}}{T} = 0$$

- For any cycle operating between T_2 and T_1 , Carnot's theorem says $\eta \leq \eta_{rev}$, so for a particular (positive) Q_2 not so much work is produced for an irreversible cycle, so more heat is rejected and $|Q_{irrev,1}| \geq |Q_{rev,1}|$. Given $Q_{irrev,1}$ and $Q_{rev,1}$ are negative we have:

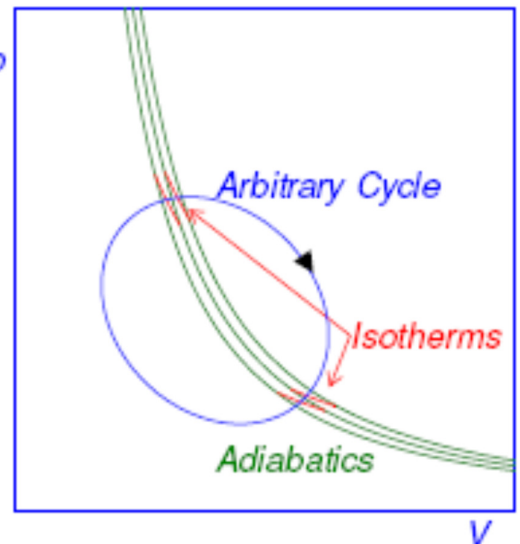
$$\frac{Q_{irrev,1}}{T_1} \leq \frac{Q_{rev,1}}{T_1} \Rightarrow \oint \frac{dQ}{T} \leq 0$$

where the equality applies to a reversible cycle working between fixed temperatures with positive dQ being heat transfer to the engine. 123

Clausius' Theorem

- Once the contents of a system are specified (eg amount of substance) one can vary two parameters – so a state may be represented uniquely by a point on a p-V diagram. A line on a p-V plot may represent a reversible or irreversible change from state to state.
- A reversible path around an arbitrary cycle of any material on a p-V diagram may be found by tiling it with small Carnot Cycles, and the integral $\oint \frac{dQ}{T}$ found by summing over the integrals around each component Carnot cycle in the limit of infinitely thin component cycles (integrals along boundaries common to two component cycles cancel out).
- From this follows Clausius' theorem which states that for any closed cycle:

$$\oint \frac{dQ}{T} \leq 0$$



(with equality if you follow round the cycle with purely reversible steps – but you can also follow round the same cycle with irreversible steps)

- What about convergence of integral over the 'zig-zags'?**

The integral of the work done by the engine: $\int p dV$ clearly converges – its just the area enclosed by the cycle. By conservation of energy this must equal the integral: $\int dQ$ (heat transfer to engine) which therefore must also converge, and since T varies only slightly over a particular 'zig-zag' the integral $\int dQ/T$ will also converge.

Entropy: the definitive definition

- If $\oint \frac{dQ_{rev}}{T} = 0$ for any reversible cycle, then splitting the integral into two parts – from A to B then onwards from B back to A we have:

$$\int_{A, \text{path1}}^B \frac{dQ_{rev}}{T} + \int_{B, \text{path2}}^A \frac{dQ_{rev}}{T} = 0 \quad \Rightarrow \quad \int_{A, \text{path1}}^B \frac{dQ_{rev}}{T} = \int_{A, \text{path2}}^B \frac{dQ_{rev}}{T}$$

- Hence the integral is independent of path and $\frac{dQ_{rev}}{T}$ must be the derivative of a **function of state** known as **Entropy, S**, units JK^{-1} .
- i.e. we can obtain the change in entropy between two states of a system by finding a reversible path between them and integrating dQ_{rev}/T along it:

$$dS = \frac{dQ_{rev}}{T} \Rightarrow \int_A^B \frac{dQ_{rev}}{T} = \int_A^B dS = S(B) - S(A)$$

- S is therefore defined up to some additive constant (**The Third Law addresses the absolute scale of entropy**).

125

Entropy in Irreversible Changes?

- For a **reversible adiabatic change**, $dQ_{rev} = 0 \Rightarrow dS = 0$. Entropy is constant - **isentropic**
- Consider going from A \rightarrow B by an **irreversible** process, and returning to A by a **reversible** change.

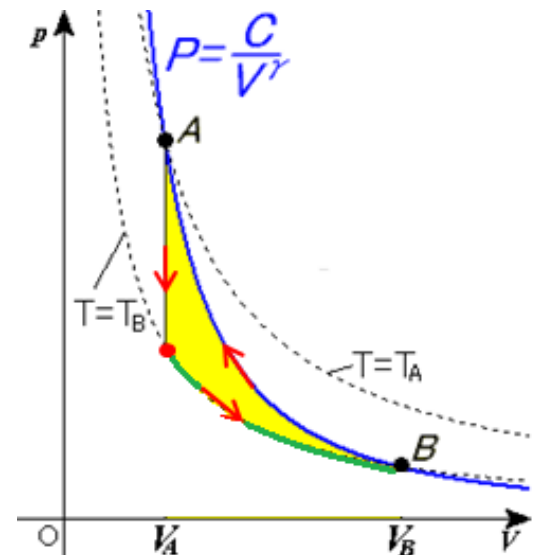
By Clausius' theorem:

$$\int_A^B \frac{dQ_{irrev}}{T} + \int_B^A \frac{dQ_{rev}}{T} \leq 0$$

$$\int_A^B \frac{dQ_{irrev}}{T} - \int_A^B \frac{dQ_{rev}}{T} \leq 0$$

$$\int_A^B \frac{dQ_{irrev}}{T} \leq \int_A^B dS \quad \text{or} \quad dS \geq \frac{dQ}{T}$$

(with equality for reversible process)



126

The law of increase of entropy

- For an isolated system, $dQ_{\text{irrev}} = 0 \Rightarrow dS \geq 0$.

The entropy of an isolated system cannot decrease, but remains constant for reversible changes and increases for irreversible ones.

- Example: Consider two systems at T_1 and T_2 ; allow heat δQ to flow from 2 \rightarrow 1. From above $\delta S_1 + \delta S_2 \geq 0$

$$\delta S_1 = \frac{\delta Q}{T_1} \Rightarrow \delta S_2 = -\frac{\delta Q}{T_2} \Rightarrow \frac{\delta Q}{T_1} - \frac{\delta Q}{T_2} \geq 0$$

- Hence, $T_2 \geq T_1$; heat can only flow from hot to cold!

127

The road to entropy: summary

- Carnot invents his cycle and thus proves you can construct at least one reversible, cyclic heat engine that operates between hot and cold reservoirs. He then uses the second law of thermodynamics to show that all reversible cyclic heat engines operating between the same temperatures have the same efficiency, and that irreversible engines are less efficient.
- The actual efficiency is derived from an ideal gas Carnot cycle and, by considering any cyclic process as broken down into notional constituent Carnot cycles, one can show that for any cyclic process involving heat transfers dQ to the system, $\oint \frac{dQ}{T} \leq 0$ (Clausius' theorem) with equality holding for reversible process.
- Since $\oint \frac{dQ_{\text{rev}}}{T} = 0$ for cyclic reversible processes, there must be a state function defined as $dS = \frac{dQ_{\text{rev}}}{T}$ and spitting a closed cycle into an irreversible path from A to B followed by a reversible one back, the fact that for an irreversible cycle $\oint \frac{dQ}{T} < 0$ means that for an irreversible process $dS > \frac{dQ}{T}$.
- For an isolated system $dQ = 0$, so entropy must always either stay the same if the process is reversible or increase if it is irreversible.

But what about entropy and no of particles?

- The arguments that lead to the development of entropy as a state function apply to cyclic processes with a fixed quantity ('N') of working material, but it is clear that **entropy is extensive for homogeneous systems** – if you double the quantity of working material, the volume, work done and heat transfer all double – so the entropy will also double.
- *But what about the law of entropy increasing for isolated systems??*
Because they are isolated, we are not considering transfer of particles in or out of them,... so the argument stands. If particles are moving around inside the system (e.g. from one side of a partitioned box where they were previously held by the partition, to filling it) – this particle motion is entirely internal to the system – so covered by the arguments that developed the law of increasing entropy.
- So – if we have particles moving from A to B, we must consider the global entropy (*i.e.* entropy of A plus the entropy of B) and this must be increasing for an irreversible change, or be constant for a reversible process.
- (Incidentally: this is why one can do a lot of thermodynamics – as in this 1B course- without worrying about changes in particle numbers – *i.e.* by considering the thermodynamics of closed systems: just put everything in a box.)

129

Entropy of the Universe

- **The universe is certainly an isolated system** (if there is something outside it, then we would say that was part of the universe). The entropy of the universe cannot decrease.
- In the 'standard' big bang model **the universe starts off tiny at very high temperatures in thermal equilibrium – a low entropy state** (heat stored at high temperature, small size). It then expands – but as it does so the 'constituents' move apart and it cools. The lower energies and fewer collisions mean **some aspects 'freeze' out**, or 'slow down' w.r.t. the overall expansion, and go out of equilibrium. e.g. nuclear reactions go out of equilibrium with the cooling photon gas, and we are left with cold low density H gas and some He. **Other irreversible processes can kick in** – collapse of gas clouds under gravity and nuclear 'ignition' in core of new stars. Gravitational/Strong Force 'potential' energy is dissipated to masses of newly created photons. In a typical analysis entropy has increased by a factor of $\sim 10^{25}$ from 'early times'.
- We shall see that the 3rd law dictates that all entropies converge to the same value (taken for simplicity as zero) as temperature approaches absolute zero.
- Thus entropy has a minimum value – so if you look back in time and can go far enough back, there will come a point at which the entropy of the universe is zero. And before that...



- This presents us with what is arguably the fact of greatest philosophical importance in the whole of science. And it is based on the only law of science for which there is pretty universal agreement that it will never be overturned.

130

Entropy and Temperature

- The definition of entropy $dS = \frac{dQ_{rev}}{T}$ gives a new insight into the meaning and significance of temperature, which can be seen to be:

$$1/T = \left(\frac{\partial S}{\partial Q} \right)_{rev}$$

- Temperature is the reciprocal of the rate of entropy change with reversible heat transfer to a system – *i.e.* when the system itself remains in internal equilibrium during the transfer process.
- For two systems to be in thermal equilibrium the global entropy must not change when heat is transferred from one to another, so for a particular transfer of heat the entropy drop of the heat source must equal the entropy increase of the heat sink.
- The condition for thermal equilibrium is that the rate at which entropy changes with heat transfer must be the same for both, and for irreversible change, the heat will transfer to the system that has the highest rate of entropy change with heat transfer (the one with the lowest temperature).

131

Entropy Examples

- Consider two equal bodies of heat capacity C and temp. T_1 and T_2 . Place them in thermal contact.

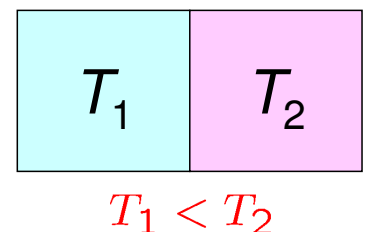
Final temperature $T_f = \frac{1}{2}(T_1 + T_2)$.

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{dQ}{T} = \int_{T_1}^{T_f} \frac{C dT}{T} = C \ln \left(\frac{T_f}{T_1} \right)$$

$$\Delta S_2 = \int_{T_2}^{T_f} \frac{dQ}{T} = \int_{T_2}^{T_f} \frac{C dT}{T} = C \ln \left(\frac{T_f}{T_2} \right)$$

$$\Delta S_{total} = C \ln \left(\frac{T_f}{T_1} \right) + C \ln \left(\frac{T_f}{T_2} \right)$$

$$= C \ln \left(\frac{T_f^2}{T_1 T_2} \right) = C \ln \left(\frac{(T_1 + T_2)^2}{4 T_1 T_2} \right) > 0$$



ΔS for irreversible processes?

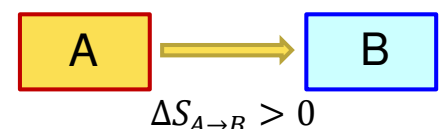
- We only know how to calculate an entropy change for reversible changes according to the rule:

$$\Delta S = \int \frac{dQ_{rev}}{T}$$

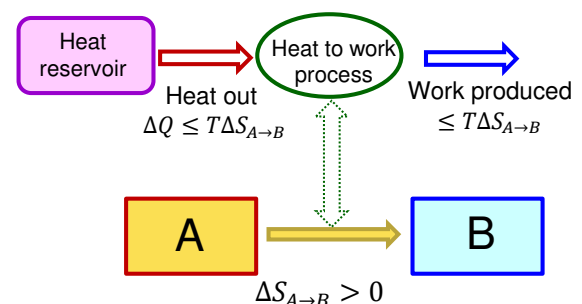
- Entropy is a state function so, to calculate the entropy change for an *irreversible* process that starts at state A and finishes at B, we can find a set of *reversible* steps that link A and B and apply the entropy formula.
- E.g.* Joule expansion (sudden expansion of a gas from V_A to V_B). It's an ideal gas, there is no temperature change—so calculate ΔS from an equivalent isothermal reversible expansion.
- E.g.* Heat Q transferred from hot body (A) to cold body (B) is irreversible—but as far as body A goes, provided all of A is at the same temperature at any one time (i.e. it is in internal thermal equilibrium), the effect is the same as transfer of heat Q to a body C in a reversible way—i.e. by maintaining the temperature of C just an infinitesimally bit lower than that of A. So, the entropy change of body A is simply $\Delta S_A = \int \frac{dQ}{T}$ whether the heat is transferred out reversibly (to a body at the same temperature) or irreversibly (to a body at a lower temperature)

So why can an irreversible process be harnessed to give work?

- Suppose we have an isolated system which undergoes an irreversible change from state A to state B (for example a gas expands to fill a box)—then its entropy increases, $\Delta S_{A \rightarrow B} > 0$



- If, somehow, you can couple the A to B conversion to a process that takes heat out of a reservoir and turns it into work, this would be allowed thermodynamically: the decrease in entropy due to the removal of heat from some reservoir could be balanced by the increase in entropy when A converts to B.



- This coupling of an irreversible process to a heat reservoir is exactly what is done when, instead of just letting a gas expand into an empty container, you expand it reversibly against a piston—i.e. convert Joule expansion to reversible isothermal expansion.
- Note that, as always, **thermodynamics does not tell you how to do the coupling of irreversible process to heat to work conversion**—merely that if you could think of a way of doing it, it would be allowed, and tells you the maximum heat you could convert to work.

2.8 Entropy and the 1st law

- For a reversible change, we can now write (for a p - V system):

$$dU = \underbrace{TdS}_{\delta Q_{\text{rev}}} - \underbrace{pdV}_{\delta W_{\text{rev}}}$$

- dU is expressed in terms of functions of state. Therefore this expression is **always true**, even for irreversible processes. This is very powerful.

- We can clearly generalise for other forms of work δW as introduced previously

$$dU = TdS + \sum_i X_i dx_i$$

135

The thermodynamic master equation

- For a p - V system and fixed no of particles we have:

$$dU = TdS - pdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

But at the start of the course we noted that the state variables of a single component system in flux that could achieve equilibrium are uniquely defined by specifying the size of the box, the number of particles and the internal energy. This means that any function of state of such a system, such as its entropy, can be expressed as a function of U, V and N , i.e.

$$S = S(U, V, N) \quad \text{and inverting gives:} \quad U = U(S, V, N)$$

From which we can deduce that we can add an extra term to our equation for dU to give what becomes the entry point of analytical thermodynamics:

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

The 'master equation' $dU = TdS - pdV + \mu dN$

Where we have defined: $\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}$

136

Master equation and chemical potential

$$dU = TdS - pdV + \mu dN$$

- This **master equation** is produced by combining the 0th (gives T) the 1st ($dU = \delta q + \delta W = \delta q - pdV$) and second laws ($TdS = \delta q_{rev}$) and the fact that a single component p - V system is defined by its V, U and N .
- It is at this point that the chemical potential (turns out to be the Gibbs free energy per particle) inauspiciously enters thermodynamics:

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

- Rearranging the master equation we have:

$$dS = \frac{dU}{T} + \frac{p}{T} dV - \frac{\mu}{T} dN$$

And we can see that:

- T relates to how fast entropy changes when we change the energy,
- p/T to how fast entropy changes when we change V
- μ/T to how fast entropy changes when we change N

So $T, p/T, \mu/T$ will control the equilibrium w.r.t movements of heat, volume and particles.

137

2.9 Heat capacities, latent heats

- Express heat capacities in terms of entropy:

$$C_V = \left(\frac{dQ}{dT} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad \text{likewise} \quad C_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

- **Latent heat** - amount of heat to convert unit mass (or mole) from one phase to another.

$$L = \Delta Q = T(S_2 - S_1)$$

where S_1 and S_2 are the entropies of the corresponding amount of the substance in the two phases.

Explains observation that melting + boiling points scale roughly as the latent heats, as the changes in the way you can order the atoms in going from one solid to liquid or liquid to gas is fairly substance and temperature independent.

	Bpt/K	Heat of Vap. (kJ/mol)	ΔS of Vap. (J/K/mole)
H₂	20	0.46	23
Ne	27	1.7	63
Butane	273	21	77
NH₃	240	23	97
H₂O	373	41	109
Al	2792	294	105
Fe	3134	340	108

- Entropy is usually different in different phases.

138

2.10 Entropy of ideal gas (I)

- Note: Introduction of entropy does not increase the number of independent thermodynamic variables; as a function of state, for fixed particle number it can be expressed in terms of any two others. Recall: a system is defined by its contents, the size of the box and its energy
- For an ideal gas we can work out the entropy change from the master equation (1st law expressed in state variables)

$$dU = C_v dT = T dS - p dV$$

$$\Rightarrow dS = \frac{C_v dT}{T} + \frac{p dV}{T} = \frac{C_v dT}{T} + \frac{nR dV}{V} \quad (\text{using } pV = nRT).$$

- Integrate along any (T, V) path- remember U and C_v for an ideal gas do not depend on V , and that this is for a fixed n :

$$S = C_v \ln T + nR \ln V + S_0(n)$$

$S_0(n)$ is the constant of integration (non-trivial to derive from Stat. Thermo.).

- The V dependence of S from can also be derived from isothermal expansion: the work done is $nRT \ln \left(\frac{V_1}{V_0} \right)$ which is equal to the reversible

heat transfer – so the entropy change is: $\Delta S = \frac{dQ_{rev}}{T} = nR \ln \left(\frac{V_1}{V_0} \right)$

139

2.10 Entropy of ideal gas (II)

$$S = C_v \ln T + nR \ln V + S_0(n)$$

- But: this expression for S is not properly extensive, and we have prior knowledge that it must be (if you double the size of the system you double the heat transfer to it and double $dS = dQ_{rev}/T$). We can use the flexibility we have with $S_0(n)$ to make it extensive.
- C_v is proportional to n , and its extensive nature can be seen explicitly if it is written in terms of the heat capacity per mole: $C_v = nC_{v,m}$
- But, when you double n , and double the volume, ' $nR \ln V$ ' becomes:

$$2nR \ln 2V = 2nR \ln V + 2nR \ln 2.$$

Doubled as required

Extra term that stops S being extensive

Make extensive by splitting the $S_0(n)$ term into $S_0(n) = nS'_0 - nR \ln n$ where S'_0 is a constant (which can be, and is, material dependent):

$$S = nC_{v,m} \ln T + nR \ln V + nS'_0 - nR \ln n$$

$$= nC_{v,m} \ln T + nR \ln \left(\frac{V}{n} \right) + nS'_0$$

140

‘Heat’ and ‘Configuration’ Entropy

● Ideal gas entropy: $S = nC_{v,m} \ln T + nR \ln(V/n) + nS'_0$

↑
‘heat’ component

←
‘configuration’ component

- For isothermal expansion of an ideal gas the volume component of the entropy increases, but the heat component does not change. **BUT** the entropy change ($dS = dQ_{\text{rev}}/T$) is determined from the reversible heat transfer to the gas (which is converted to work).
- Why does the trick of using $dS = dQ_{\text{rev}}/T$ work to give purely configurational entropy changes? We specify that the change be reversible, so if the configurational entropy of the gas increases, the entropy of something else (in this case the reservoir) must decrease by the same amount: $dS = dQ_{\text{rev}}/T$ is actually calculating the drop in reservoir entropy.
- In reversible adiabatic (= no heat transfer) expansion – the entropy remains the same: as the gas expands the configurational contribution increases, and the heat contribution decreases. So going from V_1, T_1 to V_2, T_2 :

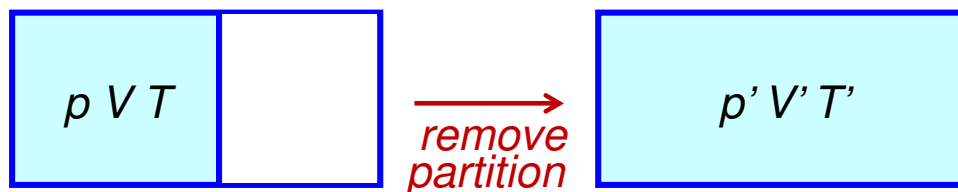
$$C_{v,m} \ln T_1 + R \ln(V_1) = C_{v,m} \ln T_2 + R \ln(V_2)$$

⇒ $T_1 V_1^{\frac{R}{C_{v,m}}} = T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ as derived previously.

141

2.11 Entropy and Joule expansion

- Expansion of gas into vacuum: $\Delta U = \Delta Q = \Delta W = 0$



- $\Delta U = 0 \Rightarrow \Delta T = 0$ for an ideal gas $\Rightarrow T = T'$.

Therefore for 1 mole of gas: $\Delta S = C_V \ln \left(\frac{T'}{T} \right) + R \ln \left(\frac{V'}{V} \right) = R \ln \left(\frac{V'}{V} \right)$

- set $V' = 2V$. $\Rightarrow \Delta S = R \ln 2$: the configuration entropy has increased

- There is no connection to a reservoir, and no corresponding drop in reservoir entropy – so the global entropy increases as expected for an irreversible process.

2.12 Entropy of mixing

- Consider two different gases separated by a partition.



- Remove partition, to allow gases to separately expand into the whole space – *i.e.* mix. Using

$$S = nC_{v,m} \ln T + nR \ln \left(\frac{V}{n} \right) + S'_0(n)$$

we have: $\Delta S = n_1 R \ln \left(\frac{V_1 + V_2}{V_1} \right) + n_2 R \ln \left(\frac{V_1 + V_2}{V_2} \right)$

which is > 0 . "**Entropy of mixing**".

143

Entropy of mixing (contd.)



$$\Delta S = n_1 R \ln \left(\frac{V_1 + V_2}{V_1} \right) + n_2 R \ln \left(\frac{V_1 + V_2}{V_1} \right)$$

- But if the two gases are the same, ΔS should be zero, which conflicts with the above result. "**Gibbs' paradox**".
- When we look at statistical thermodynamics, we shall see we have to be careful to treat distinguishable and indistinguishable particles differently.

144

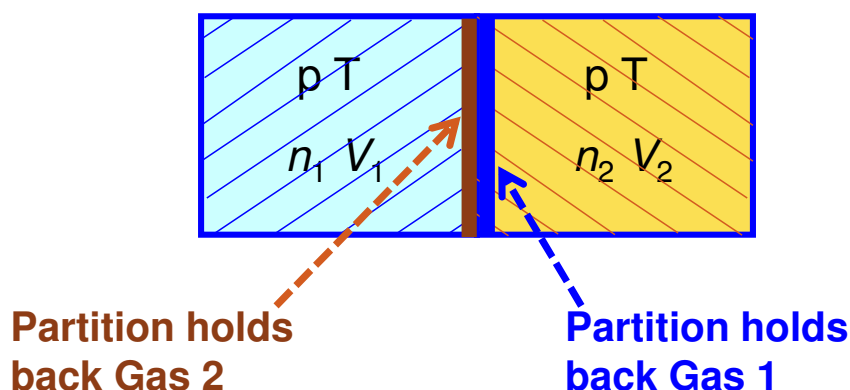
Gibbs' Paradox Explained I

- In classical **thermodynamics the entropy change for an irreversible process is determined by finding an equivalent set of reversible steps** that will take the system between identical start/end conditions and then using the defining equation for entropy change: $\Delta S = \Delta Q_{rev}/T$. **The Gibbs' paradox arises simply because this procedure has not been followed.**
- We have said quite loosely that Gas 1 (in V_1) and Gas 2 (in V_2) are separately allowed to expand into the combined volume but have not specified a series of reversible steps that would allow this to happen, and have used the formula that gives the ΔS for the isothermal expansion of a gas from V_1 to V_1+V_2 . **The first step therefore is to find a series of reversible steps that allow gas 1 and gas 2 to mix in a reversible way.** We find that such steps rely on being able to treat the 2 gases differently and no series of steps can be found if the gases are the same, so the formulae do not apply to identical gases and there is no paradox.

145

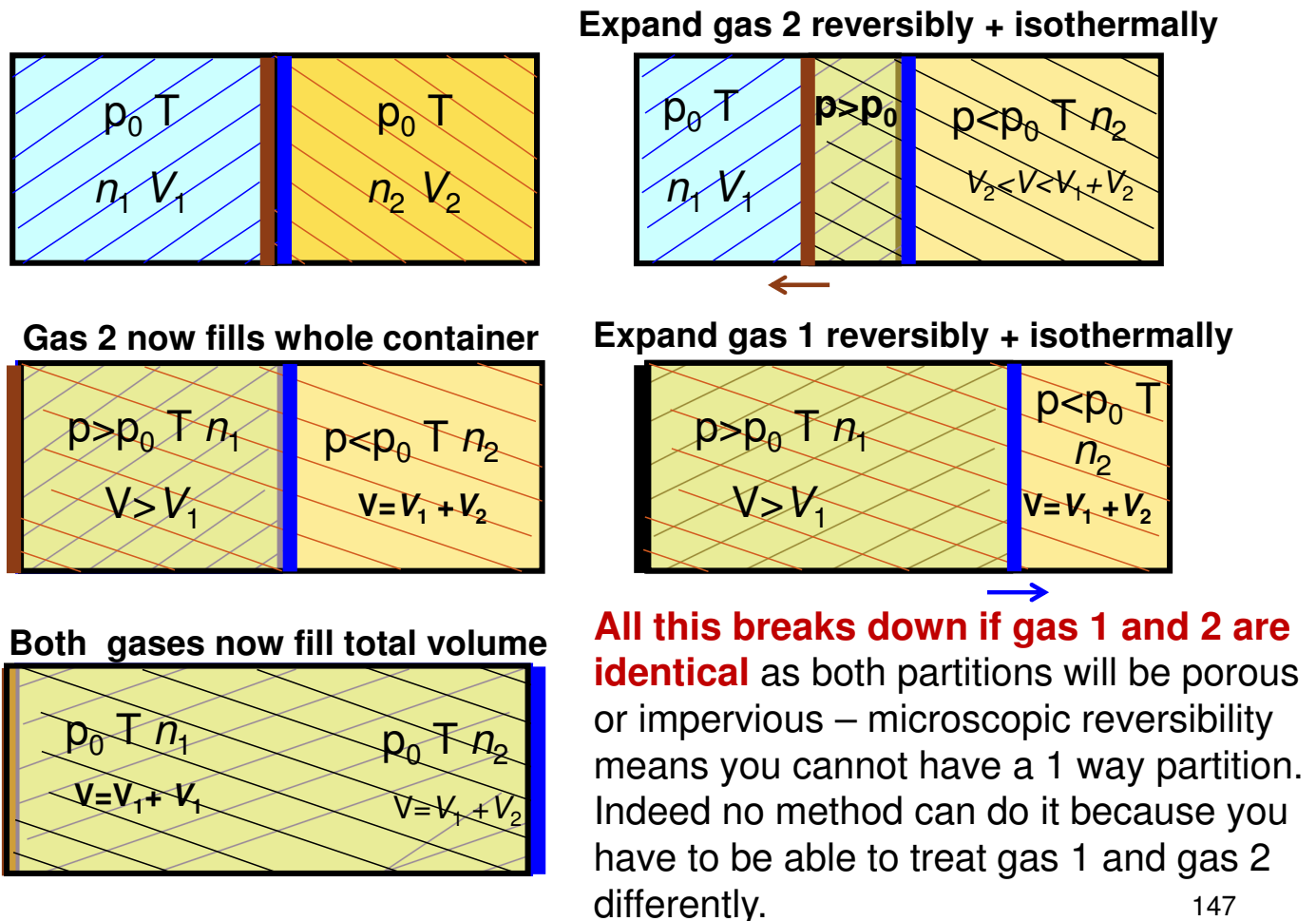
Gibbs' Paradox Explained II

- One possible reversible scheme for the mixing process is as follows. Make the partition between gas 1 and 2 a double one – with the partition on the gas 1 side permeable only to gas 1 and the partition on the gas 2 side permeable only to gas 2. One of these semipermeable partitions could be crossed by narrow channels that only allow the smaller of the two gas species to pass through and the other could be a membrane that allowed the dissolution and hence permeation of only the other species through it.



146

Gibbs' Paradox Explained III: steps for non identical case



147

Gibbs' Paradox 'discontinuity'

- There has historically been some heartache over the problem that if you consider distinguishable particles (A is red, B is white) and let the colour of A fade – there comes a point where you have to suddenly go from treating them as distinguishable to indistinguishable – so there will be a step change in the expressions for entropy.
- There are various things that are being forgotten here. The first is that this whole point of thermodynamics is produce useful equations to **describe** what happens. IF there is some process in nature that depends on a difference between particles then we need a description that handles this, and if not, then not: there is a step change in the description framework between these two cases. IF there is no process in nature that depends, for example, on the difference in masses between isotopes of an element, then there is nothing for us to describe, but as soon as we discover a property that does depend on the mass difference then we need to change our description to reflect the fact that, for example, we could now harness work from the process of mixing of the two isotopes. If you cannot tell the difference, you cannot produce work when they mix and their mixing is of no consequence in nature. The question is can *nature* tell the difference between very pale pink and white: if so they are distinguishable and if not they are not.
- Besides **whoever heard of an molecule that could continuously change its colour and fade into being another one...** there is only a point in trying to make scientific methods which describe the world as it is: if you invent a new version of nature, goodness knows what contradictions and fundamental flaws may be involved in what you propose (sometimes we don't even seem able to make a decent bike light). At least the (non human) world we have is self consistent and works, even if we don't always understand it. If there are properties of particles that can be continuously changed (for example their position or their velocity), then thermodynamics already can handle these as they will be occurring already in nature.

2.13 Entropy and degradation of energy

- The work (which must come from heat somewhere) that can be extracted from a system in some change is:

$$\delta W = \delta Q - dU \leq T_0 dS - dU$$

(T_0 is the temperature of the body from which the heat is extracted)

- δW is maximal when the equality is satisfied, *i.e.* for a reversible process. (*c.f.* Carnot's original insight)
- If entropy increases without a change in internal energy, then less of this internal energy can be converted to work. This is described as the 'degradation of energy'. Heat in a hot reservoir is stored in a low entropy system, but once it has flowed to a lower temperature it is stored in a higher entropy way and less can be converted to heat. In a gas at high pressure, a lot of internal energy can be converted to work by expanding the gas against a piston (the gas cools as you do this) – but once the gas has undergone Joule expansion – it has the same internal energy but a lower pressure – so when you expand the gas further, less work is done per increase in volume.

149

Why is work so important/useful

- Work is considered to be done when energy is transferred from one place to another by action on some constraint in a mechanical system. A rope linked to moving lorry, passed over a pulley to a weight links the motion of the lorry to the height of the weight and enables KE of the lorry to be transferred to PE of the weight and the concept of work is used to quantify the change which occurs, the amount the lorry slows as the weight rises.
- Work is also necessary to create a change or maintain a rate of change when some macroscale object/motion is linked to microscale 'degrees of freedom'.
 - A key concept was a 'switch' – we have a system 'located' by some potential energy barrier, something requiring more energy to surmount than the thermal fluctuations can supply (or are likely to supply on some accepted time scale: the larger the fluctuations the rarer they are). To get the system over this barrier requires work, which is dissipated to heat once the barrier is crossed.
 - Motion of solid on solid shows friction which corresponds to a whole series of energy barriers. Work is needed to overcome this multitude of successive barriers.
 - Motion involving fluids can be slowed by 'drag': the fluid molecules are not in a fixed position so the macroscopic KE of a macroscopic object can be dissipated into motion of individual molecules in contact with the macroscopic object. Work is needed to maintain a macro object's velocity in the presence of drag.
 - Work is also needed to force backwards what otherwise would be an irreversible change, to reduce the entropy of some part of a system: this is possible because the work is converted to heat that makes a compensating increase in the entropy in another part of the total system.
 - Work (as per above reasons) is needed to make the 'change' required to change a constraint that then enables an irreversible process to proceed. It takes work to remove an barrier or to change a configuration so that thermal contact is made between hot and cold bodies. 150

Chapter 2 - Summary

- Irreversible processes arise because we only reverse the macroscopy constraints on a system, but leave the motion of the constituents to propagate forwards.
- A process can be executed reversibly by moving in small steps from equilibrium to equilibrium.
- **The 2nd Law:** Kelvin **“No process is possible whose only effect is the complete conversion of heat into work.”** (you cannot power a ship by ‘anti dissipation’, e.g. by just extracting heat from sea water and converting it to work: dissipation goes only one way.)
- Equivalent to Clausius **“No process is possible whose effect is only to transfer heat from a colder to a hotter body.”** (i.e. heat flows only one way, from hot to cold.)
- More generally **“The direction of an irreversible process is determined by the states of the system”** (or ‘there are irreversible processes’, or ‘reversible means reversible’)
- The Carnot engine is a notional reversible cyclical process running along two isotherms connected by two adiabats with efficiency:

$$\eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$
- Carnot's Theorem: **“No engine operating between two reservoirs can be more efficient than a Carnot engine”**
- Corollary to Carnot's Theorem: **“All reversible engines operating between two temperatures have the same efficiency as a Carnot engine”**

151

Chapter 2 - Summary

- Heat engine, refrigerator, heat pump. Other cycles. Key point: $\frac{|Q_1|}{T_1} = \frac{|Q_2|}{T_2}$ for a reversible heat engine working between temperatures T_1 and T_2 . Can define a thermodynamic temperature scale in terms of Q – equivalent to ideal gas scale.
- **Clausius' Theorem** for a closed cycle, derived from Carnot's theorem and its corollary:

$$\oint \frac{dQ}{T} \leq 0$$
 where the equality applies for a reversible cycle, dQ is heat transfer TO engine
- Clausius' theorem implies a state function, entropy, defined by

$$dS \equiv \frac{dQ_{\text{rev.}}}{T}$$
- Entropy remains the same for an isolated system if it undergoes only reversible processes, but rises for irreversible ones.
- **The entropy of an isolated system cannot decrease.** The Universe by definition is an isolated system, and it is therefore hard to see how it does not have an origin from anything other than something that functions in a very different way to what we see now. The ‘start of Big Bang’ was a very low entropy state.

152

Chapter 2 - Summary

- By considering a reversible path, the First Law can be re-written as

$$dU = TdS - pdV \quad \text{for any change; not just reversible ones.}$$

- Energy, volume and no of particles define a system so $S = S(U, V, N)$ which means we have $U = U(S, V, N)$ and hence the extension of first law to give thermodynamics 'master equation'.

$$dU = TdS - pdV + \mu dN$$

defining the 'chemical potential as: $\mu = \left(\frac{\partial U}{\partial N} \right)_{V,S}$

- Entropy of an ideal gas is of the form:

$$S = nC_{v,m} \ln T + nR \ln(V/n) + S'_0(n)$$

- The requirement for irreversible change in a multiparticle system is global entropy increase. Energy is conserved, but is degraded, irreversibly dissipated as change occurs.
- Work is the 'currency' we use to quantify changes which involved the transfer of energy via the movement of a constraint and occur on the macro scale. Heat is stored in the microscale motions of the constituents and heat flow is a result of microscale motion and fluctuations.