Classical Thermodynamics

1. Introduction

1.1 Preliminaries

1.2 Reminder of key IA results

1.3 Partial differentiation

D.R. Ward; Lent 2007

1.1 Preliminaries

- What is Thermodynamics?
  The study of heat, and its relationship to other forms of energy, such as mechanical energy (kinetic and potential). Can also include other forms of energy such as electromagnetic.
- Why Classical?
  In this context, treating the systems under study as continuous; largely neglecting detailed events at atomic/molecular level.
- Obviously, the microscopic approach is more fundamental; need to model collisions and forces between molecules. e.g. describe pressure of a gas in terms of momentum changes in individual collisions (see IA course).

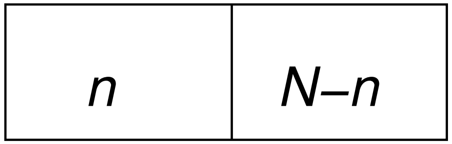
Quotes

- "Thermodynamics is the only physical theory of universal content which, within the framework of the applicability of its basic concepts, I am convinced will never be overthrown." *Albert Einstein*
- "The law that entropy always increases - the Second Law of Thermodynamics - holds, I think, the supreme position among the laws of physics. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations - then so much the worse for Maxwell's equations. If it is found to be contradicted by observation - well, these experimentalists do bungle things from time to time. But if your theory is found to be against the Second Law of Thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation." *Sir Arthur Eddington*

Statistical thermodynamics

- Macroscopic properties (such as pressure) emerge as statistical averages over many molecules; number typically $\mathcal{O}(N_{\mathrm{A}})$ – Avogadro's number.
- The above approach is called Statistical Thermodynamics, and is the main subject of Dr W Allison's *Advanced Physics* course.
- The two approaches are complementary. Although statistical approach is more fundamental, we may not have the detailed knowledge to calculate it precisely. The classical approach may often be simpler and more practical.
- n.b. Classical approach doesn't tell the full story – neglects statistical fluctuations. For example:

Statistical c.f. classical



- N atoms in a box. Classically, expect equal numbers in each half, i.e. $n = \frac{1}{2}N$.
- Statistically, numbers in each half (n and $N - n$) are given by Binomial distribution

$$P(n) = \frac{N!}{n!(N-n)!}$$

whose r.m.s.="$\sqrt{Np(1-p)}$"$= \frac{1}{2}\sqrt{N}$.

- So, classical assumption of equal numbers is likely to be inaccurate by $\sim \frac{1}{2}\sqrt{N}/\frac{1}{2}N = 1/\sqrt{N}$. Since $N \sim N_{\mathrm{A}}$, this is $\mathcal{O}(10^{-12})$; tiny.
- Classical approach works because N_{A} is so large.

Applicability of Thermodynamics

- In most of this course will be discussing gases (often ideal gases).
- This is useful pedagogically (for example the ideal gas has a nice simple equation of state, $pV = RT$), and important historically, but it is important to emphasise that thermodynamics is very fundamental in physics and has far wider validity.
- For example thermodynamics can be equally applicable to microscopic matter at very high density (e.g. atomic nuclei, neutron stars, quark-gluon plasma) and to the whole universe (big-bang cosmology etc.).

Outline of Course

1. Introduction; revision of IA material
2. Fundamentals; 0^{th} and 1^{st} laws
3. The Second Law and Entropy; heat engines
4. Analytical Thermodynamics
5. Thermodynamics of Radiation
6. Real gases
7. Phase Changes
8. Third law

Books:
C.J.Adkins *Equilibrium Thermodynamics* main recommendation (3^{rd} edition, CUP, 1983).; also
R.Bowley and M.Sánchez *Statistical Mechanics* (OUP 1996)

1.2 Revision of IA Thermal Physics

Kinetic theory of gases – basic assumptions:

- Identical particles in random motion.
- **Small** solid spheres – occupy negligible volume.
- Elastic collisions.
- No long range forces. Only forces during collisions. ⇒ no potential energy.
- Internal energy is just kinetic energy = $\frac{1}{2}mv^2$ per particle.

Kinetic Theory – key results

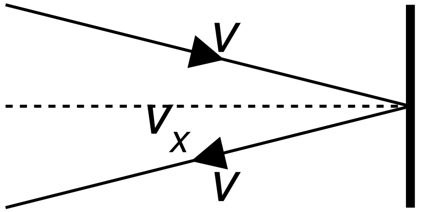
- Pressure is given by

  $$\boxed{p = \frac{1}{3} nm\overline{v^2}}$$

  where p=pressure; n=number of molecules per unit volume; m=their mass; $\overline{v^2}$=mean squared velocity.

- Flux (i.e. number of collisions per unit time per unit area) is given by

  $$\boxed{J = \frac{1}{4} n\overline{v}}$$



- Momentum change in collision $=2mv_x$
- No. hitting unit area / unit time $=nv_x f(v_x)\mathrm{d}v_x$
- Integrate: $p = \int_0^\infty 2mv_x \cdot nv_x f(v_x)\mathrm{d}v_x = nm\overline{v_x^2}$
- n.b. $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}$

Boltzmann factor

- In thermal equilibrium at temperature T, the probability of being in a state of energy E_i is
  $$\boxed{P(E_i) \propto g(E_i)e^{-E_i/kT}}$$
  where $g(E_i)$ is the degeneracy of the state E_i; k is Boltzmann's constant (often written k_{B}).
- Or, if E has a continuous distribution, the probability distribution function for E is
  $$\boxed{P(E) \propto g(E)e^{-E/kT}}$$
  where $g(E)$ is the density of states.
- The constant of proportionality is determined by normalisation of the probability to unity.

Maxwell-Boltzmann distribution

- Applied to the velocity distribution in an ideal gas:

  $$\boxed{P(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-mv_x^2/2kT}}$$

  for one component, or

  $$\boxed{P(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \cdot 4\pi v^2 \cdot e^{-mv^2/2kT}}$$

  Maxwell-Boltzmann distribution.

- By integrating:

  $$\overline{v} = \int_0^\infty P(v) v \mathrm{d}v = \sqrt{\frac{8kT}{\pi m}}$$

  and

  $$\overline{v^2} = \int_0^\infty P(v) v^2 \mathrm{d}v = 3kT/m$$

Internal energy of ideal gas

- The latter gives $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$.
- This is an example of the equipartition theorem – in thermal equilibrium, energy = $\frac{1}{2}kT$ per degree of freedom.
- Internal energy per unit volume for monatomic ideal gas $u = n \cdot \frac{1}{2}m\overline{v^2} = \frac{3}{2}nkT$ i.e. just translational kinetic energy.
- Or, for one mole; $n = N_\mathrm{A}/V$, hence the internal energy is

  $$\boxed{U = \frac{3}{2}RT}$$

  where the ideal gas constant $R \equiv N_\mathrm{A}k$.

Ideal gas equation

- From Maxwell-Boltzmann, we have $\overline{v^2} = \int_0^\infty P(v) v^2 \mathrm{d}v = 3kT/m$ and so

$$p = \frac{1}{3} nm\overline{v^2} = nkT$$

- or for one mole, $n = N_\mathrm{A}/V$, and hence

$$\boxed{pV = N_\mathrm{A}kT \equiv RT}$$

- This is the "equation of state" for an ideal gas.

Mean Free Path

- Particles in a gas undergo a random walk. As it moves, each molecule sweeps out cylinder of radius a (where a is the molecular diameter) and collides with any molecule whose centre lies within this volume.
- Yields mean free path:

  $$\lambda = 1/\sqrt{2}\pi a^2 n$$

  where the $\sqrt{2}$ results from a careful treatment of velocity distributions.
- Actual path lengths follow an exponential distribution

  $$f(x)\mathrm{d}x = \frac{1}{\lambda}e^{-x/\lambda}\mathrm{d}x$$

  of which λ is the mean.

1.3 Partial differentiation

Motivation:

- A gas (for example) can be described by (p, V, T) . But not independent; they are related by the equation of state, i.e. $pV = RT$ in the case of 1 mole of an ideal gas. A real gas would have a similar, but more complicated, equation of state.
- Can express other properties of gas as functions of *any* two of (p, V, T); e.g. internal energy $U = U(V, T)$, or $U = U(p, T)$, but can't express in terms of just one.
- Therefore functions of two variables (or sometimes more) are commonplace in Thermodynamics. Hence partial differentiation is required.

Partial differentiation

- Given some function $f(x, y)$

$$\left(\frac{\partial f}{\partial x}\right)_y \equiv \lim_{\delta x \to 0} \frac{f(x+\delta x, y) - f(x, y)}{\delta x}$$

  and likewise $\left(\frac{\partial f}{\partial y}\right)_x$

- So, for a general small change $(\delta x, \delta y)$ in (x, y):

$$\delta f = f(x+\delta x, y+\delta y) - f(x, y) = \left(\frac{\partial f}{\partial x}\right)_y \delta x + \left(\frac{\partial f}{\partial y}\right)_x \delta y + \mathcal{O}(\delta^2)$$

- Taking the limit as $\delta x,\ \delta y \to 0$:

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

Change of variables?

- Change between $f(x, y)$ and $f(x, z)$ where $z = z(x, y)$?

$$\begin{aligned}
\mathrm{d}f &= \left(\frac{\partial f}{\partial x}\right)_z \mathrm{d}x + \left(\frac{\partial f}{\partial z}\right)_x \mathrm{d}z \\
&= \left(\frac{\partial f}{\partial x}\right)_z \mathrm{d}x + \left(\frac{\partial f}{\partial z}\right)_x \left[\left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y\right] \\
&= \underbrace{\left[\left(\frac{\partial f}{\partial x}\right)_z + \left(\frac{\partial f}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y\right]}_{=\left(\frac{\partial f}{\partial x}\right)_y} \mathrm{d}x + \underbrace{\left(\frac{\partial f}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x}_{=\left(\frac{\partial f}{\partial y}\right)_x} \mathrm{d}y
\end{aligned}$$

- ⇒ "Chain Rule" $\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x$

Useful theorems

- Start from

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

- Can write $x = x(y, z)$:

$$\begin{aligned} dz &= \left(\frac{\partial z}{\partial x}\right)_y \left[\left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz\right] + \left(\frac{\partial z}{\partial y}\right)_x dy \\ &= \underbrace{\left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x\right]}_{\equiv 0} dy + \underbrace{\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y}_{\equiv 1} dz \end{aligned}$$

Useful theorems

- Hence we have the “Reciprocal Theorem”

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1 \quad \text{or} \quad \left(\frac{\partial z}{\partial x}\right)_y = 1 \Bigg/ \left(\frac{\partial x}{\partial z}\right)_y$$

- and the “Reciprocity theorem”

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

- And (from two pages ago) the Chain rule

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x$$

Classical Thermodynamics

2. Fundamentals

2.1 Basic concepts

2.2 Zeroth law of thermodynamics

2.3 First law of thermodynamics

2.4 Applications of first law

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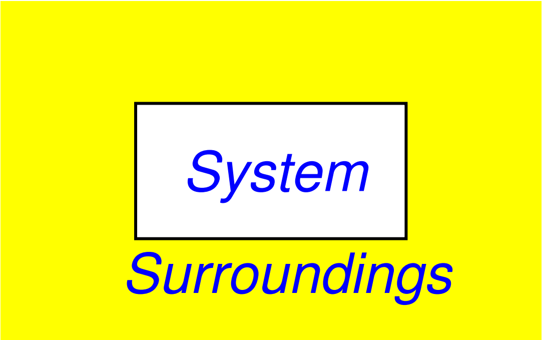
2.1 Basic ideas



- System and surroundings.
- System may exchange energy with surroundings (e.g. electrical or mechanical work, or heat). Need to specify carefully the nature of a boundary.
- If boundary walls are fixed/rigid $\Rightarrow$ no mechanical work.
- If heat cannot flow "Thermally isolated" (e.g. a thermos flask). The change is "adiabatic"
- If walls not adiabatic, so that heat can flow, the system is in "thermal contact" with its surroundings. When heat stops flowing, the system is in "thermal equilibrium" with the surroundings.

Thermodynamic variables

- Thermodynamic variables are observable properties of a system, e.g. for p, V, T for a gas, with well defined values. They fall into two categories:
- “Extensive” variables are proportional to how much stuff we are considering, e.g. volume V.
- “Intensive” variables are defined locally (i.e. for a small element of the substance) and don’t depend on the quantity of stuff. e.g. pressure, temperature.
- In Thermodynamic equilibrium the values are in a steady state. Equilibrium may be stable, unstable or metastable.
- Intensive and extensive variables form conjugate pairs, whose product has dimensions of energy.

Thermodynamic variables

Some pairs of thermodynamic variables:

System	Intensive	Extensive
Gas	p pressure	V volume
Thin wire	$\mathcal{F}$ tension	x extension
Surface film	γ surface tension	A area
Magnetic	B field	M Magnetic momen
Electric	E field	P Electric dipole
Any	T temperature	S entropy

Reversibility

- A subtle, but important concept.
- A change is reversible if an infinitesimal change in external conditions would reverse direction of change.
- Typically a very slow, quasi-static change.
- Frictionless; no viscosity, turbulence etc.
- e.g. Cylinder of gas with piston; $F = pA$ in equilibrium.

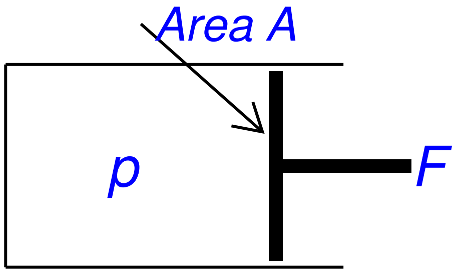
  Very small reduction in F –

  gas expands slowly.

  Reversible change → well

  defined $p - V$ curve, e.g. $pV = RT$.

  c.f. sudden change in piston – gas expands abruptly, not all at constant p, waves etc. Irreversible.



2.2 Zeroth law of thermodynamics

- Reminder – thermal equilibrium $\Rightarrow$ system and surroundings in thermal contact and no heat flow occurs.
- "0^{th} Law":

> If two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.

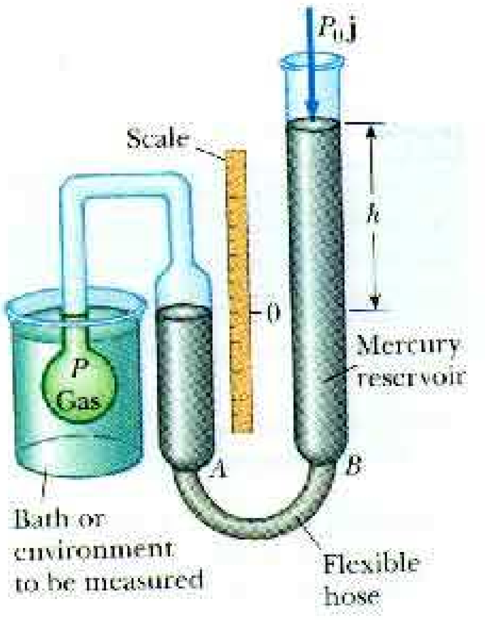
- For example, the third system could be a thermometer.
- 0^{th} Law permits the definition of temperature – i.e. temperature is that property which systems in thermal equilibrium have in common.

0^{th} Law and equation of state

- Consider three fluids A, B, C: A and C in equilibrium if $F_1(p_A, V_A, p_C, V_C) = 0$ or equivalently $p_C = f_1(p_A, V_A, V_C)$
- Likewise, B and C will be in equilibrium if $F_2(p_B, V_B, p_C, V_C) = 0$ or equivalently $p_C = f_2(p_B, V_B, V_C)$
- Hence $f_1(p_A, V_A, V_C) = f_2(p_B, V_B, V_C)$ ... (1)
- But according to 0^{th} Law, A and B also in equilibrium, so $F_3(p_A, V_A, p_B, V_B) = 0$, which doesn't involve V_C. Therefore V_C must cancel in equ.(1).
- So, equ.(1) must reduce to the form $\phi_1(p_A, V_A) = \phi_2(p_B, V_B)$ ($= \phi_3(p_C, V_C)$ by extension).
- $\Rightarrow$ there exists some function of $\phi(p, V)$ for each fluid which takes equal values when they are in equilibrium. Call this the *empirical temperature* $\phi(p, V) \equiv \theta$. $\Rightarrow$ an *equation of state* must exist.

Ideal gas temperature scale

- We can then **define** a scale of temperature using some reference system.
- One way is to use an ideal gas, so that its equation of state $pV = RT$ serves as definition of temperature.
  - e.g. a constant volume gas thermometer is a possible (though cumbersome) realisation of this.
  - May seem strange to use something non-existent and idealised as the basis of our definition, but good reasons will emerge later. Note that real gases approach ideality at low densities.



Ideal gas temperature scale

- To specify the absolute (Kelvin) temperature scale the temperature of the triple point of water (the unique pressure and temperature at which solid, liquid and vapour are all in mutual equilibrium) is defined to be $T_\mathrm{T} \equiv 273.16\,\mathrm{K}$.
- So absolute temperature T is defined by

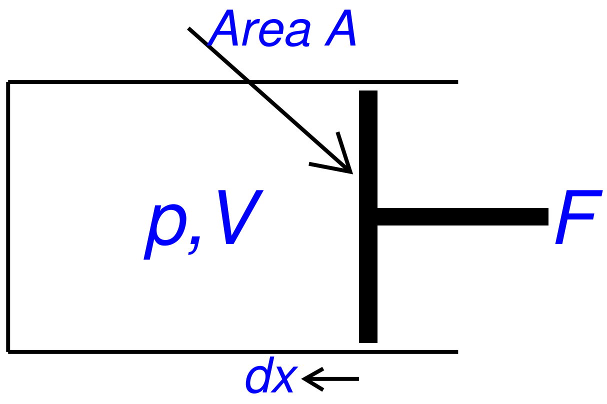
$$T(/\mathrm{K}) = 273.16\frac{\lim_{p\to 0}(pV)_T}{\lim_{p\to 0}(pV)_{T_\mathrm{T}}}$$

- In the Celsius scale, by definition, $T_\mathrm{T} \equiv 0.01°\mathrm{C}$. So absolute zero corresponds to $-273.15°\mathrm{C}$. The boiling and freezing points of water are approximately $100°\mathrm{C}$ and $0°\mathrm{C}$ respectively, at 1 atm pressure.

2.3 First Law of Thermodynamics

- Functions of State: Any thermodynamic variables which can be expressed as unique functions of other thermodynamic variables. For example, internal energy, U.
- There are two important quantities which are *not* functions of state: heat and work. We could bring about the same change in a system by various different combinations of heat and work.
- However, changes in work W and heat Q may be expressed in terms of thermodynamic variables, for reversible changes.

Mechanical work on a gas



- Force on piston $F = pA$. If we move it through distance $\mathrm{d}x \Rightarrow$ work done *on* gas $= F\mathrm{d}x = pA\mathrm{d}x$.
- Now, $A\mathrm{d}x = -\mathrm{d}V \Rightarrow \boxed{đW = -p\mathrm{d}V}$.
- Note negative sign for work done on the gas.
- The symbol đ indicates that this is not an exact differential, because W is not a function of state.

Other forms of work

- Note $đW = -p\mathrm{d}V$ applies not just for a gas, but for any compressible system under hydrostatic pressure.
- Analogous expressions for other forms of work, e.g.

Thin wire $đW = +\mathcal{F}\mathrm{d}x$

Surface tension $đW = +\gamma\mathrm{d}A$

Electric $đW = +E\mathrm{d}P$

- n.b. these involve the conjugate pairs of intensive and extensive variables introduced earlier.

The First Law of Thermodynamics

Energy is conserved if heat is taken into account

- Internal Energy U is the total energy (kinetic + potential) in a system. For a gas, $U = U(T, V)$.
- The First Law states:

$$\mathrm{d}U = \text{đ}Q + \text{đ}W \quad or$$

$$\delta U = \delta Q + \delta W$$

- For the case of a reversible change of a gas (or any $p - V$ system), this becomes

$$\mathrm{d}U = \text{đ}Q - p\mathrm{d}V$$

- In general, $\text{đ}W$ could be a sum of terms, if more than one form of work is possible. e.g. for a polar gas in an electric field.

First Law

- Is an empirical statement.
- Based on, for example, Joule's paddle wheel experiments (ca. 1850), which showed the equivalence of work and heat.
- (Superseded older "caloric" theory whereby heat was regarded as a conserved fluid.)

James Prescott Joule

Ⓒ Enquiries to Science Museum

Joule's paddle wheel apparatus

2.4 Applications – Heat Capacities

- Heat Capacity is the heat needed to cause unit increase in temperature in a system.
- n.b. The term Specific heat (capacity) is often used for heat capacity per unit mass, or per mole. Measured in J $\mathrm{K}^{-1}\mathrm{kg}^{-1}$ or J $\mathrm{K}^{-1}\mathrm{mole}^{-1}$. But people often use it loosely to mean heat capacity. Should strictly use lower case c_p or c_V for specific heats.
- Situation is not quite so simple, though. e.g. for a gas, we could be holding V constant, or p constant (or something else).
- At constant V, all heat will go into increasing internal energy of gas, while at constant p some will go into performing work on surroundings.

Heat Capacity at constant volume

- Define heat capacity at constant volume

$$C_V = \left(\frac{đQ}{\mathrm{d}T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

since, at constant V, $đW = 0$, so $\mathrm{d}U = đQ$.

- Monatomic Ideal Gas, $U = \frac{3}{2}RT$ (from IA Kinetic theory), $\Rightarrow$ $C_V = \frac{3}{2}R$ per mole.
- Likewise, Diatomic Ideal Gas (rotations unquenched) $U = \frac{5}{2}RT$, $\Rightarrow$ $C_V = \frac{5}{2}R$ per mole.

Heat Capacity at constant pressure

- Heat Capacity at constant pressure? Use First Law:

$$\begin{aligned} đQ &= \mathrm{d}U - đW = \mathrm{d}U + p\mathrm{d}V \\ &= \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + p\mathrm{d}V \end{aligned}$$

- Hence

$$\begin{aligned} C_p &\equiv \left(\frac{đQ}{\mathrm{d}T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \\ &= C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \end{aligned}$$

Heat Capacities (contd.)

- So, in general, we have

$$\boxed{C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p}$$

- In the specific case of an ideal gas, $U = U(T)$, and so $\left(\frac{\partial U}{\partial V}\right)_T = 0$. Also $pV = RT$ so, for 1 mole

$$\left(\frac{\partial V}{\partial T}\right)_p = R/p \quad \Rightarrow \quad C_p = C_V + R$$

- As an aside - mention latent heat. This is the heat (per unit mass, or per mole) needed to change the phase of a substance, e.g. liquid to vapour (latent heat of evaporation) or solid to liquid (latent heat of melting).

Gas expansions

- Need to specify what is constant in the expansion.
- e.g. Isothermal: $T = \text{const.} \Rightarrow pV = \text{const.}$.
- For an ideal gas, $U = U(T) \Rightarrow$

$$\Delta U = 0 \quad \Rightarrow \quad đQ = p\mathrm{d}V = \frac{RT}{V}\mathrm{d}V$$

$$\Rightarrow \quad \Delta Q = \int_{V_0}^{V_1} \frac{RT}{V}\mathrm{d}V = RT\ln(V_1/V_0)$$

  i.e. need to put heat in when the gas expands in order to do work on surroundings.
- Isotherms are hyperbolae on a $p - V$ diagram. Sometimes called an “Indicator diagram” – any state of a system is represented by a point in the $p - V$ plane.

Reversible Adiabatic expansion

- $đQ = 0$. $\Rightarrow$ $\mathrm{d}U = -p\mathrm{d}V$ if reversible.
- For an ideal gas:

$$\mathrm{d}U = C_V \mathrm{d}T = \frac{C_V}{R}(p\mathrm{d}V + V\mathrm{d}p) = -p\mathrm{d}V$$

$$\Rightarrow \quad C_V V \mathrm{d}p + (C_V + R)p\mathrm{d}V = C_V V \mathrm{d}p + C_p p\mathrm{d}V = 0$$

$$\Rightarrow \quad C_V \frac{\mathrm{d}p}{p} + C_p \frac{\mathrm{d}V}{V} = 0 \quad \Rightarrow \quad \frac{\mathrm{d}p}{p} + \gamma \frac{\mathrm{d}V}{V} = 0$$

- where $\gamma = C_p/C_V$. Integrating:

$$\ln p + \gamma \ln V = \mathrm{const.} \quad \Rightarrow \quad pV^{\gamma} = \mathrm{const.}$$

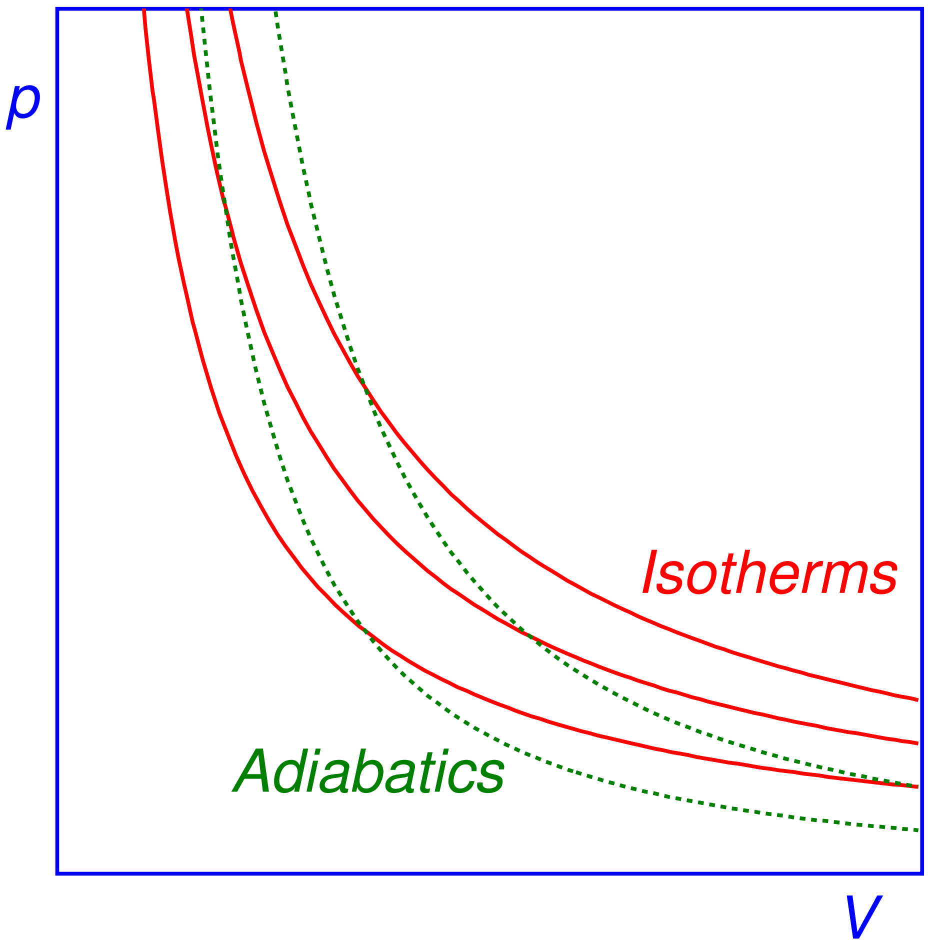
Adiabatic expansion

- We have
  $pV^\gamma = \text{const.}$
- Using $pV = RT$ we easily derive two further forms:

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

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

- See example 1 for direct derivation from kinetic theory.



Section 2: Summary

- Basic ideas – thermal isolation, thermal contact etc.
- Thermodynamic variables – intensive (e.g. T, p) or extensive (e.g. V, U).
- Reversibility. Slow, quasi-static change.
- Zeroth Law: “If two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.”
- Leads to definition of temperature. Ideal gas scale.
- Also implies existence of equation of state.

Section 2: Summary

- Functions of state. Work and heat are not state functions.
- Work: $đW = -p\mathrm{d}V$ etc.
- First Law: "Energy is conserved if heat is taken into account"
  $$\mathrm{d}U = đQ + đW = đQ - p\mathrm{d}V$$
- Empirical. Almost a definition of heat.
- Heat capacities: $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R$ for 1 mole of monatomic ideal gas.
- $C_p = C_V + R$ for 1 mole of an ideal gas.
- Reversible adiabatic expansion : $pV^\gamma = \mathrm{const.}$ where $\gamma = C_p/C_V$.

Classical Thermodynamics

3. Second Law and Entropy

3.1 The Second Law

3.2 Carnot Cycle

3.3 Thermodynamic Temperature Scale

3.4 Equivalence of Clausius and Kelvin Formulations

3.5 Other heat engines

3.6 Clausius' Theorem and Entropy

3.7–3.11 Applications of Entropy

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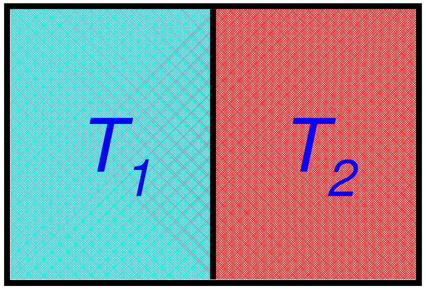
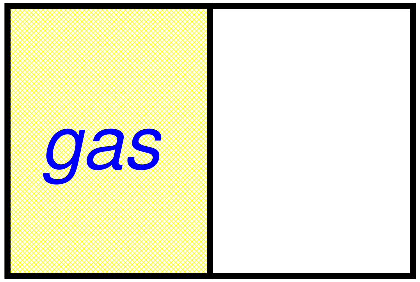
3.1 The Second Law

- The First Law was a statement of conservation of energy.
- Empirically, it is clear that not all processes permitted by the first law actually occur. e.g.



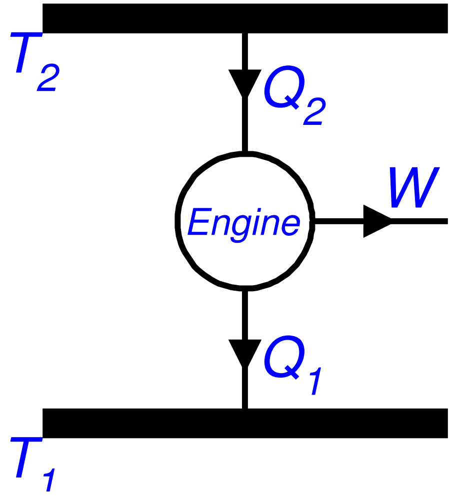
If $T_2 > T_1$ heat flows $2 \to 1$, even though $1 \to 2$ is allowed by first law.



Remove partition – gas spontaneously expands to fill whole box, even though $\Delta U = 0$ ("Joule Expansion")

Heat Engines

- There is an irreversibility in nature on the macroscopic scale, even though the underlying microscopic laws (Classical/Quantum Mechanics) are reversible.
- Heat can flow from $1 \to 2$ if we do work. How much?



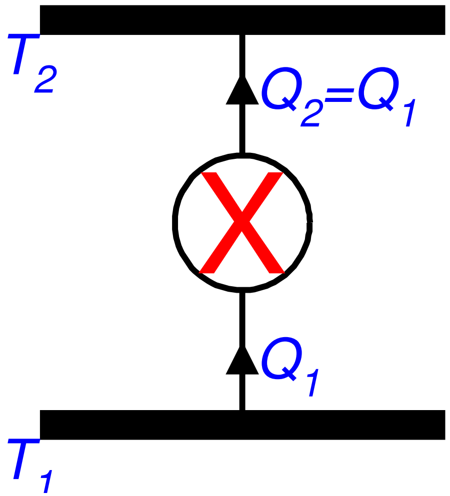
- Introduce idea of a heat engine, where engine undergoes a cyclical change, returning periodically to its initial state.
- Operate between two reservoirs, at temperatures T_2, $T_1 < T_2$; absorbing heat Q_2, doing work W and depositing heat $Q_1 = Q_2 - W$ in colder reservoir.
- How much W for a given Q_2 ?

The Second Law

Two (equivalent) statements:

Clausius' formulation

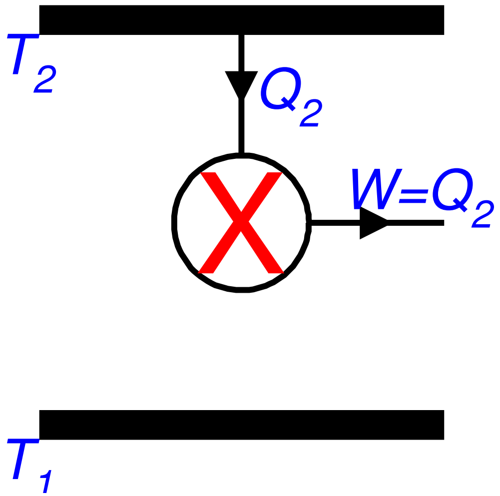
“No process is possible whose only effect is to transfer heat from a colder to a hotter body”



is impossible

Kelvin's formulation

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

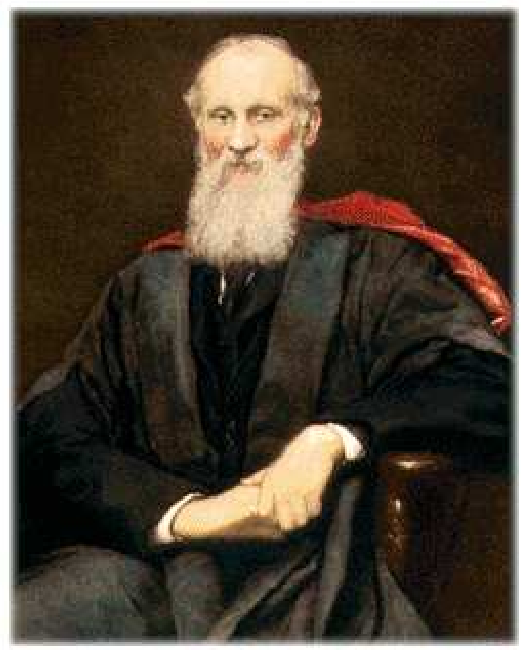


is impossible

Originators of the Second Law

Sadi Carnot

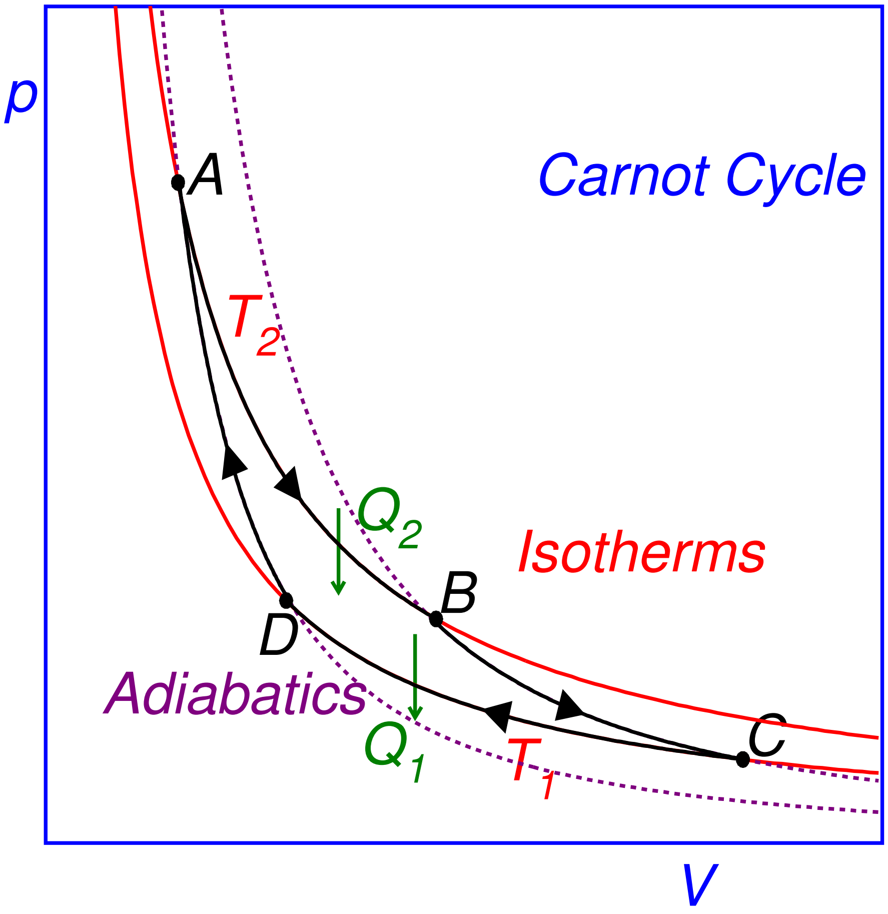
Rudolph Clausius



William Thomson
(Lord Kelvin)

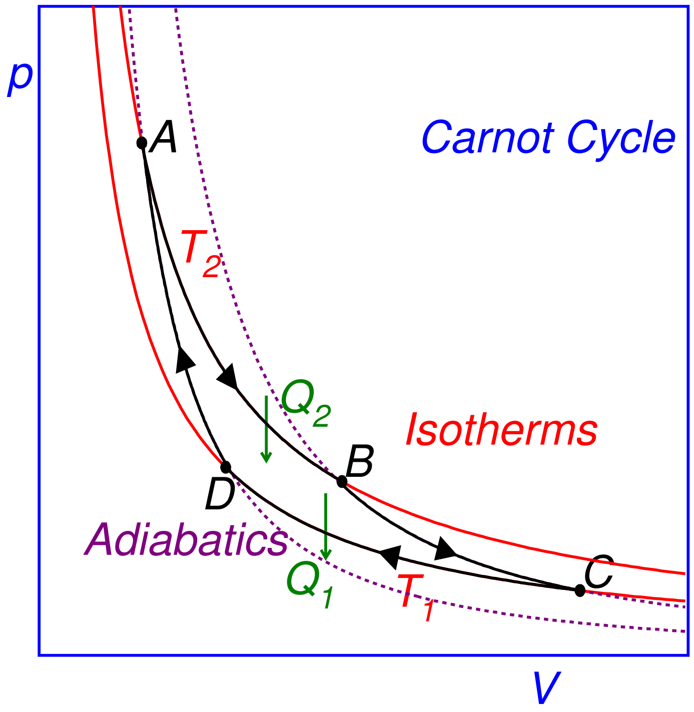
3.2 Carnot Cycle

- Working substance (not necessarily a gas) used cyclically and reversibly.
- Two isotherms, $T_1, T_2; (T_2 > T_1)$ connected by adiabatics.
- Heat absorbed Q_2 at T_2; heat deposited Q_1 at T_1.
- Work done $W = Q_2 - Q_1$ is equal to area of cycle $= \oint p\mathrm{d}V$.



Carnot Cycle in detail

- $A \rightarrow B$: Isothermal expansion; heat absorbed Q_2; equal to work done on surroundings.
- $B \rightarrow C$: Adiabatic expansion; $\Delta Q = 0$; work is done on surroundings.
- $C \rightarrow D$: Isothermal compression; heat given out Q_1; equal to work done by surroundings.
- $D \rightarrow A$: Adiabatic compression; $\Delta Q = 0$; work is done by surroundings.



Efficiency of a Carnot Cycle?

- Efficiency, η defined by

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

- Specifically, for an ideal gas, $pV = RT$, and for reversible adiabatic changes $TV^{\gamma-1} = \text{const.}$

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

- Likewise,

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

Efficiency of Carnot cycle

- Using the adiabatic equation:

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

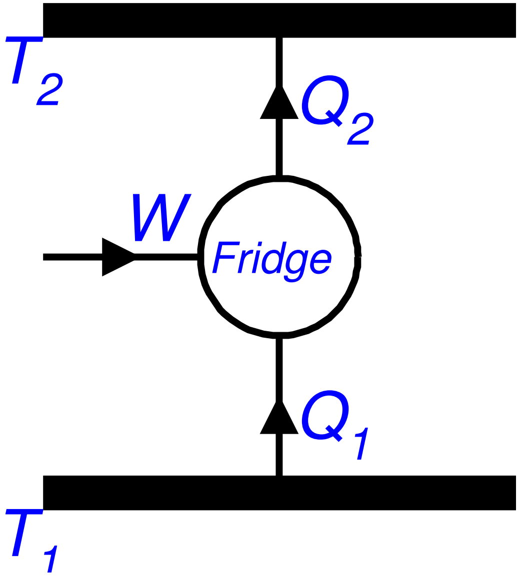
$$\Rightarrow \frac{V_B}{V_C} = \frac{V_A}{V_D} \quad \Rightarrow \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

- And hence

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

- This result is true for all Carnot cycles (shown later); not just for those involving an ideal gas.
- n.b. $T_2 > T_1$, so $0 < \eta < 1$; consistent with Kelvin's statement of the second law.

Refrigerator



- Carnot Engine run in reverse acts as a refrigerator. By doing work W, can extract heat Q_1 from reservoir at T_1. Must dump heat $Q_2 > Q_1$ at some higher temperature T_2 (hence the radiator at the back of your fridge).
- Efficiency = (heat extracted)/(work done)

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

(using previous results).

- Can, in principle, be highly efficient if $T_2 \approx T_1$.

Heat pump

- Just like refrigerator, but use Q_2 to heat your house (say), pumping heat from outside.
- In this case, relevant efficiency is

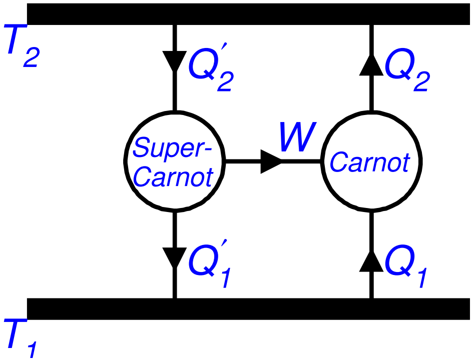
$$\eta \equiv \frac{Q_2}{W} = \frac{Q_2}{Q_2 - Q_1} = \frac{T_2}{T_2 - T_1} > 1$$

- So, potentially much more efficient than heating your house directly. However, in practice losses mean that one can't achieve anything like this efficiency.

Carnot's Theorem

No engine operating between two reservoirs can be more efficient than a Carnot engine.

- Proof: suppose we have a "super-Carnot" engine. Combine it with a Carnot engine operating in reverse.



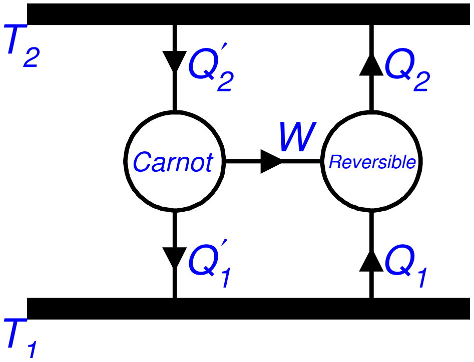
$$\eta_{\mathrm{SuperCarnot}} = \frac{W}{Q_2'} > \eta_{\mathrm{Carnot}} = \frac{W}{Q_2} \quad \text{i.e.} \quad Q_2' < Q_2$$

- The net effect is therefore transfer of heat from T_1 to T_2, which violates Clausius' formulation of the Second Law.

Carnot's theorem (contd.)

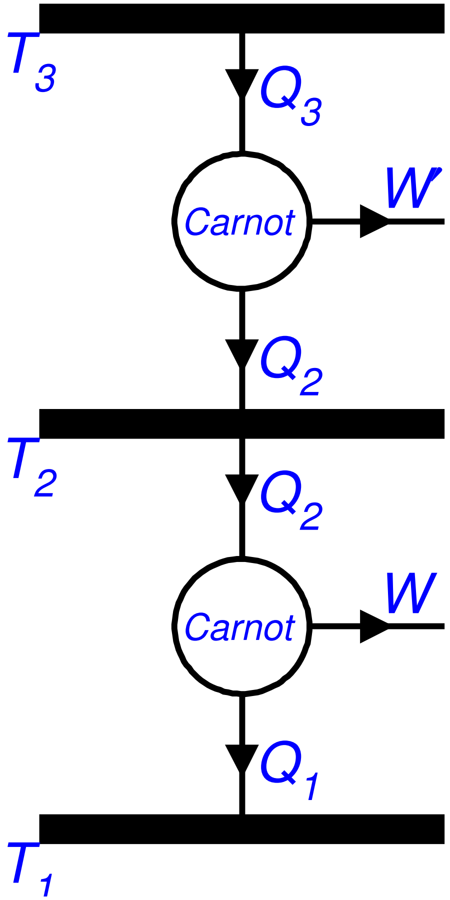
Also implies that all reversible engines operating between two temperatures have the same efficiency as a Carnot engine.

- Proof: use a Carnot engine to drive reversible engine in reverse.



- If $\eta_{\text{Carnot}} > \eta_{\text{rev.}}$, violate Clausius' formulation, as before.
- But, Carnot's theorem tells us $\eta_{\text{rev.}} \leq \eta_{\text{Carnot}}$; so we must have $\eta_{\text{rev.}} = \eta_{\text{Carnot}}$.

3.3 Thermodynamic Temperature Scale



- Carnot's Theorem ⇒ Q_2/Q_1 is the same for any reversible engine operating between T_1 and T_2.
- Can use this to define temperature scale. Label them with "empirical temperatures" $\theta_1,\ \theta_2$ such that $Q_2/Q_1 = f(\theta_1, \theta_2)$
- Consider two Carnot engines: $Q_3/Q_2 = f(\theta_2, \theta_3)$. These are equivalent to a single reversible engine operating between θ_3 and θ_1.

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

- l.h.s. independent of θ_2; ⇒ θ_2 must cancel on r.h.s.

Thermodynamic Temperature Scale

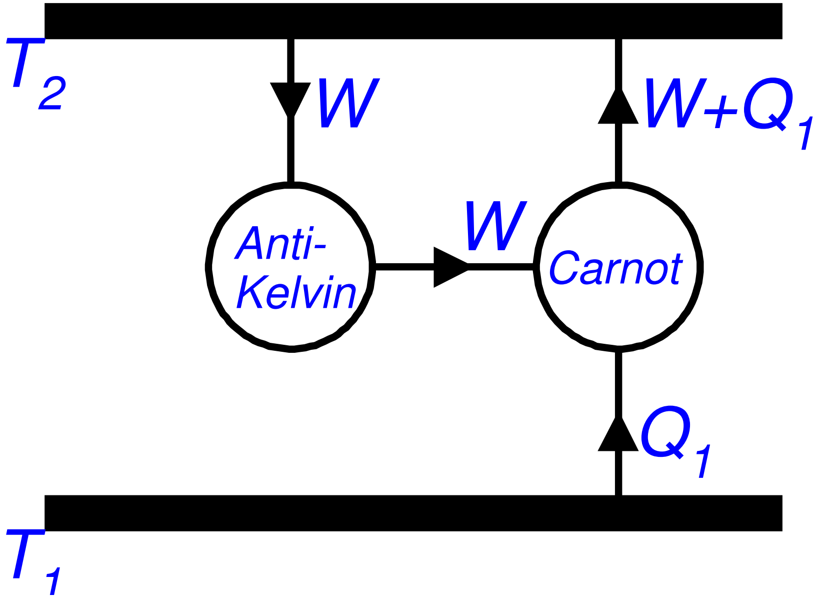
- Hence $f(\theta_1, \theta_2)$ must have the form of a ratio:

$$\frac{Q_2}{Q_1} = f(\theta_1, \theta_2) = \frac{g(\theta_2)}{g(\theta_1)} \equiv \frac{\mathcal{T}_2}{\mathcal{T}_1}$$

- This defines thermodynamic temperature $\mathcal{T}$
- But, from Carnot Cycle for ideal gas, we know that $Q_2/Q_1 = T_2/T_1$. Hence, thermodynamic temperature is identical to ideal gas temperature (up to some factor), $\mathcal{T} \equiv T$
- This is why ideal gas temperature is the “natural” choice in thermodynamics.
- Thermodynamic definition of temperature is independent of any specific choice of substance.

3.4 Clausius and Kelvin Formulations

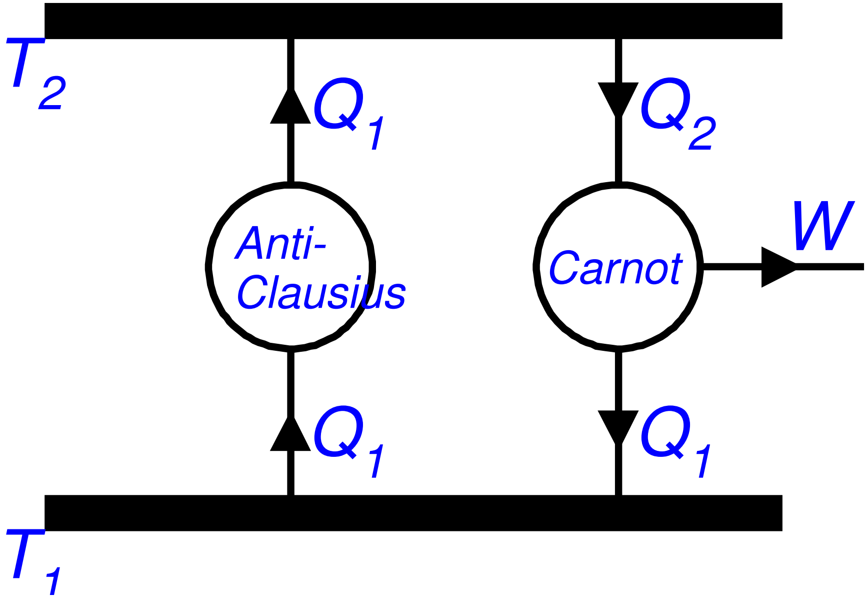
- Suppose we have an engine which violates Kelvin's formulation. Use its work to drive a Carnot engine as a heat pump.



- Net effect is to transfer heat from T_1 to T_2.
- Violates Clausius' formulation.

Clausius and Kelvin Formulations

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



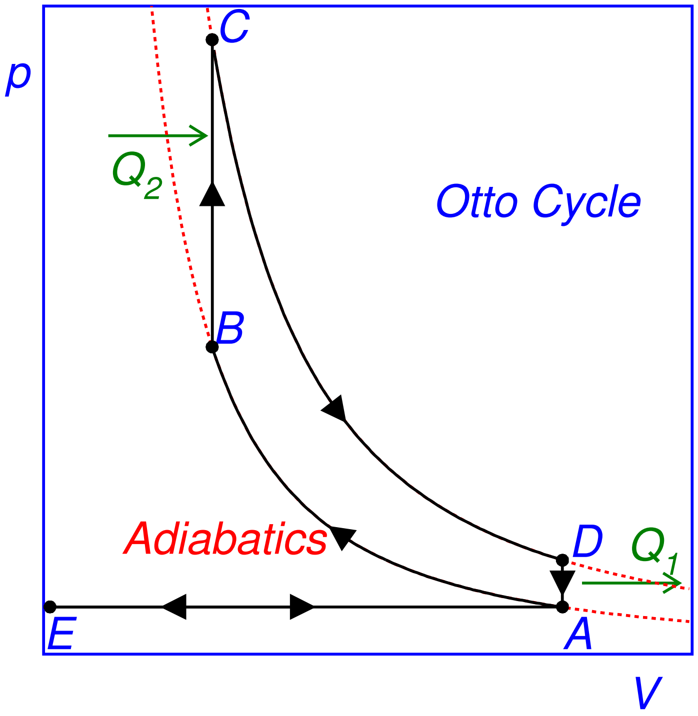
- Net effect is complete conversion of heat to work.
- Violates Kelvin's formulation.
- Hence the two formulations are equivalent.

3.5 Real heat engines

- In practice, above predictions for Carnot Engines are highly optimistic.
- Real heat engines not reversible, e.g.
    - Losses of heat through thermal conduction.
    - Friction, turbulence ⇒ irreversible.
    - Changes not slow.
- Also 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 two fixed temperatures.
- Often approximate using "Air Standard" cycles: air taken as working substance; assume ideal gas; reversible.

Air Standard Otto Cycle

- Approximates internal combustion engine.
  - $E \rightarrow A$ Intake stroke; fuel + air drawn in to cylinder.
  - $A \rightarrow B$ Compression stroke. Assumed adiabatic.
  - $B \rightarrow C$ Ignition. Heat generated by combustion of fuel.
  - $C \rightarrow D$ Power stroke; hot gas expands adiabatically.
  - $D \rightarrow A$ Open exhaust valve.
  - $A \rightarrow E$ Expel remaining gas.

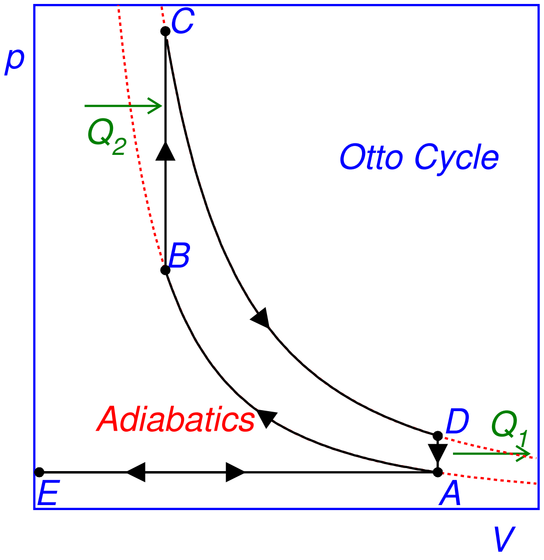


Otto Cycle – efficiency

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

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

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



- Adiabatics:

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

where the “compression ratio” $r \equiv V_A/V_B$

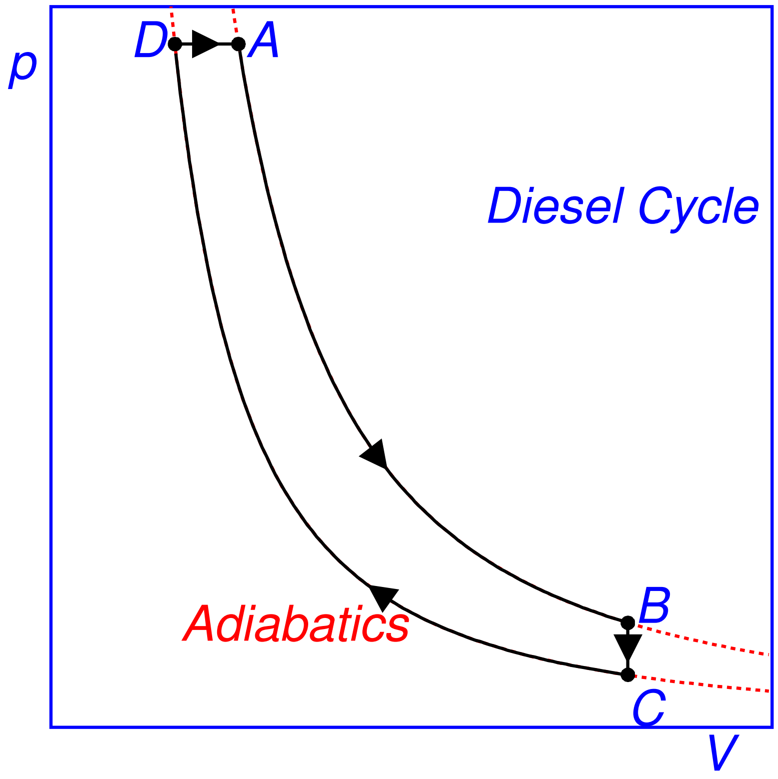
- Likewise, $T_A = T_B r^{1-\gamma}$. Hence, $\boxed{\eta = 1 - r^{1-\gamma}}$

Otto cycle – comments

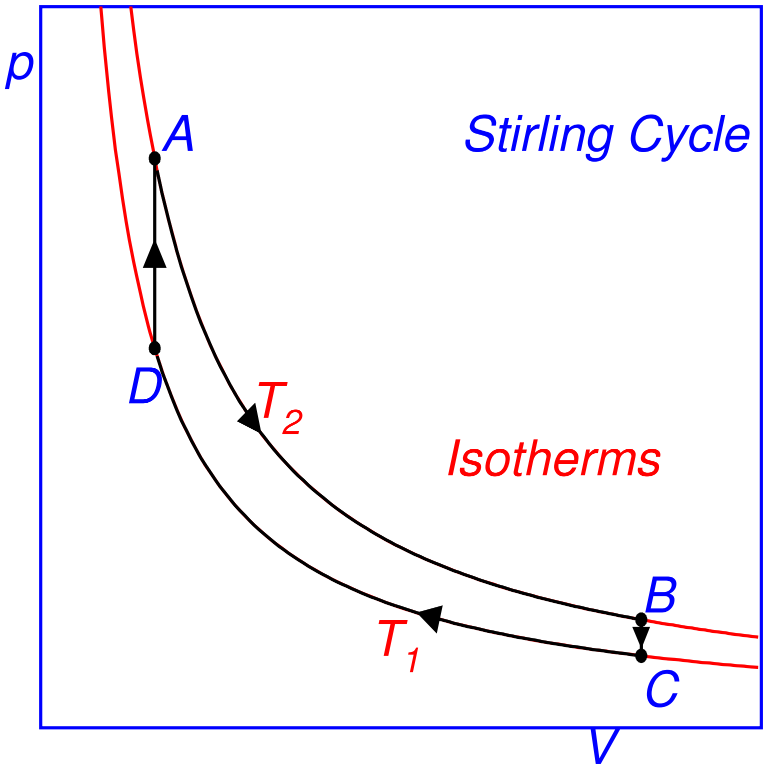
- $\eta = 1 - r^{1-\gamma}$: efficiency determined by compression ratio. Typically limited to about 8-10, otherwise “pinking” or “knocking” (premature combustion during compression; shock waves generated).
- For $\gamma = 1.4$, $r = 10$, $\eta \sim 0.6$. Efficiency of real engines likely to be only half of this.
- Diesel engine can use higher compression ratio – fuel injected after compression stroke.

Other heat engines

Diesel Cycle



Stirling Cycle



(see example)

3.6 Clausius' Theorem and Entropy

- For a Carnot Cycle:

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

- or, equivalently

$$\oint \frac{đQ}{T} = 0$$

- For any cycle operating between T_2 and T_1, Carnot's theorem says $\eta \leq \eta_{\mathrm{rev.}}$, i.e.

$$1 - \frac{Q_1}{Q_2} \leq 1 - \frac{T_1}{T_2} \quad \Rightarrow \quad \frac{Q_2}{T_2} \leq \frac{Q_1}{T_1} \quad \Rightarrow \quad \oint \frac{đQ}{T} \leq 0$$

where the equality applies to a reversible cycle.

Clausius' theorem

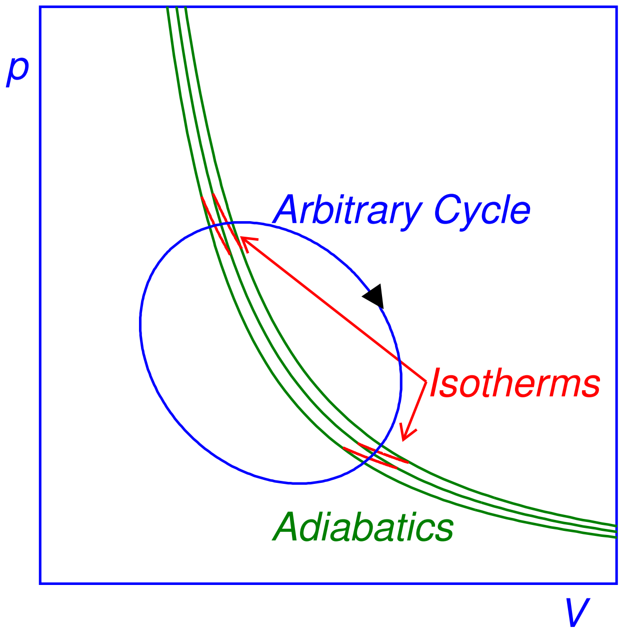
- Clausius' theorem states

$$\oint \frac{đQ}{T} \leq 0$$

  for any arbitrary cycle.

- Prove it by "tiling" the arbitrary cycle with small Carnot cycles. Since $\oint \frac{đQ}{T} \leq 0$ for each, it is also true for the sum of them, i.e. for the overall cycle. Again, equality if reversible.

- This is not a very rigorous proof. See Adkins for a better way.



Entropy

- If $\oint \frac{đQ}{T} = 0$ for any reversible cycle, this means $\int_A^B \frac{đQ}{T}$ is independent of path from A to B.
- Hence $\frac{đQ_{\mathrm{rev.}}}{T}$ must be the derivative of a function of state. Call it Entropy, S. Units J K^{-1}.
- i.e. for a reversible change

$$\mathrm{d}S \equiv \frac{đQ_{\mathrm{rev.}}}{T} \quad \Rightarrow \quad \int_A^B \frac{đQ}{T} = \int_A^B \mathrm{d}S = S(B) - S(A)$$

- Thus defines S up to some additive constant.
- (The Third Law (see later) addresses the absolute scale of entropy).

Entropy in irreversible changes?

- For a reversible adiabatic change, $đQ_{\mathrm{rev.}} = 0 \Rightarrow \mathrm{d}S = 0$. Entropy is constant; “isentrope”
- Consider going from $A \to B$ by an irreversible process, and returning to A by a reversible change. By Clausius' theorem:

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

$$\Rightarrow \quad \int_A^B \frac{đQ_{\mathrm{irrev.}}}{T} - \int_A^B \frac{đQ_{\mathrm{rev.}}}{T} \leq 0$$

$$\Rightarrow \quad \int_A^B \frac{đQ_{\mathrm{irrev.}}}{T} \leq \int_A^B \mathrm{d}S \quad \text{or} \quad \mathrm{d}S \geq \frac{đQ_{\mathrm{irrev.}}}{T}$$

n.b. T is the temperature at which heat is extracted.

The "Arrow of Time"

- For an isolated system, $đQ = 0 \Rightarrow \mathrm{d}S \geq 0$.
- The entropy of an isolated system cannot decrease.
- The universe is certainly an isolated system. The entropy of the universe cannot decrease.
- Now start to see the connection between the Second Law and the directionality of nature.
- Example: Consider two systems at temperatures T_1 and T_2; allow heat δQ to flow from $2 \to 1$. From above $\delta S_1 + \delta S_2 \geq 0$

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

- Hence, $T_2 \geq T_1$; heat flows from hot to cold!

Entropy examples

- Consider two equal bodies of heat capacity C and temperatures T_1 and T_2. Place them in thermal contact. Final temperature $T_f = \frac{1}{2}(T_1 + T_2)$.

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{đQ}{T} = \int_{T_1}^{T_f} \frac{C\mathrm{d}T}{T} = C\ln\left(\frac{T_f}{T_1}\right)$$

$$\Delta S_2 = \int_{T_2}^{T_f} \frac{đQ}{T} = \int_{T_2}^{T_f} \frac{C\mathrm{d}T}{T} = C\ln\left(\frac{T_f}{T_2}\right)$$

$$\begin{aligned}\Delta S_{\mathrm{total}} &= C\ln\left(\frac{T_f}{T_1}\right) + C\ln\left(\frac{T_f}{T_2}\right)\\ &= C\ln\left(\frac{T_f^2}{T_1T_2}\right) = C\ln\left(\frac{(T_1+T_2)^2}{4T_1T_2}\right) > 0\end{aligned}$$

Entropy examples

- Consider a body of heat capacity C and initial temperature T_1. Place in reservoir (of heat capacity $\gg C$) at fixed temperature T_0.

$$
\begin{aligned}
\Delta S_{\text{body}} &= C \ln\left(\frac{T_0}{T_1}\right) \qquad \text{as above} \\
\Delta S_{\text{res.}} &= \frac{C(T_1 - T_0)}{T_0} \\
\Delta S_{\text{universe}} &= C\left[\frac{(T_1 - T_0)}{T_0} + \ln\left(\frac{T_0}{T_1}\right)\right] > 0
\end{aligned}
$$

3.7 Entropy and the First Law

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

$$\mathrm{d}U = \underbrace{T\mathrm{d}S}_{đQ_{\mathrm{rev.}}} \underbrace{-p\mathrm{d}V}_{đW_{\mathrm{rev.}}}$$

- This is now expressed in terms of functions of state. Therefore it is always true, even for irreversible processes. This is very powerful.
- We can clearly generalise for other forms of work $đW$ as introduced previously

$$\mathrm{d}U = T\mathrm{d}S + \sum_i X_i \mathrm{d}x_i$$

3.8 Heat Capacities; Latent Heats

- Express heat capacities in terms of entropy:

$$C_V = \left(\frac{đQ}{\mathrm{d}T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad ; \text{ likewise } \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

- 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.

- Entropy is usually different in different phases.

Entropy of Ideal Gas

- n.b. Introduction of entropy hasn't increased the number of independent thermodynamic variables; being a function of state, it will be expressible in terms of any two others.
- e.g. Ideal Gas — First Law ⇒:

$$\mathrm{d}U = C_V \mathrm{d}T = T\mathrm{d}S - p\mathrm{d}V$$

$$\Rightarrow \quad \mathrm{d}S = \frac{C_V \mathrm{d}T}{T} + \frac{p\mathrm{d}V}{T} = \frac{C_V \mathrm{d}T}{T} + \frac{R\mathrm{d}V}{V}$$

(for one mole; using $pV = RT$).

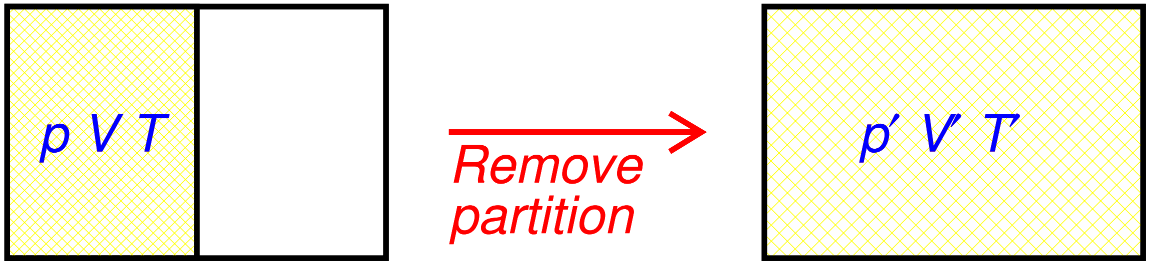
- Integrate:

$$S = C_V \ln T + R \ln V + S_0$$

where S_0 is the constant of integration (non-trivial to calculate).

3.9 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 $\Rightarrow T = T'$. So:

$$\Delta S = C_V \ln\left(\frac{T'}{T}\right) + R\ln\left(\frac{V'}{V}\right) = R\ln\left(\frac{V'}{V}\right)$$

- Suppose we double the size of the box; $V' = 2V$. $\Rightarrow$ $\Delta S = R\ln 2$.
- n.b. change in entropy is not necessarily associated with heat flow. Of course the Joule expansion is an irreversible process.

3.10 Statistical interpretation of Entropy

- Consider this Joule expansion statistically.
- After expansion, each molecule equally likely to be in either half of the box; they could all be at the same end (like they started) but highly unlikely.
- $N = N_{\mathrm{A}}$ molecules. Only one way of having them all at the same end (probability $= \frac{1}{2}^{N}$), while the number of ways of having equal numbers in each half is ${}_{N/2}C_N$.
- i.e. the relative likelihood of this configuration is greater by a factor

$$W =_{N/2} C_N = \frac{N!}{(\frac{1}{2}N)!(\frac{1}{2}N)!}$$

Statistical interpretation ...

$$W = {}_{N/2}C_N = \frac{N!}{(\frac{1}{2}N)!(\frac{1}{2}N)!}$$

- Simplify this using Stirling's approximation:

$$\ln N! \approx N \ln N - N$$

$$\begin{aligned} \ln W &= N \ln N - N - 2\left[\tfrac{1}{2}N \ln(\tfrac{1}{2}N) - \tfrac{1}{2}N\right] \\ &= N\left(\ln N - \ln(\tfrac{1}{2}N)\right) = N \ln 2 \end{aligned}$$

Statistical interpretation ...

- Compare with entropy change in Joule expansion

$$\Delta S = R \ln 2 = N_{\mathrm{A}} k \ln 2 = k \ln W$$

- Suggests a connection between entropy and the number of configurations available to the system.
- In fact $S = k \ln W$ is a general result in statistical mechanics, though we have only proved it in one specific case.
- Entropy is a measure of the disorder of a system. More configurations $\Rightarrow$ higher entropy.
- The universe tends inexorably towards greater disorder. Can only increase order of one part of the universe by increasing disorder of another.

3.11 Entropy and degradation of energy

- The work which can be extracted from a system in some change is

$$đW = đQ - \mathrm{d}U \leq T_0 \mathrm{d}S - \mathrm{d}U$$

  where T_0 is the temperature at which heat is extracted.
- $đW$ is maximal when the equality is satisfied, i.e. for a reversible process.
- Increase of entropy corresponds to conversion of energy into a form (e.g. frictional heating) which is less useful for conversion to work.
- Energy is degraded into a less useful form, even though it is still conserved (First Law).

Section 3 – Summary

- The Second Law: Clausius ”No process is possible whose effect is only to transfer heat from a colder to a hotter body”.
- Equivalent to Kelvin: “No process is possible whose only effect is the complete conversion of heat into work”
- Carnot engine – reversible cyclical process; two isotherms connected by two adiabatics.

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

- Heat engine, refrigerator, heat pump. Other cycles.
- Carnot’s Theorem “No engine operating between two reservoirs can be more efficient than a Carnot engine”

Section 3 – Summary

- Thermodynamic temperature scale – equivalent to ideal gas scale.
- Clausius' Theorem:

  $$\oint \frac{đQ}{T} \leq 0$$

  where the equality applies for a reversible cycle.
- Entropy – defined by

  $$\mathrm{d}S \equiv \frac{đQ_{\mathrm{rev.}}}{T}$$

- Entropy is a function of state.
- The entropy of an isolated system cannot decrease. Directionality of time.

Section 3 – Summary

- First Law can be written

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

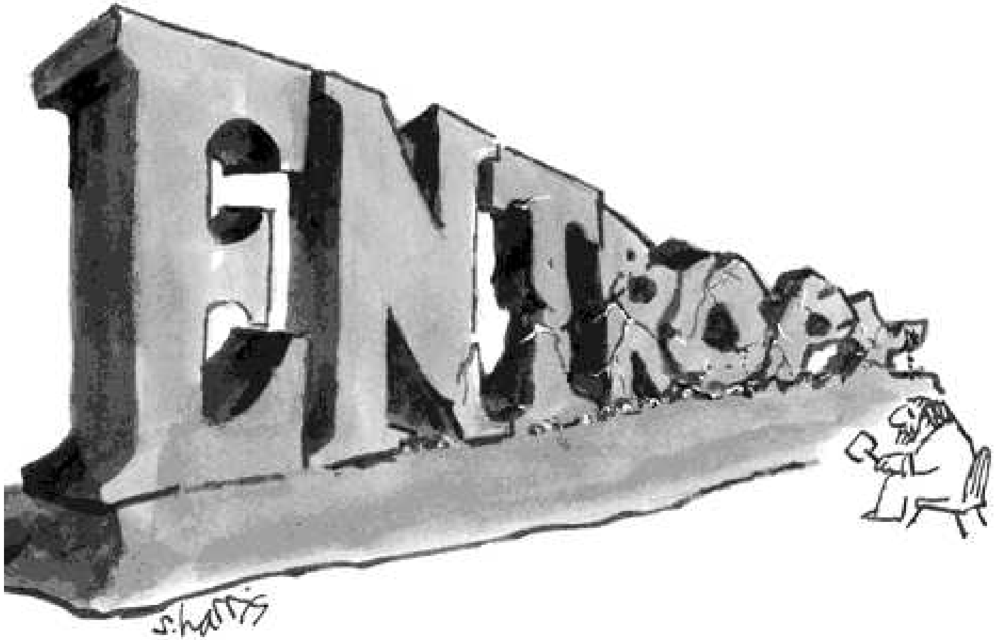
  for any change; not just reversible.

- Entropy of ideal gas

$$S = C_V \ln T + R \ln V + S_0$$

- Entropy change in Joule expansion – leads to statistical interpretation of entropy $S = k \ln W$.
- Entropy can be regarded as a measure of disorder.

Entropy according to Sidney Harris



Entropy $\equiv$ disorder

Entropy can't decrease