Temperature and Entropy

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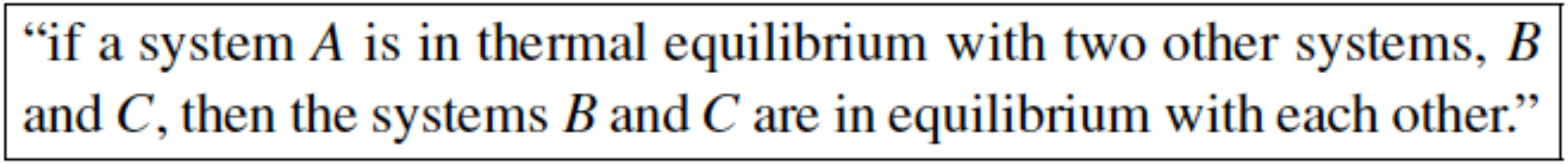
Boltzmann’s tomb with his definition of entropy engraved on it.

The second law of thermodynamics can be used
to prove the existence of
a new function of state known as entropy
which allows to determine quantitatively
- whether a process is reversible
- whether it can occur naturally or not

7.1 The Zeroth Law and Empirical Temperature

The zeroth law:



"if a system *A* is in thermal equilibrium with two other systems, *B* and *C*, then the systems *B* and *C* are in equilibrium with each other."

Two systems are in thermal equilibrium if
no heat is transferred between them
when they are placed in thermal contact

The Zeroth Law means that we can assign a label to any system, the label being the value shown on a thermometer when it is thermal equilibrium with the system.

We call the label temperature.

Temperature is a function of state which determines whether one system will be in thermal equilibrium with another.

7.1.1 Empirical temperature scales

We need a thermometer, a device with some easily measured property, X, that varies with temperature, such as the length of the mercury column in a mercury-in-glass thermometer.
The temperature is some function of X, θ(X).

We choose: $\theta(X) = aX + b$

where *a* and *b* are constants, fixed using two easily reproduced calibration temperatures.

For instance, the Centigrade temperature scale assigns values of 0 C for the temperature of ice in equilibrium with water (known as the ice point) and 100 C for the temperature of boiling water (the steam point). Letting the values of X at these two points be X_0 and X_{100},
the Centigrade temperature is defined as:

$$\theta = 100\left(\frac{X - X_0}{X_{100} - X_0}\right)$$

The Centigrade scale is not very good for two reasons:

1. the ice and steam points are not well defined as both depend upon pressure, and dissolved air makes a difference to the ice point.
2. any errors made during the calibration are amplified when extrapolating to very low temperatures.

Temperatures are now defined by setting θ(X=0) = 0 (so that b = 0) and choosing one other calibration point.

A good choice is the triple point, the unique temperature (and pressure) at which ice, water and water vapour co-exist in equilibrium.

Temperatures are thus given by:

$$\theta = 273.16\left(\frac{X}{X_{\mathrm{TP}}}\right)$$

where X_{TP} is the value of X at the triple point

The trouble with empirical temperatures is that, except at the calibration points, the temperature depends upon the thermometer.

For instance, the rate at which the length of a mercury-in-glass thermometer changes will slow dramatically once the mercury shrinks to be inside the bulb.

The temperature can thus depend upon the substance (mercury versus alcohol for instance), and the exact dimensions of the thermometer.

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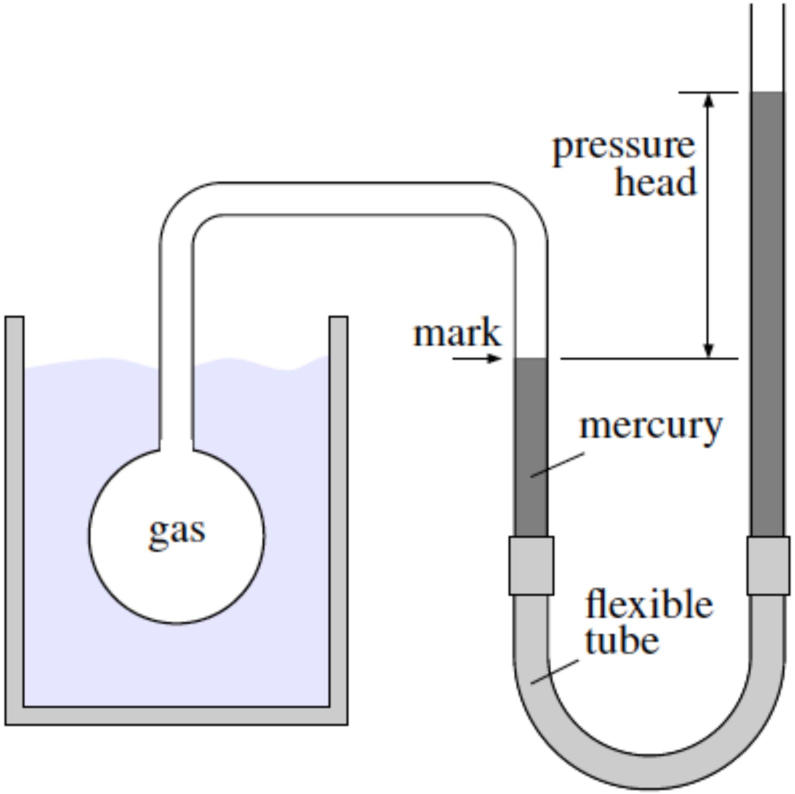
a very unsatisfactory situation

7.1.2 The ideal gas scale

In constant volume gas thermometers, the volume of a quantity of gas is kept constant, while the pressure is measured.



The height of the rightmost tube is adjusted to hold the mercury at the level of the mark, keeping the gas volume constant.

The pressure is read from the difference in the heights of the mercury in different tubes.

For an ideal gas, $PV = n_m RT_I$, so if V is constant, T α P

the pressure is used for X, and T for θ, so:

$$\theta = 273.16\left(\frac{X}{X_{\mathrm{TP}}}\right) \xrightarrow{\text{becomes}} T_{\mathrm{I}} = 273.16\left(\frac{P}{P_{\mathrm{TP}}}\right)_{\rho\to 0}$$

The units of this scale are Kelvin, symbol K.
The measurement is carried out in the limit of zero density since that is when gases tend to the ideal case.

Constant volume gas thermometers are not very convenient, but they can be used to calibrate more convenient thermometers.

The Celsius temperature scale is directly related to the ideal gas scale by:

$$t = T_{\mathrm{I}} - 273.15$$

The triple point has temperature 0.01C by definition

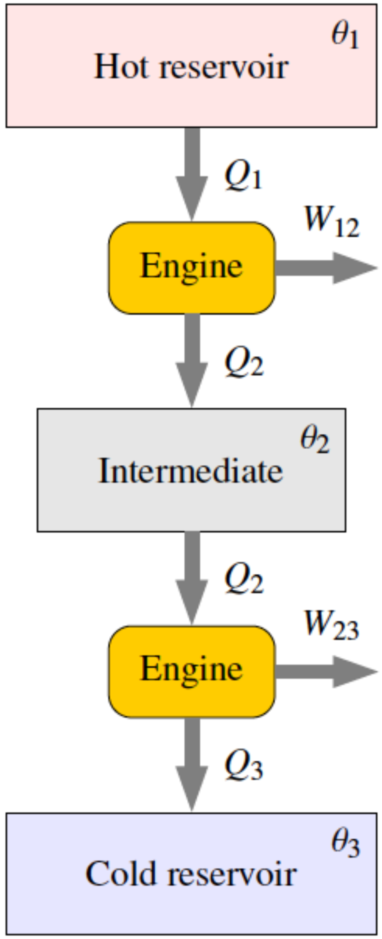
7.2 Thermodynamic temperature

Carnot's theorem says that all reversible engines running between the same two reservoirs have the same efficiency, regardless of their construction.

Therefore we can say that the efficiency and the ratio of heat input to output is a function of the reservoir temperatures only:

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

where θ_1 and θ_2 are the empirical temperatures of the hot and cold reservoirs respectively



The function *f* will depend upon the particular empirical temperature scale in use, but Q_1/Q_2 does not, as long the reservoir temperatures do not vary.

two Carnot engines run between reservoirs at temperatures θ_1 and θ_3 via an intermediate stage at temperature θ_2

There is no net flow of heat into or out of the intermediate reservoir, in which case we can also think of the two engines combined into a single engine producing total work $W_{12} + W_{23}$.

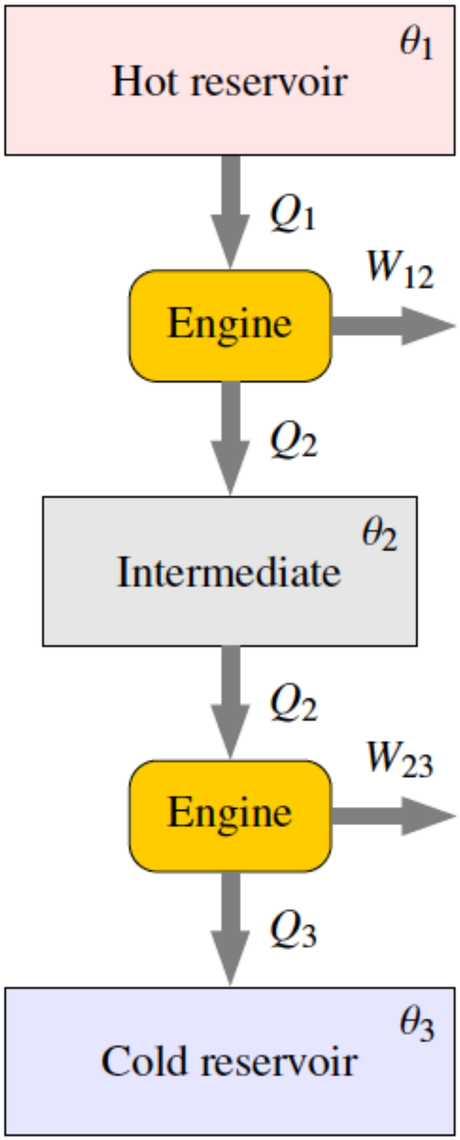
The ratios of heat input to output of the two engines considered separately and the two considered as one are given by:

$$\frac{Q_1}{Q_2} = f(\theta_1, \theta_2), \qquad \frac{Q_1}{Q_3} = f(\theta_1, \theta_3).$$

$$\frac{Q_2}{Q_3} = f(\theta_2, \theta_3),$$

$$\Downarrow$$

$$f(\theta_1, \theta_3) = f(\theta_1, \theta_2) f(\theta_2, \theta_3)$$



$$f(\theta_1, \theta_3) = f(\theta_1, \theta_2) f(\theta_2, \theta_3)$$

θ_2 appears on the right-hand side but it does not appear on the left

the only way that this can be true for arbitrary θ_2 is if the function f is of the form:

$$f(\theta_1, \theta_2) = \frac{g(\theta_1)}{g(\theta_2)}$$

where *g* is a function of the empirical temperature

let's use T = *g(*θ*)* for our temperature

⇓

$$\frac{Q_1}{Q_2} = f(\theta_1, \theta_2) \quad \text{becomes} \quad \boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}}$$

where T_1 and T_2 are the *thermodynamic temperatures* of the reservoirs

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

the ratio of thermodynamic temperatures of two reservoirs is the ratio of heats exchanged during the operation of a reversible engine running between them.

This defines thermodynamic temperatures up to a multiplicative constant.

If a calibration point is defined, then the scale is uniquely determined.
The triple point of water is defined to have T = 273.16K,
the number chosen so that there are 100K between the ice and steam points, consistent with the standard usage of the Centigrade scale.

7.2.1 Temperature and hotness

We know from the Second Law that if Q_1 is extracted from the hotter reservoir then some work can be obtained and therefore

$$Q_2 < Q_1 \quad \Rightarrow \quad T_2 < T_1$$

This implies that the hotter reservoir has the higher temperature, as expected.

(but we could have defined it the other way round, reversing the ordering of temperature and hotness).

7.3 Efficiencies of Engines, Heat Pumps and Refrigerators

What is the maximum efficiency of
an engine, heat pump or refrigerator?

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

for an engine

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

a heat engine running between the steam point (T_1 = 373 K) and the ice point (T_2 = 273 K) has a maximum efficiency of 27%.

to increase the efficiency one wants to maximise the temperature difference between the reservoirs

For heat pumps we are interested in the reverse, i.e. the ratio of heat dumped to the hot reservoir to the work input:

$$\eta_{\mathrm{HP}} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$$

for small temperature differences, the efficiency is high

For instance to heat a house to 18C with a river flowing by of temperature 8C, η_{HP} = 29%

One issue is the efficiency in the transfer of the heat.

in refrigerators we are interested in the amount of heat extracted from the cold reservoir per unit work:

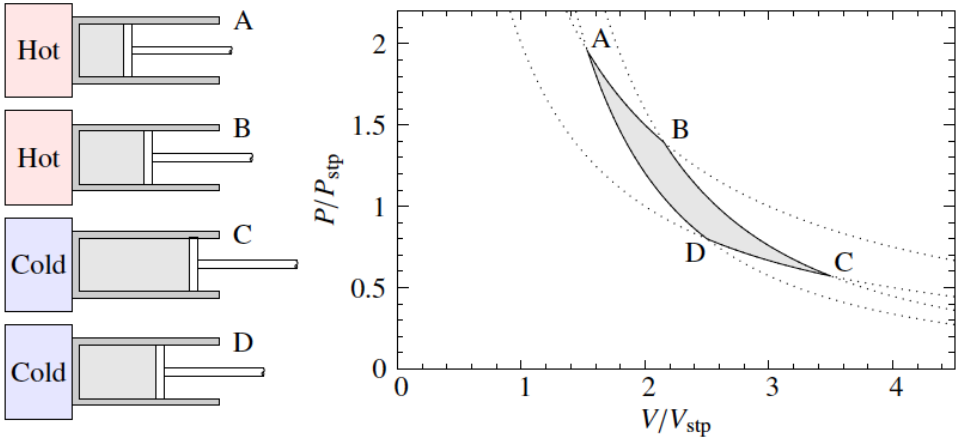
$$\eta_R = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

high efficiency when T_1-T_2 is small

7.4 Goodbye to T_I

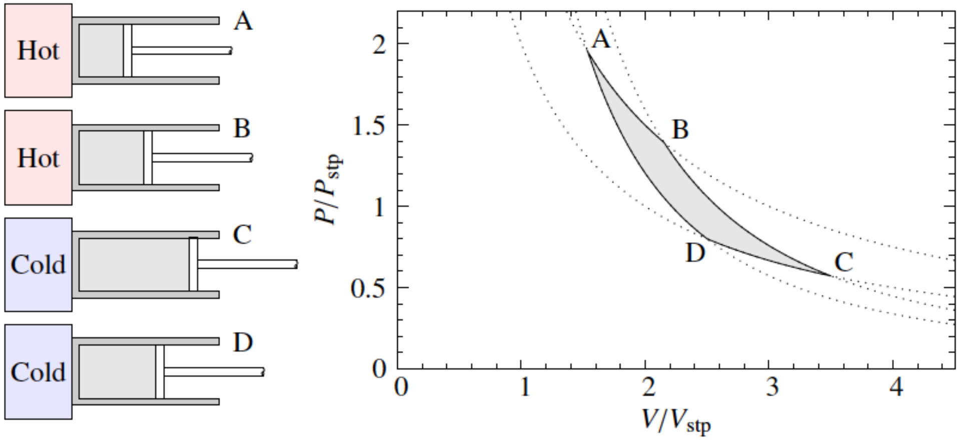
Is there an easier way to measure the thermodynamic temperature?

Let's go back to the Carnot engine:



If we consider the transition from A to B,
the gas is in contact with a hot reservoir and expands isothermally

all heat absorbed in an isothermal expansion of an ideal gas is converted to work,
so the work performed in this stage gives the heat absorbed Q_1



We know that the work is given by:

$$W_R = -n_m R T_{\mathrm{I}} \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = -n_m R T_{\mathrm{I}} \left[\ln V\right]_{V_1}^{V_2} = n_m R T_{\mathrm{I}} \ln\left(\frac{V_1}{V_2}\right)$$

Considering the transition from A to B,
$V_1 = V_A$, and $V_2 = V_B$, and $T_I = (T_I)_1$:

$$Q_1 = n_m R (T_{\mathrm{I}})_1 \ln \frac{V_B}{V_A}$$

heat absorbed

Considering the transition from C to D:

$$Q_2 = n_m R (T_{\mathrm{I}})_2 \ln \frac{V_C}{V_D}$$

heat released

Combining the results obtained:

$$Q_1 = n_m R (T_\mathrm{I})_1 \ln \frac{V_B}{V_A} \qquad Q_2 = n_m R (T_\mathrm{I})_2 \ln \frac{V_C}{V_D}$$

$$\frac{Q_1}{Q_2} = \boxed{\frac{T_1}{T_2}} = \frac{(T_\mathrm{I})_1}{(T_\mathrm{I})_2} \frac{\ln(V_B/V_A)}{\ln(V_C/V_D)}$$

this is the definition of thermodynamic temperature

$T_1/T_2=(T_\mathrm{I})_1/(T_\mathrm{I})_2$

if $\ln(V_B/V_A)/\ln(V_C/V_D)=1$

the equivalence between the thermodynamic and ideal gas scales

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{(T_\mathrm{I})_1}{(T_\mathrm{I})_2}\frac{\ln(V_B/V_A)}{\ln(V_C/V_D)}$$

remembering that points B and C, and points D and A are connected by reversible adiabatic transitions for which we know that $T_I V^{\gamma-1}$ = constant

$$\begin{aligned}(T_\mathrm{I})_1 V_B^{\gamma-1} &= (T_\mathrm{I})_2 V_C^{\gamma-1} \\ (T_\mathrm{I})_1 V_A^{\gamma-1} &= (T_\mathrm{I})_2 V_D^{\gamma-1}\end{aligned}$$

Dividing these two equations shows that $V_B/V_A = V_C/V_D$ and so:

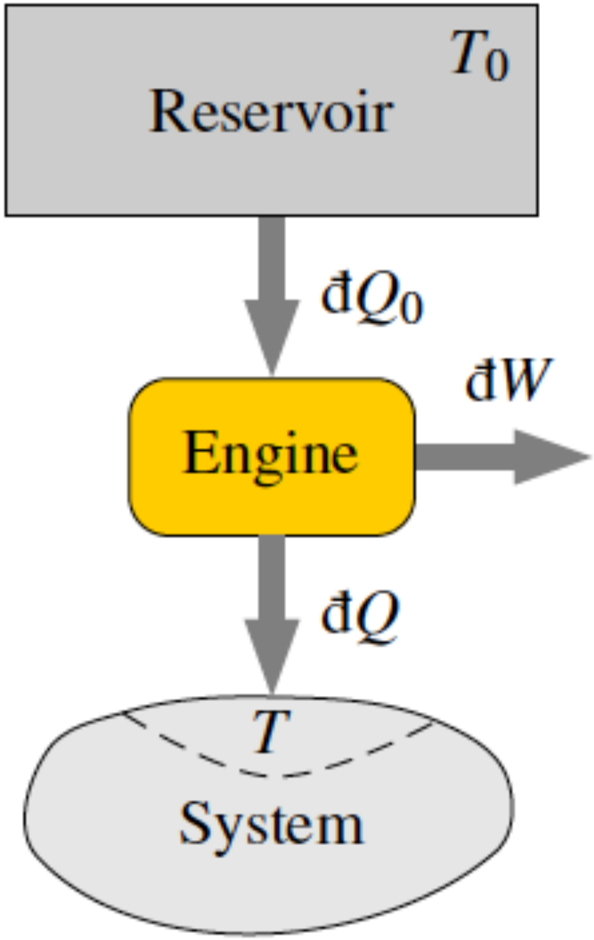
$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{(T_\mathrm{I})_1}{(T_\mathrm{I})_2}$$

the ideal gas temperature scale is identical to the thermodynamic temperature scale.

From now on, there will be no more T_I, but just T instead.

7.5 Entropy

Let's consider a Carnot's engine:



For each infinitesimal cycle of the Carnot engine the heat transferred from the reservoir is:

$$đQ_0 = T_0 \frac{đQ}{T}$$

where T_0 is positive.

By making each cycle infinitesimally small we can consider T to be fixed over the cycle.

The engine runs between a reservoir at temperature T_0 and a part of the system at temperature T .

Now we take the system through a large cycle, encompassing many complete cycles of the Carnot engine,
returning everything to its initial state, so that the internal energy (of system plus Carnot engine) is unchanged.

⇓

Hence the total heat Q_0 extracted from the reservoir is equal to the work done by the system and the Carnot engine.
By the Kelvin-Planck statement of the Second Law these must be less than or equal to zero or we would have converted heat completely into work with no other effect.
Therefore, the heat transferred to the system:

$$\text{đ}Q_0 = T_0 \frac{\text{đ}Q}{T} \quad \Rightarrow \quad Q_0 = \oint \text{đ}Q_0 = T_0 \oint \frac{\text{đ}Q}{T} \leq 0$$

Given that T_0 is positive:

$$\boxed{\oint \frac{\text{đ}Q}{T} \leq 0}$$

Clausius' inequality

$$\boxed{\oint \frac{\text{đ}Q}{T} \leq 0}$$

In general, the different parts of the system might not be in thermal equilibrium with each other and it might be impossible to define a temperature for the system as a whole.

Here, T is the temperature at which heat is supplied to the system

If we consider a reversible process, we can run the cycle in reverse, therefore, every heat transfer +Q becomes -Q:

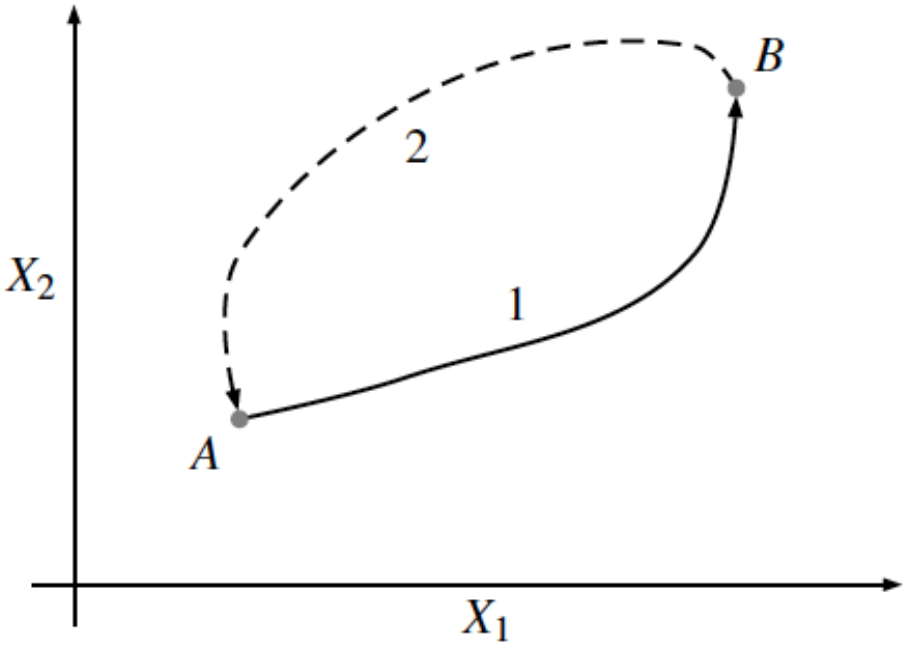
⬇

$$\oint \text{đ}Q/T \geq 0$$

If $\oint \frac{\text{đ}Q}{T} \leq 0$ and $\oint \text{đ}Q/T \geq 0$ ➡ $\oint \frac{\text{đ}Q_R}{T} = 0,$

Clausius's inequality becomes an equality for reversible changes

Consider a system taken through a cycle from A to B via path 1 and then back to A via path 2, reversibly:



$$\oint \frac{đQ_R}{T} = \left(\int_A^B \frac{đQ_R}{T}\right)_1 + \left(\int_B^A \frac{đQ_R}{T}\right)_2 = 0$$

$$\Downarrow$$

$$\left(\int_A^B \frac{đQ_R}{T}\right)_1 = \left(\int_A^B \frac{đQ_R}{T}\right)_2$$

$$\left(\int_A^B \frac{\text{đ}Q_R}{T}\right)_1 = \left(\int_A^B \frac{\text{đ}Q_R}{T}\right)_2$$

the value of this integral is independent of the path taken

there must be a function of state *S*, such that:

$$S_B - S_A = \int_A^B \frac{\text{đ}Q_R}{T}$$

the new function of state is called the entropy

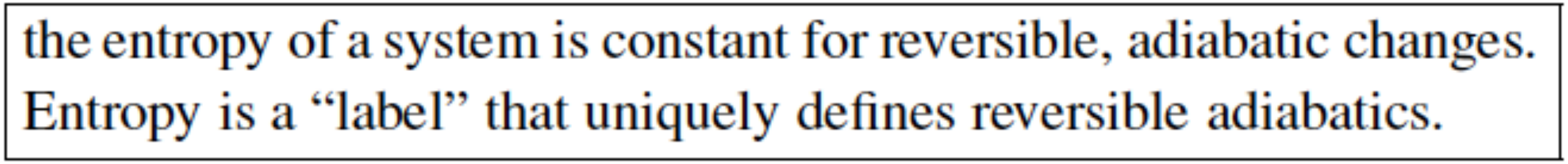
A change of entropy in the system is given by:

$$\boxed{\mathrm{d}S = \frac{\text{đ}Q_R}{T}}$$

where the R is a reminder that this only applies to
reversible transfer of heat
and T is the temperature at which heat is supplied to the system.

$$\boxed{\mathrm{d}S = \frac{\text{đ}Q_R}{T}}$$

if a change is reversible and adiabatic as well ($\text{đ}Q = 0$), then $dS = 0$



the entropy of a system is constant for reversible, adiabatic changes. Entropy is a “label” that uniquely defines reversible adiabatics.

Now consider that path 1 is irreversible while path 2 remains reversible. Then from Clausius's inequality:

$$\oint \frac{\text{đ}Q}{T} = \left(\int_A^B \frac{\text{đ}Q}{T}\right)_1 + \left(\int_B^A \frac{\text{đ}Q_R}{T}\right)_2 \leq 0$$

Given that $S_B - S_A = \displaystyle\int_A^B \frac{\text{đ}Q_R}{T} \;\Longrightarrow\; \left(\int_B^A \frac{\text{đ}Q_R}{T}\right)_2 = S_A - S_B$

$$\Downarrow$$

$$S_B - S_A \geq \int_A^B \frac{\text{đ}Q}{T}$$

And for an infinitesimal heat transfer: $\boxed{\text{đ}Q \leq T\,\mathrm{d}S}$

7.6 The Increase of Entropy and Heat Death of the Universe

For an isolated system $\text{đ}Q = 0$, so Clausius' inequality becomes:

$$\boxed{\text{đ}Q \le T\,\mathrm{d}S} \quad \Rightarrow \quad \mathrm{d}S \ge 0$$

the entropy of an isolated system can never decrease

This result imposes a direction in which processes can occur.
Applied to the Universe as a whole, the entropy will carry on increasing until it can no longer do so, by which point the Universe will be in a state of equilibrium and it will no longer be possible to extract work from any process.
This is the so-called heat death of the Universe.

The increase of entropy gives us another way to decide whether a process is reversible or not:

reversible processes do not change the total entropy of the Universe

7.7 Calculations Involving Entropy

Since entropy is a function of state, it does not matter how you calculate the change as long as the system begins and ends in an equilibrium state.

Therefore, you might as well make things simple and do things reversibly when you can.

7.7.1 Heat engines

In a heat engine, the hot reservoir has heat Q_1 removed so:

$$\Delta S_1 = -\frac{Q_1}{T_1}$$

Similarly:

$$\Delta S_2 = \frac{Q_2}{T_2}$$

So the total entropy change after a cycle is:

$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

If the engine is reversible:

$$Q_1/T_1 = Q_2/T_2 \text{ and } \Delta S = 0$$

If the engine is irreversible, then it is less efficient,
or, equivalently, Q_2 is larger for a given Q_1
than in the case of a reversible engine

⇩

$\Delta S > 0$

Irreversible engines are therefore entropy sources

7.7.2 Entropy Change during a Change of Phase

The change of a liquid to a gas or solid to liquid
is called a change of phase.

This involves latent heat, heat absorbed at constant temperature.

This implies that an increase of entropy has occurred, with no change in temperature.

Let us consider to bring a mass m of liquid to boil, this requires to provide an amount of heat to the system:

$$Q = mL$$

where L is latent heat of vaporisation, at temperature T_b (boil).
Therefore:

$$\Delta S_l = \frac{mL}{T_b}$$

$$\Delta S_l = \frac{mL}{T_b}$$

In this case, an entropy increase is associated with increasing disorder

It is only the entropy of the substance that has increased
the entropy of the Universe could stay constant if the process was carried out reversibly because then you would have supplied
heat Q at temperature T_b,
and so the entropy of the surroundings would have dropped by ΔS_l.

7.7.3 Hot objects placed in water

Consider to heat a lump of iron to temperature T_{Fe}, and then place it into a large quantity of water of temperature T_W.
The final temperature will be about T_W.
Such a process is irreversible

we expect the total entropy to increase.

If we consider that the temperature of the water hardly changes, the heat transferred from the iron to the water is:

$$Q = m_{Fe}C_{Fe}(T_{Fe} - T_W)$$

the change in entropy for the water:

$$\Delta S_W = m_{Fe}C_{Fe}\frac{T_{Fe} - T_W}{T_W}$$

as the iron loses heat, it cools down
so the temperature T that we use in the relation $dS = \text{đ}Q_R/T$ changes as a function of time.
We therefore need to integrate.
Remembering that

$$\text{đ}Q = m_{Fe}C_{Fe}\,dT$$

$$\Downarrow$$

the change in entropy for the iron:

$$\Delta S_{\mathrm{Fe}} = \int_{T_{\mathrm{Fe}}}^{T_{\mathrm{W}}} \frac{m_{\mathrm{Fe}} C_{\mathrm{Fe}}\, dT}{T} = -m_{\mathrm{Fe}} C_{\mathrm{Fe}} \ln \frac{T_{\mathrm{Fe}}}{T_{\mathrm{W}}}$$

The total entropy change of the Universe is then:

$$\delta S = \Delta S_{\mathrm{W}} + \Delta S_{\mathrm{Fe}} = m_{\mathrm{Fe}} C_{\mathrm{Fe}} \underbrace{\boxed{\left(\frac{T_{\mathrm{Fe}} - T_{\mathrm{W}}}{T_{\mathrm{W}}} - \ln \frac{T_{\mathrm{Fe}}}{T_{\mathrm{W}}} \right)}}_{>0}$$

entropy increases

7.7.4 Isothermal Expansion of Gas

During the isothermal expansion of an ideal gas, the heat absorbed equals the work performed by the gas.

Therefore:

$$\text{đ}Q_R = T\,\mathrm{d}S = P\,\mathrm{d}V$$

$$\Delta S_{\text{gas}} = \int_{V_1}^{V_2} \frac{P\,\mathrm{d}V}{T}$$

For an ideal gas,
$PV = n_m RT$

$$\Delta S_{\text{gas}} = n_m R \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = n_m R \ln \frac{V_2}{V_1}.$$

since entropy is a function of state, this formula is correct regardless of how the volume change is carried out, as long as we start and end in equilibrium at temperature T.

7.7.5 Joule Expansions

Joule expansions are classic examples of irreversible changes.

In this case no heat is transferred, so the surroundings do not change their entropy.

However, in expanding from V_1 to V_2, the entropy of the gas does change according to:

$$\Delta S = n_m R \ln \frac{V_2}{V_1}$$

this is the change of entropy of the Universe,
and since $V_2 > V_1$, then $\Delta S > 0$ as expected.

7.8 Generating Entropy

Any irreversibility generates entropy

Entropy is not conserved

The sun, which is a huge entropy source,
generates $4*10^{26}$Watt at a temperature of T = $15*10^6$K at its centre.

This corresponds to an entropy generation rate of:

$$\frac{4 \times 10^{26}\,\mathrm{W}}{15 \times 10^{6}\,\mathrm{K}} = 2.67 \times 10^{19}\,\mathrm{J\,K^{-1}\,s^{-1}}$$

All this power is radiated at its surface at a temperature of 5700 K, so entropy is generated at:

$$\frac{4 \times 10^{26}\,\mathrm{W}}{5700\,\mathrm{K}} = 7.02 \times 10^{22}\,\mathrm{J\,K^{-1}\,s^{-1}}$$

between the core and the surface
irreversible heat transfer processes have generated entropy.

7.9 Statistical Interpretation of Entropy

Entropy shows in which direction processes can occur
and distinguishes reversible adiabatic processes,
but *what is it?*

The increase of entropy during a Joule expansion indicates that it is irreversible.
Gas molecules in a box of volume V will never spontaneously all move to volume V/2.

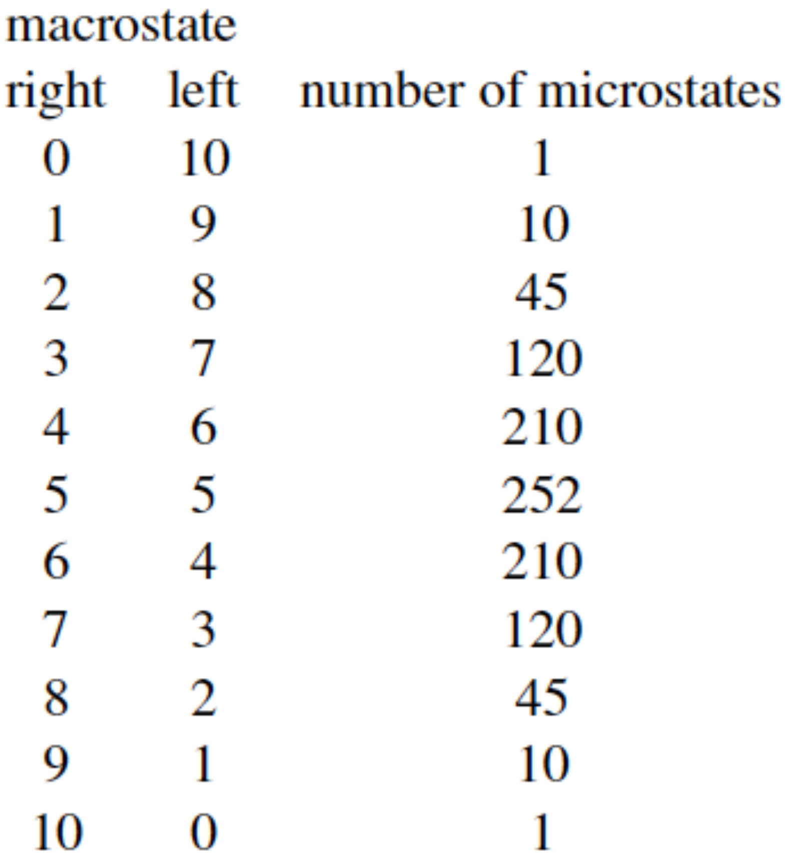
Let us count the number of ways in which we can distribute N molecules into two halves of a box.
At the microscopic level, each molecule can be in either the left or right half (but not both), and there are 2^N possibilities in total: these are the distinct microstates.

At a macroscopic level, all that matters is how many molecules are in each half: we can label these macrostates by the number or fraction of the molecules in, say, the right half of the box (since the total number is fixed).

The number of ways in which we can have n molecules out of N on the right is simply the number of combinations of n distinguishable objects drawn from N:

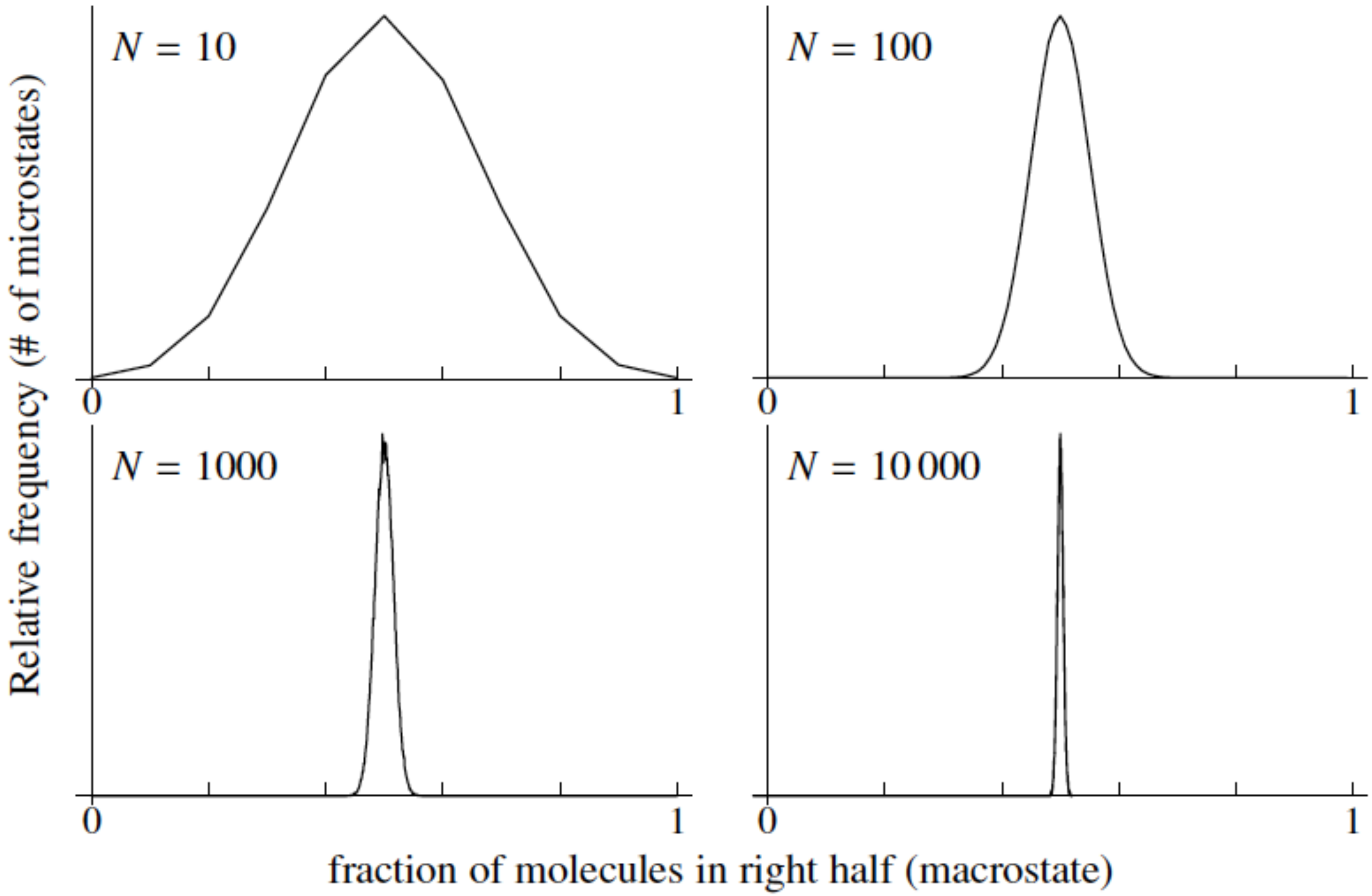
$$\frac{N!}{(N-n)!\,n!}$$

If there are N = 10 molecules in total, for example, there are 11 possible macrostates, with microstates distributed as follows:



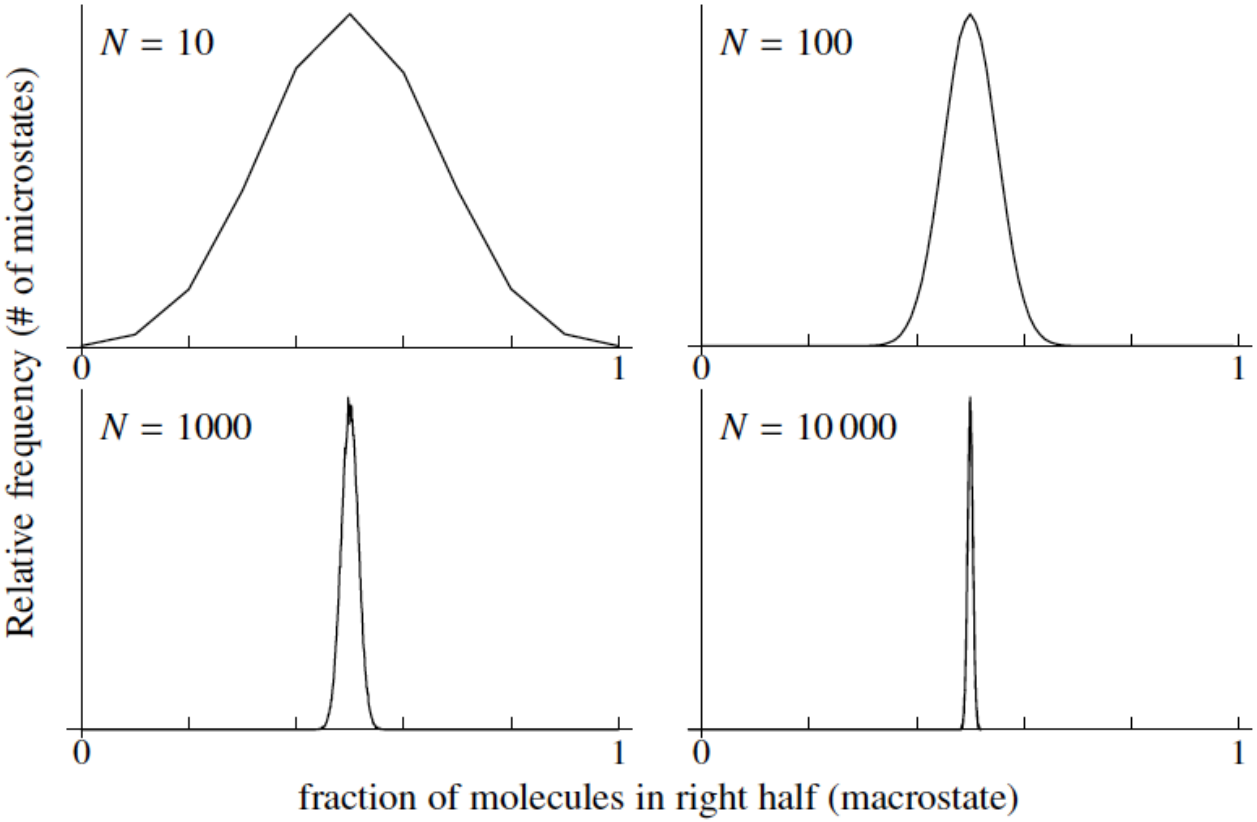
macrostate		
right	left	number of microstates
0	10	1
1	9	10
2	8	45
3	7	120
4	6	210
5	5	252
6	4	210
7	3	120
8	2	45
9	1	10
10	0	1

Multiplicity distributions for states of N = 10, 100, 1000 and 10 000 molecules distributed in two halves of a box



As N increases it becomes less and less probable to have anything other than (almost) equal numbers in the two halves.

What you can see is that as N increases,
there is a sharper and sharper peak centred at 50% occupancy.
This should make it easy to believe that with N = 10^{23} molecules
you essentially always find a macrostate with equal occupancy in the two halves of the box.



All this suggests that entropy may be related to the number of ways of arranging molecules, which is known as the multiplicity, W.

The multiplicity of a macrostate
is the number of microstates which correspond to it.

For N molecules expanding from volume V_1 to V_2 (so V_1 and V_2 label the macrostates), the multiplicity changes by:

$$\frac{W_2}{W_1} = \left(\frac{V_2}{V_1}\right)^N$$

If we take the natural logarithm: $$\ln \frac{W_2}{W_1} = N \ln \frac{V_2}{V_1}$$

Remembering that for the Joule expansion: $$\Delta S = n_m R \ln \frac{V_2}{V_1}$$

If we suppose that we can write S = k lnW, where k is a constant:

$$\begin{aligned} \Delta S &= S_2 - S_1 = k(\ln W_2 - \ln W_1) \\ &= k \ln \frac{W_2}{W_1} = kN \ln \frac{V_2}{V_1} = n_m N_A k \ln \frac{V_2}{V_1} = n_m R \ln \frac{V_2}{V_1} \end{aligned}$$

This is exactly the same as:

$$\Delta S = n_m R \ln \frac{V_2}{V_1}$$

S = k lnW

Boltzmann relation

entropy as a measure of the number of microscopic arrangements or microstates of a system W

The Universe is always changing to a more probable configuration, in the sense of more available microstates.
The new configurations are so much more probable that the change is irreversible.

7.10 Summary

- In the hands of Clausius and Kelvin, Carnot's theorem led to the definition of an absolute, as opposed to empirical, temperature scale.

- A new function of state was recognised, called entropy.
  The entropy change of a system absorbing heat đQ, with the heat transfer occurring at temperature T, is Clausius' inequality in the form dS ≥ đQ/T.

- When the change is reversible, this reduces to $dS = đQ_R/T$ where T is the temperature of the system.

- The important consequence of Clausius' inequality is that the entropy of an isolated system always increases.

- Following Boltzmann: a system always tends towards states of greater multiplicity given external constraints.