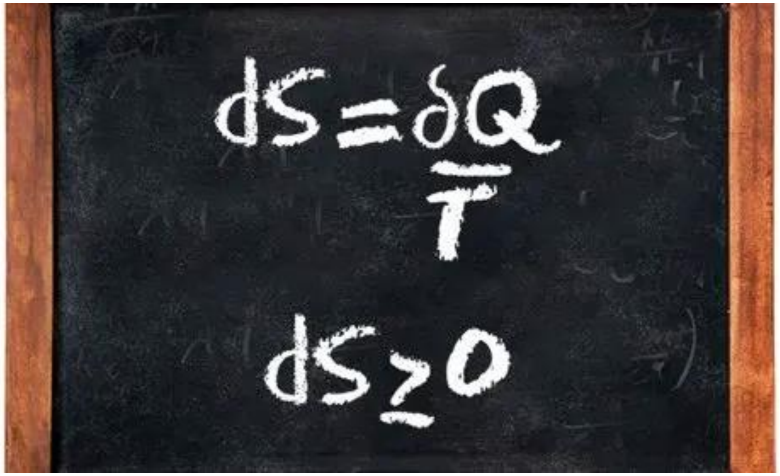
Picture taken from https://www.theguardian.com/science/2013/dec/01/what-is-the-second-law-of-thermodynamics



Second law of Thermodynamics

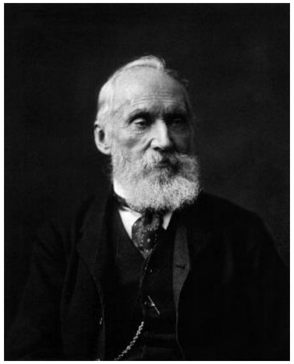
Carnot's Theorem

Entropy

Clausius' Theorem

Second law of thermodynamics

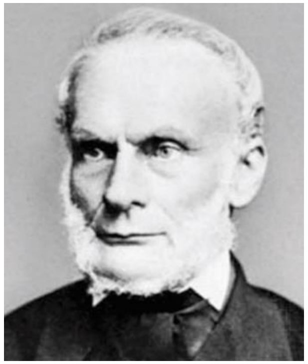
No process is possible whose sole result is the complete conversion of heat into work.



Lord Kelvin

https://commons.wikimedia.org/w/index.php?curid=376221

No process is possible whose sole result is the transfer of heat from a colder to a hotter body.



Rudolf Clausius

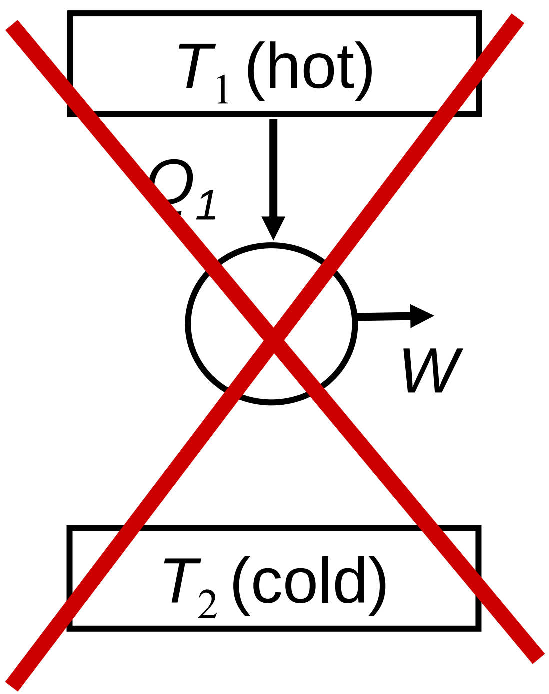
https://opentextbc.ca/chemistry/chapter/16-2-entropy/

Second law of thermodynamics

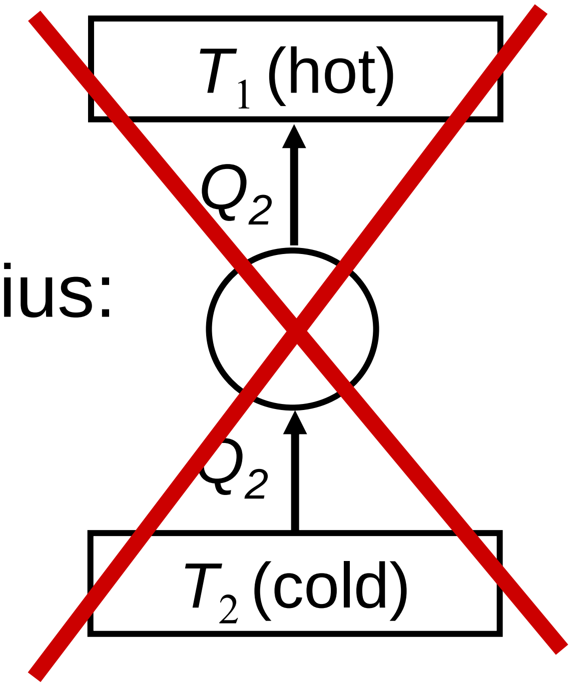
Complete conversion of heat into work

Only transfer of heat from a colder to a hotter body

Kelvin:



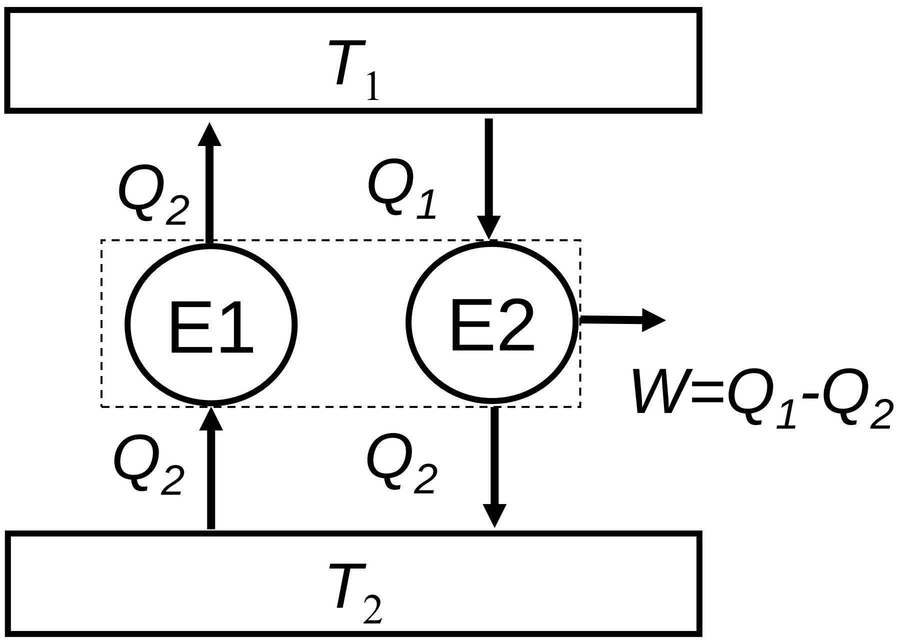
Clausius:



Proof that Clausius ≡ Kelvin

Suppose we have an engine E1 that violates Clausius and a normal engine E2.

Make E2 output Q_2 to the cold bath.



Now look at E1+E2 as one engine: compare to Kelvin violator.

It's the same.

So, if C. is not obeyed, K. is not.

Homework: can you show the equivalence starting from a Kelvin violator?

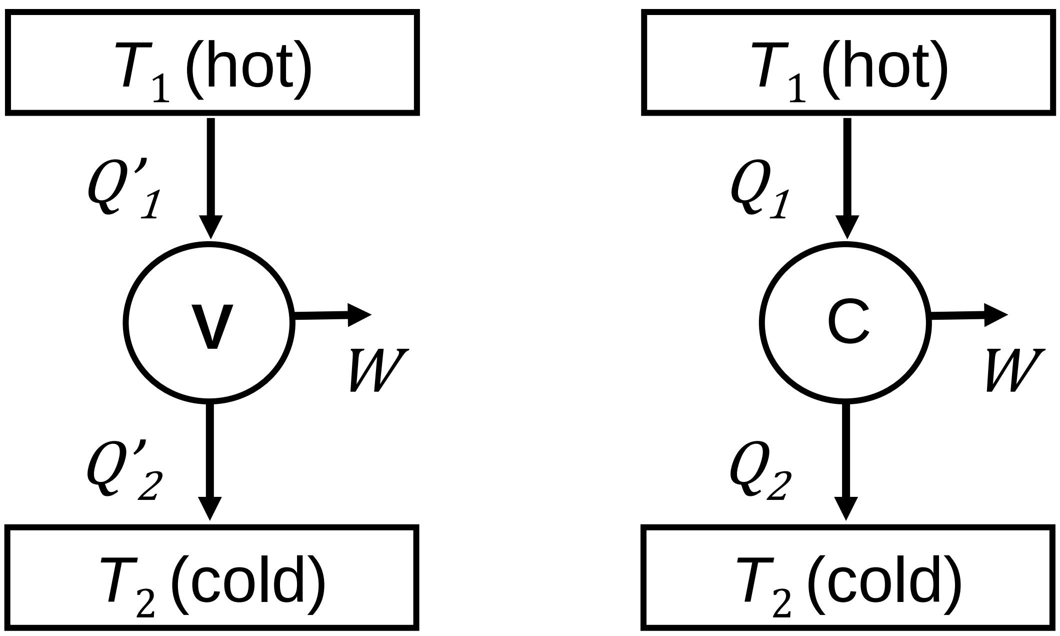
Carnot's theorem (1824)

No engine operating between two given heat reservoirs can be more efficient than a Carnot engine operating between the same two baths.

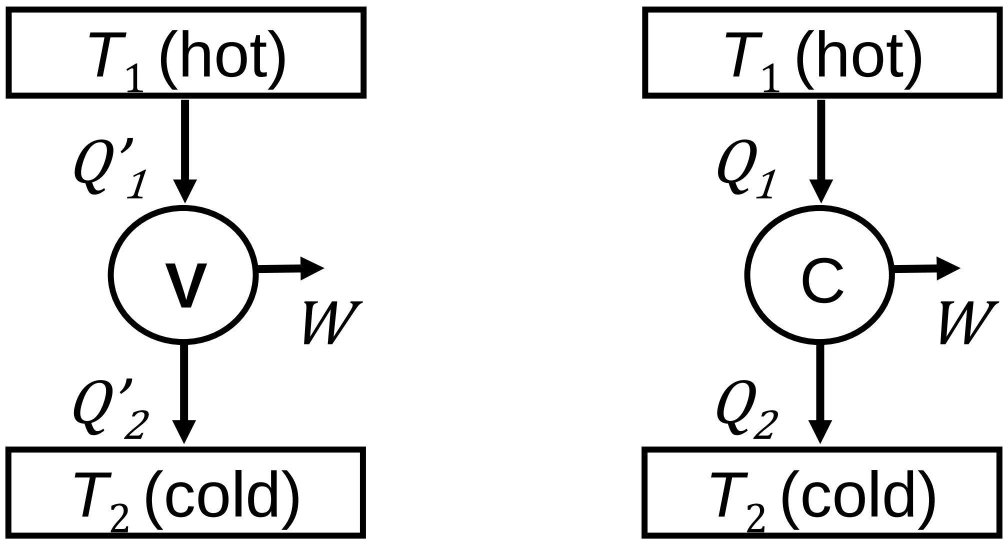
-a consequence of the 2nd law.

$$\eta_{\text{Carnot}} \geq \eta_{\text{other}}$$

Proof: Assume engine **V** is more efficient



Carnot's theorem

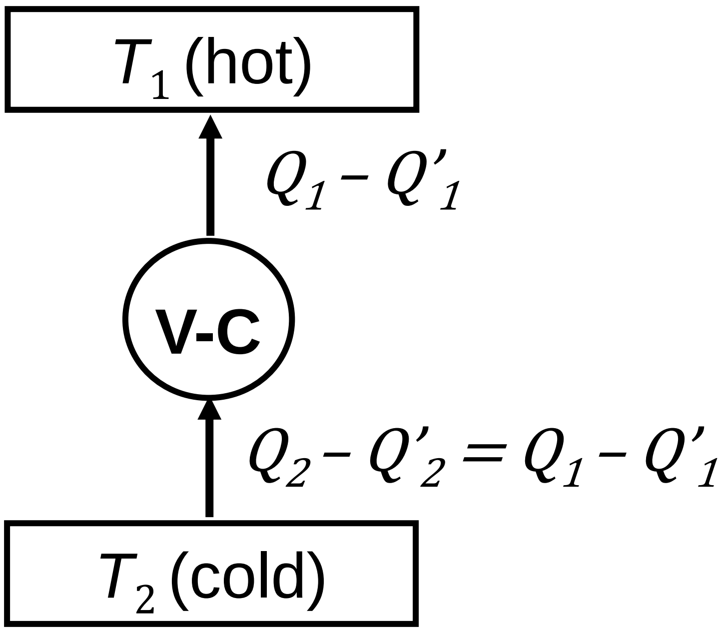


1st law: $W = Q'_1 - Q'_2 = Q_1 - Q_2$

$\Rightarrow$ $\underbrace{Q_1 - Q'_1}_{\text{positive if } Q'_1 < Q_1,\ \frac{W}{Q'_1} > \frac{W}{Q_1},\ \eta_V > \eta_C} = Q_2 - Q'_2$

Carnot's theorem

Put the two together, reverse the Carnot engine and drive it by **V**:



net result is taking $Q_1 - Q'_1$ from cold to hot body:

violates Clausius Principle

unless $Q_1 = Q'_1$ and hence $\eta_V = \eta_C$

$\Rightarrow$ Carnot engine has highest possible efficiency

$\Rightarrow$ ALL reversible engines have the same efficiency η_C

Note: this is slightly different to what we've just proven. See Blundell & Blundell p126 for full proof.

Towards (classical) entropy

We stated that $\eta_{\text{Carnot}} \geq \eta_{\text{other}}$

Substituting in, $1 - \frac{Q_2^C}{Q_1^C} \geq 1 - \frac{Q_2^O}{Q_1^O}$ and therefore $\frac{Q_2^C}{Q_1^C} \leq \frac{Q_2^O}{Q_1^O}$

$$\frac{Q_2^C}{Q_1^C} = \frac{\mathrm{T}_2}{\mathrm{T}_1} \text{ so that we obtain } \frac{Q_2^O}{\mathrm{T}_2} \geq \frac{Q_1^O}{\mathrm{T}_1}$$

What does this mean? Recall, Q_1 and Q_2 are heats entering and leaving system so, taking heat flow into the system as positive,

$$\frac{Q_1^O}{\mathrm{T}_1} - \frac{Q_2^O}{\mathrm{T}_2} \leq 0; \quad \text{generalising this, } \boxed{\sum_{\text{cycle}} \frac{Q^O}{\mathrm{T}} \leq 0}$$

where the equality applies for reversible cycles.

Entropy and Clausius' theorem

Without proof, shall generalise this result to Clausius' theorem:

For any closed cycle, $\oint_{\text{cycle}} \frac{đQ}{T} \leq 0$

where the equality holds for reversible cycles.

For an infinitesimal reversible change, define a new variable *S,* the *entropy*, given by

$$\mathrm{d}S = \frac{đQ_{\text{rev}}}{T}$$

For a finite, reversible change

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{đQ_{\text{rev}}}{T}$$

Units of entropy are $\mathrm{JK^{-1}}$

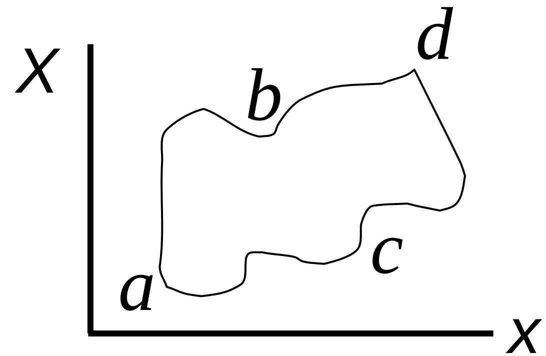
Not usually direct measureable.

Entropy

Entropy is a function of state

Proof

For a reversible cycle, $\oint_{\text{rev cycle}} \frac{đQ}{T} = 0$



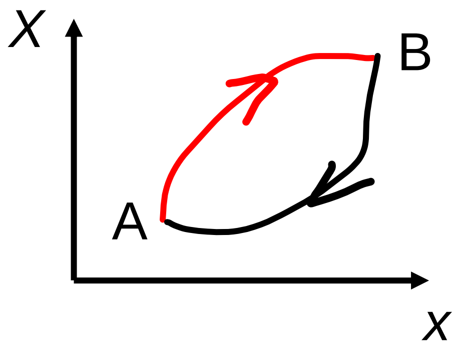
Example, $\oint_{abdca} \mathrm{d}S = \int_{abd} \mathrm{d}S + \int_{dca} \mathrm{d}S = 0$

Therefore, $\int_{abd} \mathrm{d}S = \int_{acd} \mathrm{d}S$

So, the entropy change is path-independent for any reversible path; <u>entropy is a function of state</u> (and thus d*S* is an exact differential).

Entropy in irreversible changes

Clausius theorem says $\oint_{\text{cycle}} \frac{đQ}{T} \leq 0$



$$\int_{\mathrm{A}}^{\mathrm{B}} \frac{đQ}{T} + \int_{\mathrm{B}}^{\mathrm{A}} \frac{đQ_{\text{rev}}}{T} \leq 0$$

$$\int_{\mathrm{A}}^{\mathrm{B}} \frac{đQ}{T} \leq \int_{\mathrm{A}}^{\mathrm{B}} \frac{đQ_{\text{rev}}}{T}$$

$$\Rightarrow \qquad \frac{đQ}{T} \leq \frac{đQ_{\text{rev}}}{T} = \mathrm{d}S$$

For thermally isolated system $đQ = 0$

Therefore $\mathrm{d}S \geq 0$ (equality for reversible process $\leftrightarrow$ S is constant)

In the universe $đQ = 0$ (assumption)

So $\mathrm{d}S > 0$ (certainly irreversible):

In the end: all (thermal) processes are heading towards the “heat death of the Universe”.