The Second Law

▲ First Law showed the equivalence of work and heat

$\Delta U = q + w$, $\oint dU = 0$ for cyclic process $\Rightarrow$ $q = -w$

Suggests engine can run in a cycle and convert heat into useful work.

▲ Second Law

- Puts restrictions on useful conversion of q to w
- Follows from observation of a directionality to natural or spontaneous processes
- Provides a set of principles for
  - determining the direction of spontaneous change
  - determining equilibrium state of system

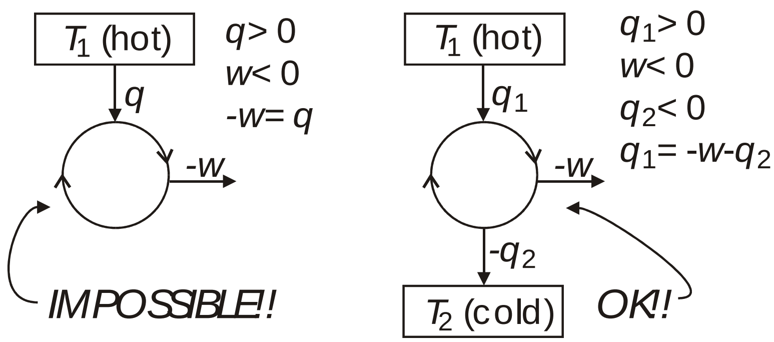
Need a definition:

Heat reservoir Definition: A very large system of uniform T, which does not change regardless of the amount of heat added or withdrawn.

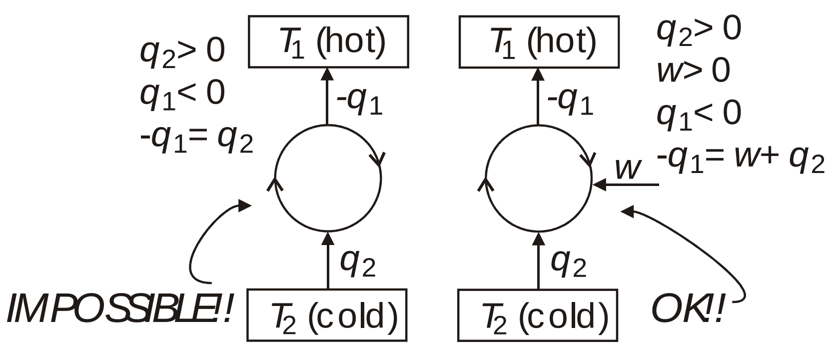
Also called a heat bath. Real systems can come close to this idealization.

Two classical statements of the Second Law:
Kelvin
Clausius
and a Mathematical statement

I. Kelvin: It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it to work in the surroundings without at the same time transferring some heat to a colder reservoir.



II. Clausius: It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfers it to a hot reservoir without at the same time converting some work into heat.



Alternative Clausius statement: All spontaneous processes are irreversible.

(e.g. heat flows from hot to cold spontaneously and irreversibly)

Mathematical statement: $\boxed{\oint \frac{đq_{rev}}{T} = 0 \quad and \quad \oint \frac{đq_{irrev}}{T} < 0}$

$\int \frac{đq_{rev}}{T}$ is a state function $= \int dS \quad \rightarrow \quad dS = \frac{đq_{rev}}{T}$

$S \equiv$ ENTROPY

$$\oint dS = 0 \quad \rightarrow \quad \Delta S = S_2 - S_1 = \int_1^2 \frac{q_{rev}}{T} > \int_1^2 \frac{q_{irrev}}{T}$$

for cycle $[1] \xrightarrow{irrev} [2] \xrightarrow{rev} [1]$

$$\int_1^2 \frac{q_{irrev}}{T} + \int_2^1 \frac{q_{rev}}{T} = \oint \frac{q_{irrev}}{T} < 0$$

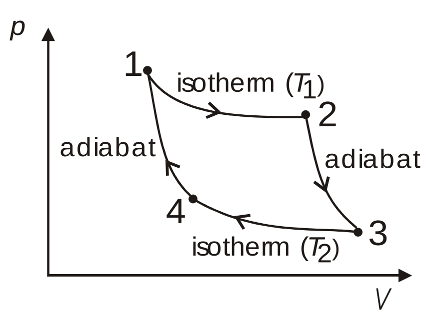
$$\int_1^2 \frac{q_{irrev}}{T} - \Delta S < 0 \Rightarrow \Delta S > \int_1^2 \frac{q_{irrev}}{T}$$

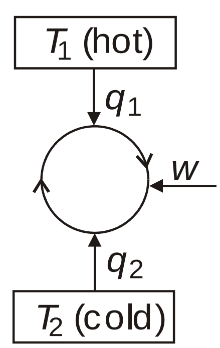
Kelvin and Clausius statements are specialized to heat engines.
Mathematical statement is very abstract.

Let's Link them through analytical treatment of a heat engine.

The Carnot Cycle - a typical heat engine

All paths are <u>reversible</u>





$1 \rightarrow 2$ isothermal expansion at T_1 (hot) $\Delta U = q_1 + w_1$
$2 \rightarrow 3$ adiabatic expansion (q = 0) $\Delta U = w_1'$
$3 \rightarrow 4$ isothermal expansion at T_2 (cold) $\Delta U = q_2 + w_2$
$4 \rightarrow 1$ adiabatic compression (q = 0) $\Delta U = w_2'$

$$\text{Efficiency} = \frac{\text{work output to surroundings}}{\text{heat in at } T_1 \text{ (hot)}} = \frac{-\left(w_1 + w_1' + w_2 + w_2'\right)}{q}$$

1st Law $\Rightarrow \oint dU = 0 \Rightarrow q_1 + q_2 = -\left(w_1 + w_1' + w_2 + w_2'\right)$

$$\therefore \boxed{\text{Efficiency} = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1}}$$

Kelvin: $q_2 < 0 \rightarrow$ Efficiency $\equiv \varepsilon < 1$ (< 100%)

$-w = q_1\varepsilon$ = work output

Note: if the cycle were run in reverse, then $q_1 < 0$, $q_2 > 0$, $w > 0$.
It's a refrigerator!

$\boxed{\text{Carnot cycle for an ideal gas}}$

$1 \rightarrow 2$ $\Delta U = 0; \quad q_1 = -w_1 = \int_1^2 p dV = RT_1 \ln\left(\frac{V_2}{V_1}\right)$

$2 \rightarrow 3$ $q = 0; \quad w_1' = C_V\left(T_2 - T_1\right)$

Rev. adiabat $\Rightarrow \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma - 1}$

$3 \rightarrow 4$ $\Delta U = 0; \quad q_2 = -w_2 = \int_3^4 p dV = RT_2 \ln\left(\frac{V_4}{V_3}\right)$

$4 \rightarrow 1$ $q = 0; \quad w_2' = C_V\left(T_1 - T_2\right)$

Rev. adiabat $\Rightarrow \left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma - 1}$

$$\frac{q_2}{q_1} = \frac{T_2 \ln(V_4/V_3)}{T_1 \ln(V_2/V_1)}$$

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \quad \Rightarrow \quad \left(\frac{V_4}{V_3}\right) = \left(\frac{V_1}{V_2}\right) \quad \Rightarrow \quad \boxed{\frac{q_2}{q_1} = -\frac{T_2}{T_1}}$$

or $\quad \dfrac{q_1}{T_1} + \dfrac{q_2}{T_2} = 0 \quad \Rightarrow \quad \boxed{\oint \dfrac{đq_{rev}}{T} = 0}$

this illustrates the link between heat engines to the mathematical statement of the second law

Efficiency $\quad \boxed{\varepsilon = 1 + \dfrac{q_2}{q_1} = 1 - \dfrac{T_2}{T_1}} \quad \rightarrow 100\%$ as $T_2 \rightarrow 0$ K

For a <u>heat engine</u> (Kelvin): $\quad q_1 > 0,\ w < 0,\ T_2 < T_1$

Total work out $= -w = \varepsilon q_1 = \left(\dfrac{T_1 - T_2}{T_1}\right) q_1 \quad \Rightarrow \quad (-w) < q_1$

<u>Note</u>: In the limit $T_2 \rightarrow 0$ K, $(-w) \rightarrow q_1$, and $\varepsilon \rightarrow 100\%$ conversion of heat into work. 3rd law will state that we can't reach this limit!

For a <u>refrigerator</u> (Clausius): $\quad q_2 > 0,\ w > 0,\ T_2 < T_1$

Total work <u>in</u> $= w = \left(\dfrac{T_2 - T_1}{T_1}\right) q_1$

But $\quad \dfrac{q_1}{T_1} = -\dfrac{q_2}{T_2} \quad \Rightarrow \quad w = \left(\dfrac{T_1 - T_2}{T_2}\right) q_2$

<u>Note</u>: In the limit $T_2 \rightarrow 0$ K, $w \rightarrow \infty$. This means it takes an infinite amount of work to extract heat from a reservoir at 0 K $\Rightarrow$ 0 K cannot be reached (3rd law).

- The efficiency of any reversible engine has to be the same as the Carnot cycle, this can be shown by running the reversible engine as a refrigerator, using the work output of a Carnot engine to drive it so that the total work out is zero, and showing that, if the efficiency of the reversible engine is higher, then the second law is broken.

Additionally:

- We can approach arbitrarily closely to any cyclic process using a series of only adiabats and isotherms.

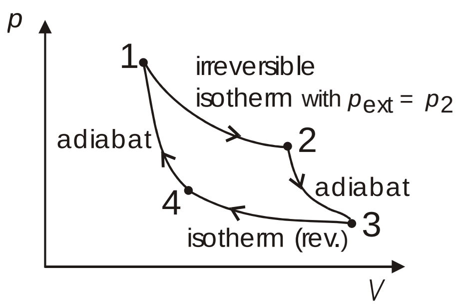
∴ So, for <u>any</u> <u>reversible</u> cycle $\boxed{\oint \frac{đq_{rev}}{T} = 0}$

- This is consistent with the mathematical statement of the second law, which defines <u>Entropy</u>, a function of state, with

$$dS = \frac{đq_{rev}}{T} \quad \Rightarrow \quad \Delta S = S_2 - S_1 = \int_1^2 \frac{đq_{rev}}{T}$$

Note: Entropy is a state function, but to calculate ΔS from q <u>requires</u> a reversible path.

- An <u>irreversible</u> Carnot (or any other) cycle is less efficient than a reversible one.



$1 \rightarrow 2$

$$(-w)_{irrev} < (-w)_{rev} \quad \Rightarrow \quad w_{irrev} > w_{rev}$$

$$\Delta U = q_{irrev} + w_{irrev} = q_{rev} + w_{rev}$$

$$\therefore \quad \boxed{q_{irrev} < q_{rev}}$$

** An irreversible isothermal expansion requires less heat than a reversible one. **

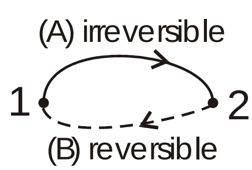
$$\varepsilon_{irrev} = 1 + \frac{q_2^{rev}}{q_1^{irrev}} < 1 + \frac{q_2^{rev}}{q_1^{rev}} = \varepsilon_{rev} \qquad (q_2 < 0)$$

also $\dfrac{đq_{irrev}}{T} < \dfrac{đq_{rev}}{T} \quad \Rightarrow \quad \boxed{\oint \dfrac{đq_{irrev}}{T} < 0}$

- This leads to the <u>Clausius inequality</u>

$$\boxed{\oint \frac{đq}{T} \le 0} \quad \text{contains} \begin{cases} \oint \dfrac{đq_{rev}}{T} = 0 \\ \oint \dfrac{đq_{irrev}}{T} < 0 \end{cases}$$

- Important corollary: The entropy of an <u>isolated</u> system <u>never</u> decreases



(A): The system is <u>isolated</u> and <u>irreversibly</u> (spontaneously) changes from [1] to [2]

(B): The system is brought into contact with a heat reservoir and <u>reversibly</u> brought back from [2] to [1]

Path (A): $q_{irrev} = 0$ (isolated)

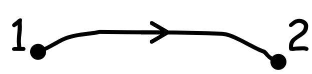
Clausius $\oint \dfrac{đq}{T} \le 0 \quad \Rightarrow \quad \overbrace{\cancel{\int_1^2 \dfrac{đq_{irrev}}{T}}}^{=0!} + \int_2^1 \dfrac{đq_{rev}}{T} \le 0$

$$\Rightarrow \quad \int_2^1 \frac{đq_{rev}}{T} = S_1 - S_2 = -\Delta S \le 0$$

$$\therefore \quad \boxed{\Delta S = S_2 - S_1 \ge 0}$$

This gives the direction of spontaneous change!

For isolated systems	$\Delta S > 0$	Spontaneous, irreversible process
	$\Delta S = 0$	Reversible process
	$\Delta S < 0$	Impossible



$\Delta S = S_2 - S_1$ <u>independent</u> of path

But! $\Delta S_{surroundings}$ <u>depends</u> on whether the process is reversible or irreversible

(a) <u>Irreversible</u>: Consider the universe as an isolated system containing our initial system and its surroundings.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$
$$\therefore \quad \Delta S_{surr} > -\Delta S_{sys}$$

(b) <u>Reversible</u>:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S'_{surr} = 0$$
$$\therefore \quad \Delta S'_{surr} = -\Delta S_{sys}$$

$\Delta S_{universe} \ge 0$ for any change in state (> 0 if irreversible, = 0 if reversible)