5.60 Thermodynamics & Kinetics
Spring 2008

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**

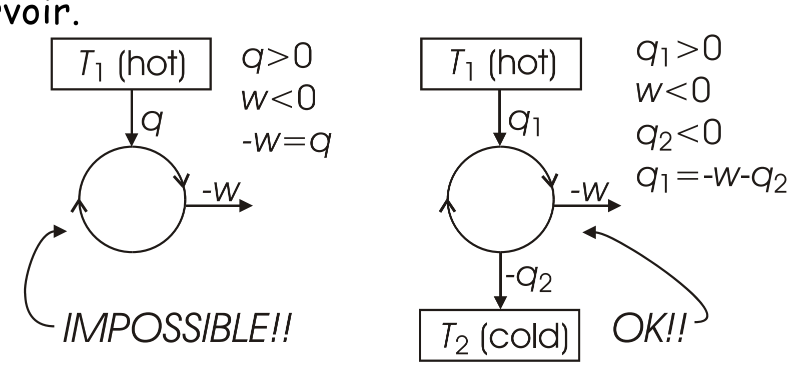
- Puts restrictions on useful conversion of q to w
- Follows from observation of a directionality to natural or spontaneous processes
- Provides a set of principles for
  - determining the direction of spontaneous change
  - determining equilibrium state of system

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reservoir Definition: A very large system of uniform T, which does not change regardless of the amount of heat added or withdrawn.

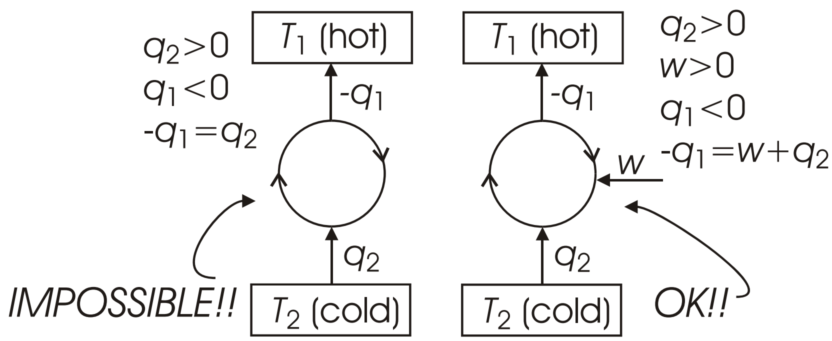
Also called heat bath. Real systems can come close to this idealization.

Different statements of the Second Law

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.



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



<u>Alternative Clausius statement</u>: All spontaneous processes are irreversible.
(e.g. heat flows from hot to cold spontaneously <u>and</u> irreversibly)

<u>Mathematical statement</u>:

$$\oint \frac{đq_{rev}}{T} = 0 \quad and \quad \oint \frac{đq_{irrev}}{T} < 0$$

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

$$S \equiv \text{ENTROPY}$$

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

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

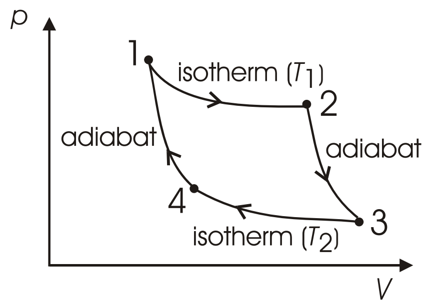
$$\int_1^2 \frac{q_{irrev}}{T} + \int_2^1 \frac{q_{rev}}{T} = \oint \frac{q_{irrev}}{T} < 0$$

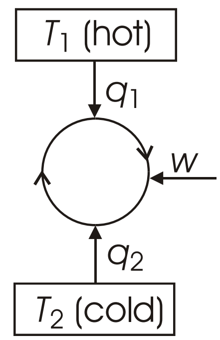
$$\int_1^2 \frac{q_{irrev}}{T} - \Delta S < 0 \Rightarrow \Delta S > \int_1^2 \frac{q_{irrev}}{T}$$

Kelvin and Clausius statements are specialized to heat engines.
Mathematical statement is very abstract.
Link them through analytical treatment of a heat engine.

The Carnot Cycle - a typical heat engine

All paths are <u>reversible</u>





1 → 2 isothermal expansion at T_1 (hot) $\Delta U = q_1 + w_1$

2 → 3 adiabatic expansion (q = 0) $\Delta U = w_1'$

3 → 4 isothermal compression at T_2 (cold) $\Delta U = q_2 + w_2$

4 → 1 adiabatic compression (q = 0) $\Delta U = w_2'$

$$\text{Efficiency} = \frac{\text{work output to surroundings}}{\text{heat in at } T_1 \text{ (hot)}} = \frac{-(w_1 + w_1' + w_2 + w_2')}{q_1}$$

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

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

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

$-w = q_1\varepsilon$ = work output

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

Carnot cycle for an ideal gas

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

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

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

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

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

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

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

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

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

links heat engines to mathematical statement

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

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

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

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

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

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

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

Note: In the limit $T_2 \to 0$ K, $w \to \infty$. 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).