

*5.92 Energy Environment and Society
(a Project Based First Year Subject supported by the d'Arbeloff Program)*

Session 1.4. Energy Basics (continued)

1. Discussion of team projects and project selections
2. Summary of thermodynamics concepts and applications

Readings and Assignments

D. Goodstein, "Out of Gas" (Norton, 2004): Chapter 2, "Energy Myths and a Brief History of Energy", pp. 41 – 56
Practice Problems on First and Second Laws of Thermodynamics (due Feb. 21)

Supplementary recommended text (on library reserve)

J.B. Fenn, "Engines, Energy, and Entropy" (W.H. Freeman and Co., 1982)

Thermodynamics is about the flow of energy

Thermodynamics was first developed to explain how much *heat* could be used to do *work* ... eventually we learned that these laws apply to every material and energy transformation everywhere in the universe!

- **Describes macroscopic properties of equilibrium systems**
(you don't need to know anything about atoms and molecules – but it helps!)
- **Entirely Empirical**
(cannot be proven logically, but can be derived using statistical mechanics)
- **Built on Four Laws and “simple” mathematics**
(but we will not assume you have had 18.02!)

0th Law → **Defines Temperature (T)**
"The common sense Law"

1st Law → **Defines Energy (U), Heat (q), Work (w)**
"You can break even, but you can't win"

2nd Law → **Defines Entropy (S)**
"You have to go to 0 K to break even"
"Everything wants to be as imperfect as possible"

3rd Law → **Gives Numerical Value to Entropy**
"You can't get to 0 K" (so you can never break even)

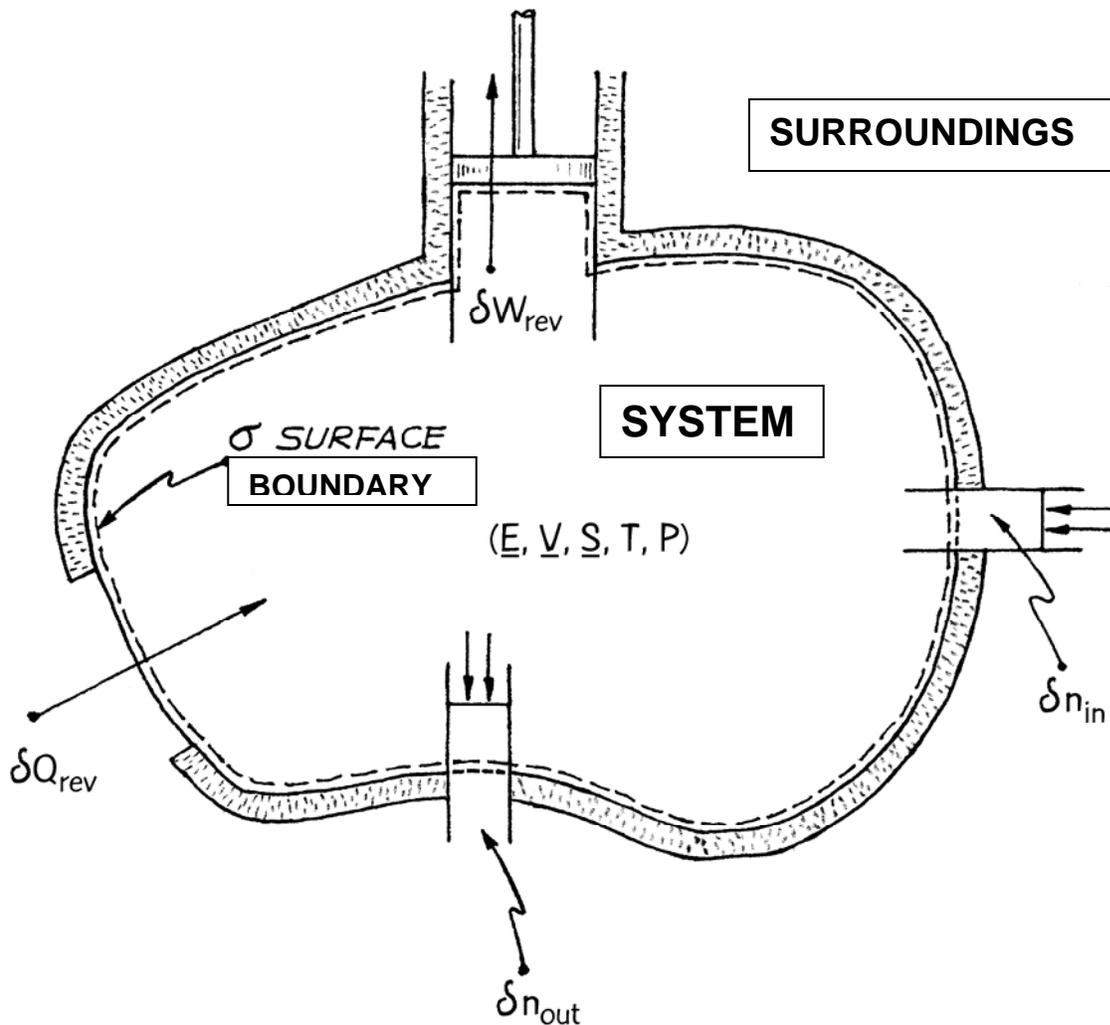
These laws are UNIVERSALLY VALID , they cannot be circumvented.

"From BTU's and calories
Producing foot-pounds, ergs, and joules
Heat Engines must, to serve our needs
Obey inexorable rules."

-- J.B. Fenn, "Engines, Energy, and Entropy"

Definitions:

- **System:** The part of the Universe that we are interested in
(everything inside the boundary)
- **Surroundings:** The rest of the Universe
(everything else outside the boundary)
- **Boundary:** The surface dividing the System from the Surroundings

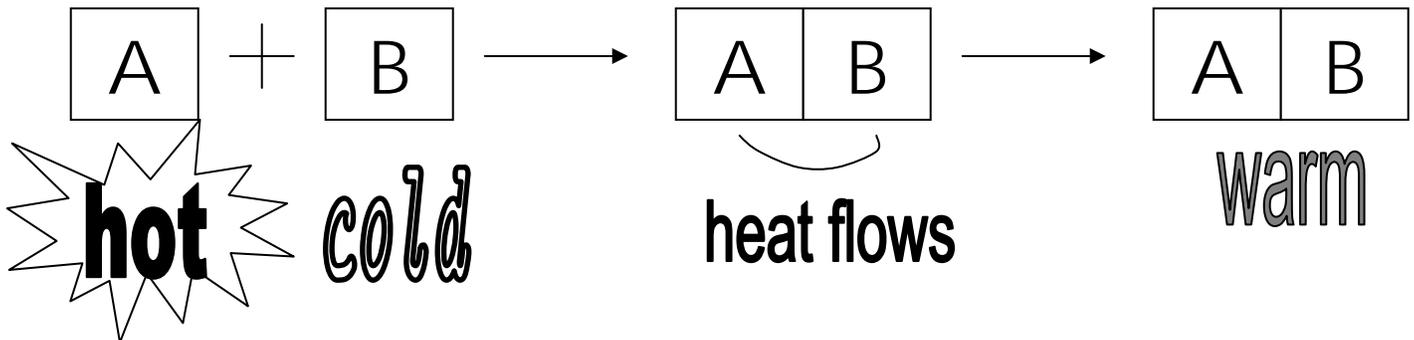


In order to describe a system we have to specify a small number of macroscopic properties ("state variables"), such as

Pressure	p	Energy	U (or E)
Volume	V	Enthalpy	H
Temperature	T	Entropy	S

Temperature is defined by the Zeroth Law of Thermodynamics:

Thermal Equilibrium (when heat stops flowing)



When a hot object is placed in thermal contact with a cold object, heat flows from the warmer to the cooler object. This continues until they are in thermal equilibrium (no more heat flow). We say, at this point, that both bodies have the same "temperature".

This intuitively straightforward idea is formalized in the 0th Law of thermodynamics and is made practical through the development of thermometers and temperature scales.

==== ZERO'th LAW of Thermodynamics ====

If A and B are in thermal equilibrium and B and C are in thermal equilibrium, then A and C are in thermal equilibrium.

B acts like (is) a thermometer, and A, B, and C are all at the same temperature.

For thermodynamics calculations, we have to use the Absolute (Kelvin) temperature scale:

$$T \text{ (K)} = T \text{ (}^\circ\text{C)} + 273.15$$

Work, Heat, and the First Law

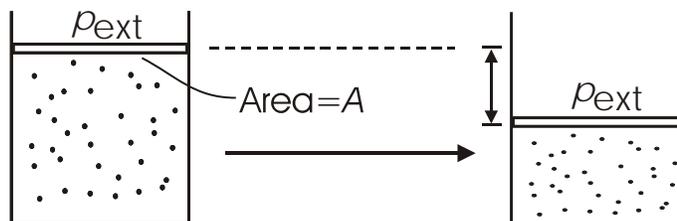
- Work:**

$$w = F \cdot \ell$$

↑ applied constant force ↑ distance ℓ

Expansion work

$$F = p_{ext} A$$



$$w = -(p_{ext} A) \ell = -p_{ext} \Delta V$$

convention:

$w > 0$ means that the surroundings do work to the system (compression, $\Delta V < 0$).
 If the system does work on the surroundings (expansion, $\Delta V > 0$), then $w < 0$.

Work is *not* a property of the state of the system!

$$w = -p_{ext} dV \quad \text{means } \textit{not} \text{ an exact differential}$$

which means that

$$\text{the integral } w = -\int_1^2 p_{ext} dV \quad \text{depends on the path!!!}$$

See Non Lecture # 1 for an example calculation of the path dependence of w

- Heat:** "q"

The quantity that flows between the system and the surroundings, which results in a change of temperature of the system and/or the surroundings.

Sign convention: If heat enters the system, then q is positive.

Remember this: $w > 0$ if work done on system
 $q > 0$ if heat added to system
 w and q are both forms of energy

Units of q and w : 1 calorie = heat needed to raise 1 g H₂O by 1°C at T = 15°C
 1 Joule = 4.184 calories
 1 BTU = 252 calories = 1,055 Joules
 1 "quad" = 10¹⁵ BTU = 1.055 exaJoules

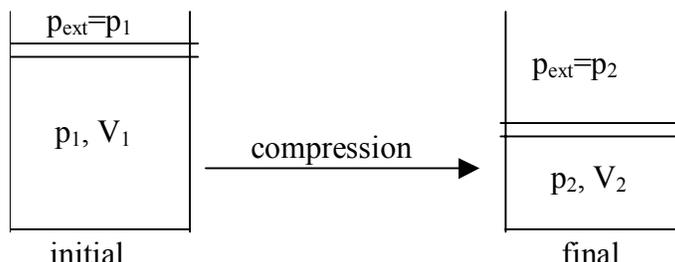
Heat capacity amount of q needed to raise a substance's temperature by ΔT
 heat capacity of water = 1 cal K⁻¹ g⁻¹ = 4.184 J K⁻¹ g⁻¹ = 75.3 J K⁻¹ mole⁻¹

Non Lecture #1: Path dependence of work

Example: assume a reversible process so that $p_{ext} = p$ (p same as p_{ext} everywhere and at all times inside the system)

$$\text{Ar}(g, p_1, V_1) = \text{Ar}(g, p_2, V_2)$$

Compression $V_1 > V_2$ and $p_1 < p_2$

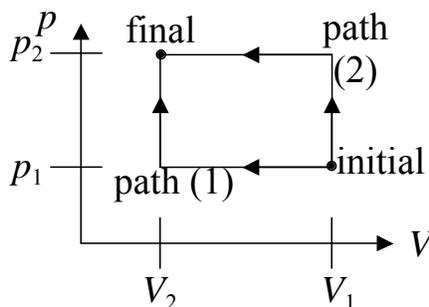


Two paths:

- (1) First $V_1 \rightarrow V_2$ at $p = p_1$ then $p_1 \rightarrow p_2$ at $V = V_2$
- (2) First $p_1 \rightarrow p_2$ at $V = V_1$ then $V_1 \rightarrow V_2$ at $p = p_2$

$$\text{Ar}(g, p_1, V_1) = \text{Ar}(g, p_1, V_2) = \text{Ar}(g, p_2, V_2) \quad \text{path (1)}$$

$$\text{Ar}(g, p_1, V_1) = \text{Ar}(g, p_2, V_1) = \text{Ar}(g, p_2, V_2) \quad \text{path (2)}$$



$$w_{(1)} = -\int_{V_1}^{V_2} p_{ext} dV - \int_{V_2}^{V_2} p_{ext} dV$$

$$= -\int_{V_1}^{V_2} p_1 dV = -p_1(V_2 - V_1)$$

$$w_{(1)} = p_1(V_1 - V_2)$$

$$w_{(2)} = -\int_{V_1}^{V_1} p_{ext} dV - \int_{V_1}^{V_2} p_{ext} dV$$

$$= -\int_{V_1}^{V_2} p_2 dV = -p_2(V_2 - V_1)$$

$$w_{(2)} = p_2(V_1 - V_2)$$

(Note $w > 0$, work is done on system to compress it)

$$w_{(1)} \neq w_{(2)} !!!$$

(because $p_1 \neq p_2$)

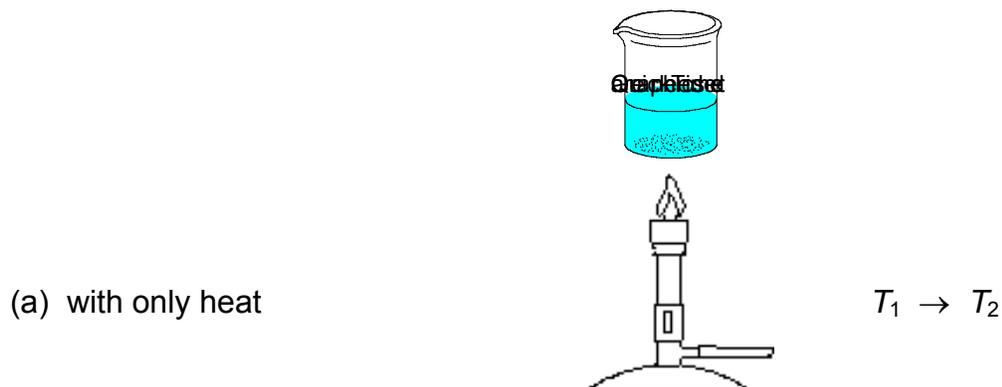
Note for the closed cycle [path (1)] - [path (2)], $\oint d w \neq 0$

w is not a state function

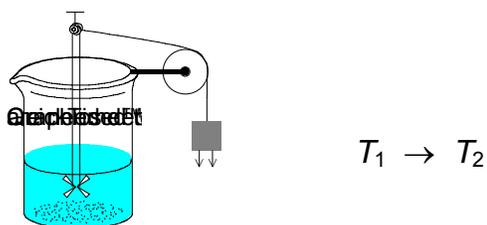
you cannot write $w = f(p, V)$

closed cycle

The equivalence of work and heat was demonstrated by Joule's experiments on raising the temperature of a known amount of water (see Goodstein, Chapter 2, for detail)



(b) with only work (weight falls, propeller rotates, viscous friction heats water):



The First Law of Thermodynamics: Conservation of Energy

$$dU = \delta q + \delta w$$

or

Mathematical statement:

$$\Delta U = q + w$$

or

$$-\int \delta q = \int \delta w$$

$$\Delta U_{system} = q + w$$

$$\Delta U_{surroundings} = -q - w$$

$$\Rightarrow \Delta U_{universe} = \Delta U_{system} + \Delta U_{surroundings} = 0$$

U is a "state function", value depends only on properties of system (p, V, T, etc.)

Enthalpy H = U + pV, useful to measure energy changes in processes taking place at constant pressure

For example, the ΔH of vaporization of water at p = 1 atmosphere = 2400 J/gram = 43.2 kJ/mole.

Clausius statement of 1st Law:

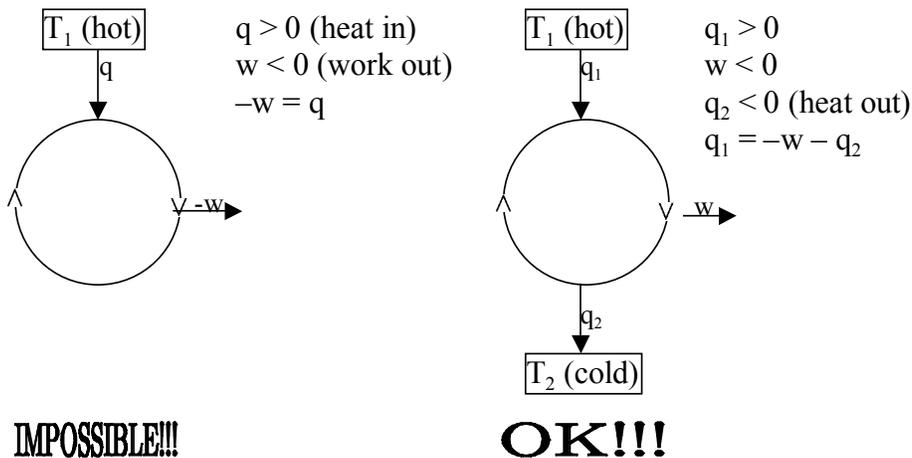
The energy of the universe is conserved.

The First Law tells us that a properly designed engine can run in a cycle by converting heat into useful work. The work obtained cannot exceed the heat. But can all of the heat be converted into work?

Heat reservoir A very large system of uniform T . This T of the reservoir does not change regardless of the amount of heat added or withdrawn. Also called heat bath. Real systems can come close to this idealized definition.

Different statements of the Second Law

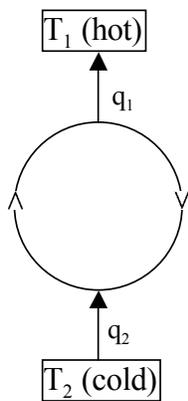
Kelvin: It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it to work in the surroundings without simultaneously transferring some heat to a colder reservoir.



Arrows show direction of actual energy flow, q and w are positive when heat is added to system or work is done on system.

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.

Clausius' statement is similar to Kelvin's, but for an engine operating in the opposite direction (as a refrigerator or heat pump). The two statements of the second law may be proven to be equivalent by connecting a Kelvin heat engine to a Clausius heat pump, then showing that violation of either statement will lead to violation of the other.

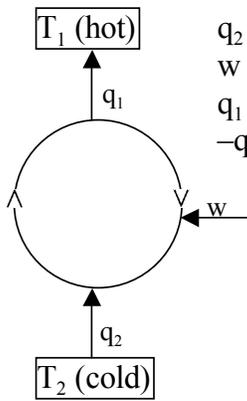


$$q_2 > 0 \text{ (heat in)}$$

$$q_1 < 0 \text{ (heat out)}$$

$$-q_1 = q_2$$

IMPOSSIBLE!!!



$$q_2 > 0$$

$$w > 0 \text{ (work in)}$$

$$q_1 < 0$$

$$-q_1 = w + q_2$$

OK!!!

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

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

CLAUSIUS THEOREM

$$\int \frac{dq_{rev}}{T} \text{ is a state function} = \int dS \rightarrow dS = \frac{dq_{rev}}{T}$$

S ≡ ENTROPY

Kelvin and Clausius statements are specialized to heat engines.

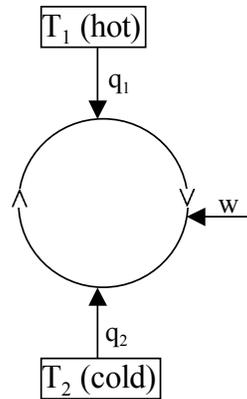
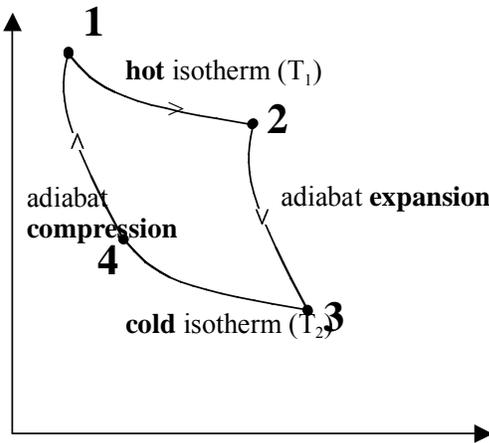
Mathematical statement seems very abstract.

Link them through analytical treatment of a heat engine. It turns out that the Carnot¹ Cycle is both a fundamental standard against which all other cycles may be evaluated, and all properties of a Carnot Cycle may be calculated. (See Non-Lecture 2 for explicit calculation of work and heat changes for a Carnot cycle in which the working fluid is an ideal gas. The overall result does not depend on the choice of the working fluid – see Non Lecture 3.)

¹ Nicholas Leonhard Sadi Carnot. b. 1796. Published "*Reflections on the Motive Power of Heat and on Machines*" (his only publication) in 1824. d. of cholera in 1832.

The Carnot Cycle

- an idealized heat engine in which all paths are *reversible*



1 → 2	isothermal expansion at T ₁ (hot)	$\Delta U = q_1 + w_1$	(q ₁ > 0, w ₁ < 0)
2 → 3	adiabatic expansion (q = 0)	$\Delta U = w'_1$	(w' ₁ < 0)
3 → 4	isothermal compression at T ₂ (cold)	$\Delta U = q_2 + w_2$	(q ₂ < 0, w ₂ > 0)
4 → 1	adiabatic compression (q = 0)	$\Delta U = w'_2$	(w' ₂ > 0)

The signs of q₁, q₂, and w cannot all be positive. When run as a **heat engine** (converts heat input to work output), we will find that q₁ > 0, q₂ and w < 0. When run as a **heat pump** (converts work input to transfer of heat from a cold to a hot reservoir), q₂ and w are > 0, q₁ < 0.

$$1^{\text{st}} \text{ Law} \quad \Rightarrow \oint dU = 0 \Rightarrow q_1 + q_2 = -(w_1 + w'_1 + w_2 + w'_2)$$

$\text{Efficiency as heat engine} = \varepsilon = \frac{\text{total work out}}{\text{heat in from hot reserv. at } T_1} = \frac{-(w_1 + w'_1 + w_2 + w'_2)}{q_1} = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1}$

Efficiency

$\varepsilon = 1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$

but $\varepsilon \rightarrow 100\%$ only as $T_2 \rightarrow 0 \text{ K}$

For a heat engine (Kelvin)

(heat from hot reservoir converted to work by system)

$$q_1 > 0, w < 0, T_2 < T_1$$

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

Note: In the limit $T_2 \rightarrow 0 \text{ K}$, $(-w) \rightarrow q_1$ and $\varepsilon \rightarrow 100\%$ conversion of heat into work.
Can we cool the cold reservoir to $T_2 = 0 \text{ K}$?

For a heat pump (i.e. refrigerator) (Clausius)

(pumps heat from cold reservoir $q_2 > 0$ to hot reservoir $q_1 < 0$)

$$q_2 > 0, w > 0, T_2 < T_1$$

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

$$q_1 < 0, w > 0, T_2 - T_1 < 0$$

But

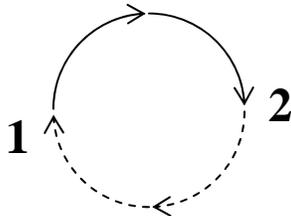
$$\frac{q_1}{T_1} = -\frac{q_2}{T_2} \Rightarrow w = \left(\frac{T_2 - T_1}{T_1} \right) \left(\frac{-T_1 q_2}{T_2} \right) = \left(\frac{T_1 - T_2}{T_2} \right) q_2$$

But in the limit $T_2 \rightarrow 0 \text{ K}$, $w \rightarrow \infty$. This means it takes an infinite amount of work to extract heat from a reservoir at 0 K. This implies that 0 K cannot be reached (a form of the Third Law).

Finally, the entropy of an isolated system **never** decreases.

(A) irreversible (isolated) (A)

The system is isolated and irreversibly (spontaneously) changes from [1] to [2]



(B)

The system is brought into contact with a heat reservoir and reversibly brought back from [2] to [1]

(B) reversible (not isolated)

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

$$\text{Clausius: } \oint \frac{dq}{T} \leq 0 \Rightarrow \int_1^2 \frac{dq_{irrev}}{T} + \int_2^1 \frac{dq_{rev}}{T} \leq 0$$

Definition of ΔS for the $1 \rightarrow 2$ change of state of an isolated system:

$$\Rightarrow \int_2^1 \frac{dq_{rev}}{T} = S_1 - S_2 = -\Delta S \leq 0$$

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

This gives the direction of spontaneous change!

If $S_2 > S_1$, isolated system goes spontaneously and irreversibly from $1 \rightarrow 2$.

For isolated systems	$S > 0$	Spontaneous, irreversible process
	$S = 0$	Reversible process
	$S < 0$	Impossible! No exceptions!

Non Lecture 2: Carnot Cycle for an Ideal Gas

$$1 \rightarrow 2 \quad \begin{array}{l} \text{isotherm} \\ \text{(expansion @ } T_1) \end{array} \quad {}^2 U = 0; \quad q_1 = -w_1 = \int_1^2 p dV = RT_1 \ln\left(\frac{V_2}{V_1}\right) > 0$$

$$2 \rightarrow 3 \quad \begin{array}{l} \text{adiabatic} \\ \text{(expansion)} \end{array} \quad q = 0; \quad w'_1 = C_v (T_2 - T_1) < 0$$

$$\text{Reversible adiabatic} \quad \Rightarrow \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1} < 1$$

$$3 \rightarrow 4 \quad \begin{array}{l} \text{isotherm} \\ \text{(compression at} \\ T_2 < T_1) \end{array} \quad {}^2 U = 0; \quad q_2 = -w_2 = \int_3^4 p dV = RT_2 \ln\left(\frac{V_4}{V_3}\right) < 0$$

$$4 \rightarrow 1 \quad \begin{array}{l} \text{adiabatic} \\ \text{(compression)} \end{array} \quad q = 0; \quad w'_2 = C_v (T_1 - T_2) > 0$$

$$\text{Reversible adiabatic} \quad \Rightarrow \quad \left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma-1} > 1$$

$$\frac{q_2}{q_1} = \frac{T_2 \ln(V_4/V_3)}{T_1 \ln(V_2/V_1)} \quad \dots \text{here comes the crucial trick!}$$

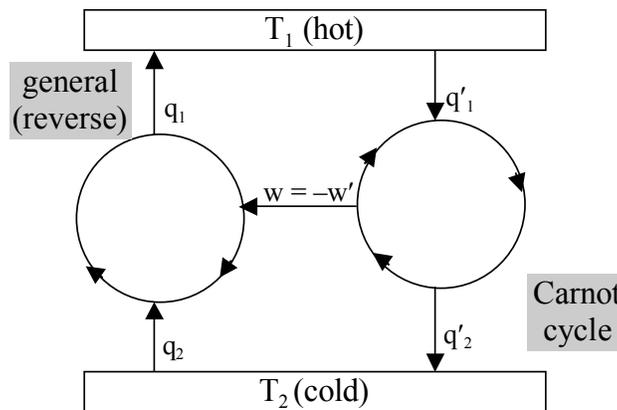
$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \Rightarrow \left(\frac{V_4}{V_3}\right) = \left(\frac{V_1}{V_2}\right) \Rightarrow \boxed{\frac{q_2}{q_1} = -\frac{T_2}{T_1}}$$

$$\text{or} \quad \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \Rightarrow \boxed{\oint \frac{dq_{rev}}{T} = 0} \text{ we have a state function!}$$

This provides a link between (ideal gas) heat engines and the mathematical statement of the Second Law! But it is not a proof of the Second Law. It tells us that entropy, efficiency, and reversibility are inter-related via the Second Law.

Non-Lecture 3: Entropy and the Clausius Inequality

We want to show that the efficiency of any reversible engine is the same as that for a reversible Carnot engine where the gas in the Carnot engine is ideal. We do this by connecting the general engine to the Carnot engine, one acting as a heat engine (using heat from a hot reservoir to produce work) and the other acting as a heat pump or refrigerator (using work to pump heat from a cold to a hot reservoir). The two engines connected together produce no net work. Work output from the heat engine is used as work input to the heat pump. First we set up the Carnot engine as a heat engine and run the general engine in reverse as a heat pump. We assume that the general engine is less efficient than the Carnot engine and show that this assumption is in violation of the Second Law. Then we set up the general engine as a heat engine and run the Carnot engine in reverse as a heat pump. We assume that the general engine is more efficient than the Carnot engine and show that this assumption violates the Second Law. Since the general engine cannot be less or more efficient than the Carnot engine (because **each** would violate the Second Law), the efficiencies are identical.



Right Engine:
$$\varepsilon' = \frac{\text{work out}}{\text{heat from } T_1 \text{ in}} = \frac{-w'}{q'_1} = 1 - \frac{T_2}{T_1}$$

Left Engine
$$\varepsilon = \frac{\text{work in}}{\text{heat to } T_1 \text{ out}} = \frac{w}{-q_1}$$

Since $w = -w'$, the total work from the two engines = $w' + w = 0$

We assume that $\varepsilon < \varepsilon' \Rightarrow \frac{-w'}{q'_1} > \frac{w}{-q_1}$ (both quantities are positive)

$$\frac{w}{q'_1} > \frac{w}{-q_1} \quad (-w' \text{ replaced by } w)$$

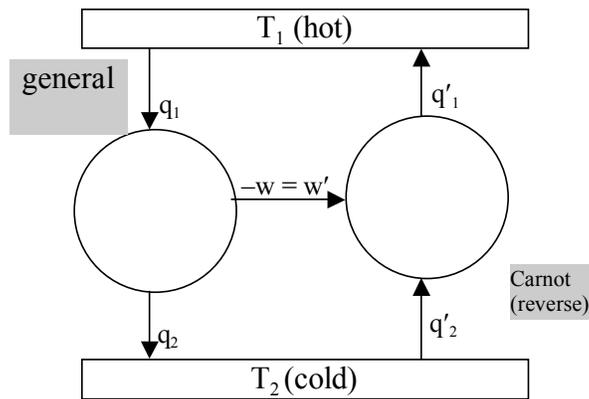
$$\frac{1}{q'_1} > \frac{1}{-q_1} \Rightarrow q'_1 < -q_1 \quad (\text{both sides divided by } w > 0)$$

We add q_1 to both sides of inequality

$$q_1 + q'_1 < q_1 - q_1 = 0$$

Net heat has been input into hot reservoir without net work! Assumption $\varepsilon < \varepsilon'$ must be invalid.

Now reverse the direction of operation of both engines.



Right Engine:
$$\varepsilon' = \frac{\text{work in}}{\text{heat to } T_1 \text{ out}} = \frac{w'}{-q'_1} = 1 - \frac{T_2}{T_1}$$

Left Engine
$$\varepsilon = \frac{\text{work out}}{\text{heat from } T_1 \text{ in}} = \frac{-w}{q_1}$$

Since $-w = w'$, the total work from the two engines = $w' + w = 0$

We assume that $\varepsilon > \varepsilon' \Rightarrow \frac{-w}{q_1} > \frac{w'}{-q'_1}$ (both quantities are positive)

$$\frac{-w}{q_1} > \frac{-w}{-q'_1}$$

$$\frac{1}{q_1} > \frac{1}{-q'_1} \Rightarrow q_1 < -q'_1$$

We add $-q_1$ to both sides of the inequality and multiply both sides by -1 , reversing the sense of the inequality.

$$q_1 + q'_1 < 0$$

Net heat is input into hot reservoir without net work! Assumption $\varepsilon > \varepsilon'$ must be invalid. Thus we have shown that both $\varepsilon < \varepsilon'$ and $\varepsilon > \varepsilon'$ lead to violation of the second law. Thus $\varepsilon = \varepsilon'$.