LECTURE HANDOUT

The Discovery of Entropy and its Significance

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Clausius's statement of the two laws of thermodynamics (1865):

The energy of the universe is constant,
the entropy strives toward a maximum.

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Rival Theories of Heat

(Carnot) Caloric Theory of Heat = Conservation of Heat. Heat is a subtle material substance that can neither be created nor destroyed.

(Clausius) Mechanical Theory of Heat. Heat is essentially motion, a form of energy uniformly convertible into mechanical work.

Note: *Both* theories are compatible with the principle of the conservation of energy.

Carnot's Flawed Reductio ad absurdum
(false statement underlined)

To prove: *A reversible heat engine, operating between two fixed temperatures, is the most efficient means of deriving work from heat regardless of the working substance employed.*

Let it be given that we have a reversible heat engine, Engine I.

Now suppose that there is a second engine, Engine II, more efficient than the first.

Consider the following cyclical processes, all taking place between the same two fixed temperatures:

Process A: *Engine I* absorbs heat Q at the furnace while doing work W.

Process B: *Engine I reversed* discharges heat Q at the furnace while consuming work W.

Process C: *Engine II* absorbs heat Q at the furnace while doing work $W+\Delta W$.

Combine Processes B and C: The net work done is ΔW, while the furnace neither gains nor loses any heat. <u>Since heat cannot be created or destroyed, the refrigerator also neither gains nor loses any heat.</u> (*False Principle of the Conservation of Heat*)

But it is impossible for a machine to do work without consuming or transporting anything. (*True Principle of the Conservation of Energy*)

Therefore our supposition that Engine II is more efficient than Engine I must be false. *Q.E.D.*

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Carnot's Reductio Freed of Error
(new principle underlined)

Process D: *Engine I reversed* discharges heat $Q+\Delta Q$ at the furnace while consuming work $W+\Delta W$.

Combine Processes D and C: The net work done is zero, while the net heat transferred to the furnace is ΔQ. *The heat must have come from the refrigerator.*

<u>But it is impossible to transfer heat from a cold body to a hot body without consuming work.</u> (*New Thermodynamic Principle*)

Therefore our supposition that Engine II is more efficient than Engine I must be false. *Q.E.D.*

Isothermal processes occur at constant temperature.

Adiabatic processes occur without passage of heat into or out of the body.

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Four Phases of the Simple Carnot Cycle:

1-2 **Isothermal expansion:** The gas expands while heat is absorbed from the furnace (body *A*) at constant temperature T_A. **Expansive work is done by the engine**.

2-3 **Adiabatic expansion**: The gas is removed from body *A* and continues to expand without passage of heat; its temperature spontaneously falls until it reaches the temperature T_B of the refrigerator (body *B*). **Expansive work is done by the engine**.

3-4 **Isothermal compression**. The gas is in contact with the refrigerator (body *B*) and maintained at its temperature T_B. It is compressed while discharging heat into the refrigerator. **Work is consumed by the engine.**

4-1 **Adiabatic compression**: The gas is removed from body *B* and the compression continues without passage of heat; its temperature spontaneously rises until it reaches the temperature T_A of the furnace (body *A*), at which point the cycle begins again. **Work is consumed by the engine.**

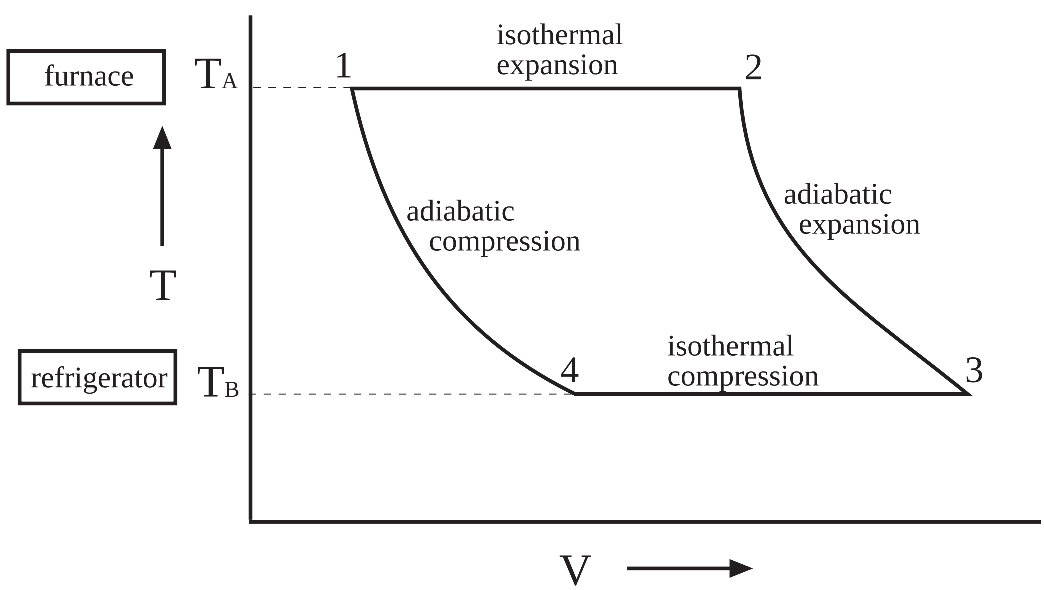

Diagram of the Simple Carnot Cycle

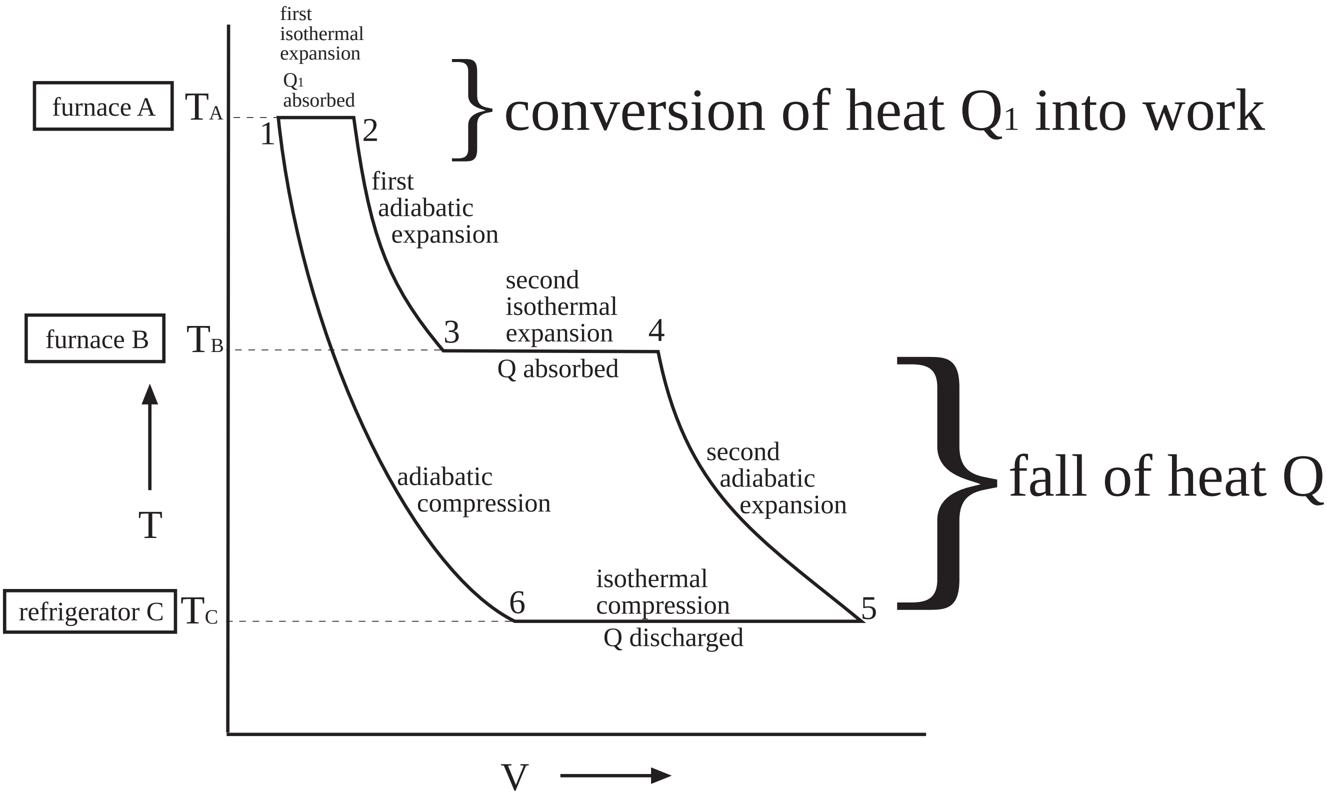

Diagram of Clausius's Complex 6-point Carnot Cycle

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Clausius's Transformations and their Equivalence Values

Transformations of the First Kind:

- conversion of heat *Q* into work at temperature *T*: value $= -\frac{Q}{T}$
- conversion of work into heat *Q* at temperature *T*: value $= +\frac{Q}{T}$

Transformations of the Second Kind:

- fall of heat *Q* from temperature T_1 to temperature T_2: value $= Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

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efficiency of a perfect (i.e., reversible) simple Carnot engine is $= \left(\frac{T_1 - T_2}{T_1}\right)$

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Clausius's analytic statement of the second law of thermodynamics:

$$\sum \frac{Q}{T} = \int \frac{dQ}{T} \geq 0$$