SECOND LAW OF THERMODYNAMICS II

Intended Learning Outcomes – after this lecture you will learn:

1. reversible processes, reversible engine and the Carnot cycle
2. efficiency of the Carnot engine as an upper bound for other heat engines
3. definition of absolute temperature by Carnot efficiency
4. consistency of ideal gas temperature and absolute temperature
5. entropy and the second law of thermodynamics (optional)

Textbook Reference: Ch 20.6

Reversible Processes

A **reversible** thermodynamic process is an *idealized* process whose direction can be reversed by making only an infinitesimal change in the conditions of the system.

- ⚠ Throughout a reversible process the system must be very close to equilibrium at any instant, called an **equilibrium process** (*but* not exactly in equilibrium, otherwise no change, no process)
- ⚠ Heat flow due to a finite temperature difference is necessarily irreversible because an infinitesimal change in the temperatures cannot reverse heat flow.
- ⚠ How to understand reversible *isothermal* heat flow – the temperature difference must be *infinitesimal* so that as heat flows, the two bodies are still *infinitesimally* close to equilibrium. The rate of heat flow is *infinitesimally* small, and the time taken to finish the process is *infinitely* long!

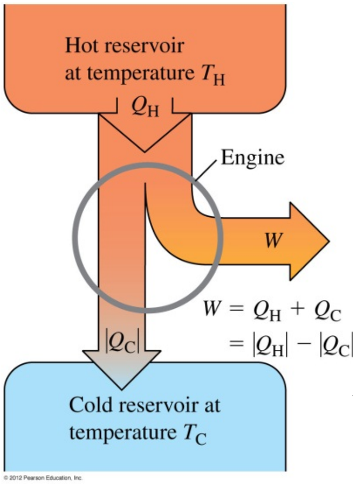
Reversible engine and Carnot cycle

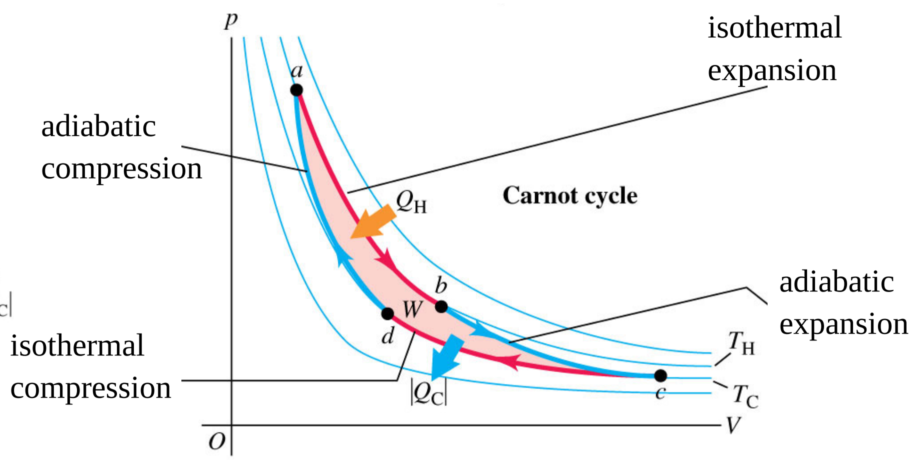
Recall: heat flow between two objects with different temperatures is irreversible.

Suppose all processes in a cycle of an engine are reversible, then:

1. Heat flow between the reservoirs and the working substance of the engine must take place when the working substance is in thermal equilibrium with the reservoirs (isothermal processes) – Processes $a \rightarrow b$ and $c \rightarrow d$
2. When the working substance and the reservoirs are not in thermal equilibrium (i.e., not at the same temperature) with the reservoirs, heat flow must be forbidden (adiabatic) – Processes $b \rightarrow c$ and $d \rightarrow a$

Such a reversible cycle ($a \rightarrow b \rightarrow c \rightarrow d$) is called a **Carnot cycle**.





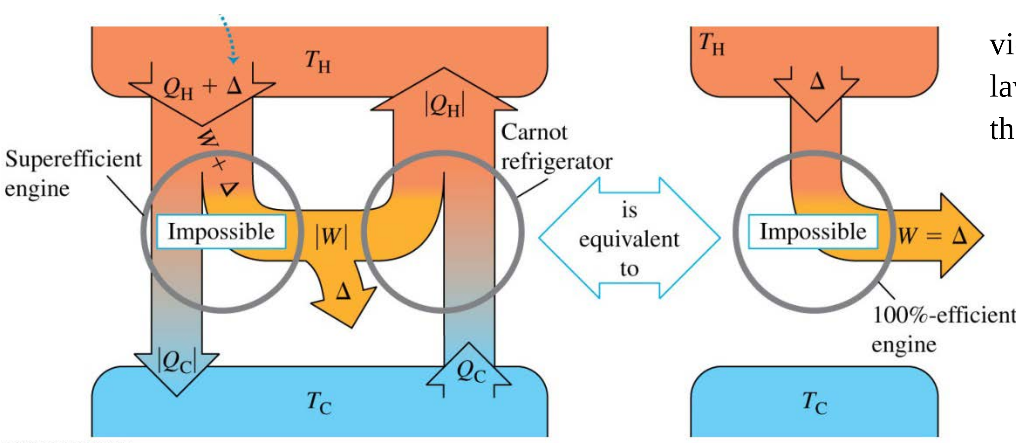
Conclusion: A reversible cycle involving two fixed reservoirs is a Carnot cycle
An engine running a Carnot cycle is called a **Carnot engine**.

Maximum efficiency

Theorem: No engine can be more efficient than a reversible (Carnot) engine operating between the same two reservoirs

Proof:

- If such a superefficient engine exists, then compared to a Carnot engine operating between the same reservoirs and dump the same amount of heat $|Q_C|$ to the cold reservoir, it takes more heat $Q_H + \Delta$ from the hot reservoir and does more work $W + \Delta$ (by comparing their efficiency $1 - \left|\frac{Q_C}{Q_H}\right| < 1 - \left|\frac{Q_C}{Q_H+\Delta}\right|$)
- since Carnot engine is reversible, turn it into a refrigerator with the same $|Q_H|$, $|Q_C|$, and $|W|$ (⚠ doesn't work for any other irreversible engine)
- operate the superefficient engine alongside with the Carnot refrigerator:



violates second law of thermodynamics

⚠ A Carnot engine is the *most efficient* heat engine operating between the two heat reservoirs, but the *most impractical* one. Since the working substance is assumed to be in thermal equilibrium in every step, it runs very slowly to allow time to establish thermal equilibrium.

Carnot efficiency and definition of absolute temperature

$$e_{\text{carnot}} = 1 - \left|\frac{Q_{\text{C}}}{Q_{\text{H}}}\right|$$

Carnot showed that the efficiency of a Carnot engine depends *only* on the two reservoirs chosen. (For example, it does not depend on the working substance chosen)→ For two given reservoirs

$$\left|\frac{Q_{\text{H}}}{Q_{\text{C}}}\right| = \text{Constant}$$

Define absolute temperatures of the two reservoirs by

$$\frac{T_{\text{H}}}{T_{\text{C}}} = \left|\frac{Q_{\text{H}}}{Q_{\text{C}}}\right|$$

⚠ this definition of temperature is "absolute" in the sense that it depends on "absolutely" nothing besides the two reservoirs

Hence,

$$\boxed{e_{\text{Carnot}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}} = \frac{T_{\text{H}} - T_{\text{C}}}{T_{\text{H}}}}$$

⚠ It defines the temperature ratio only. To fix the scale, choose the triple point of water and define its temperature to be 273.16 K exactly.

⚠ $e_{\text{Carnot}} < 1$ unless $T_{\text{C}} = 0$, which is forbidden by the **Third Law of Thermodynamics**

Carnot Refrigerator

The coefficient of performance

$$\boxed{K = \frac{|Q_{\text{C}}|}{|Q_{\text{H}}| - |Q_{\text{C}}|} = \frac{T_{\text{C}}}{T_{\text{H}} - T_{\text{C}}}}$$

Example 20.2 P. 683

A Carnot engine takes 2000 J of heat from the hot reservoir and discards 1400 J of heat to the cold reservoir. The temperature ratio of the two reservoirs should be defined as

$$\frac{T_{\text{H}}}{T_{\text{C}}} = \left|\frac{Q_{\text{H}}}{Q_{\text{C}}}\right| = \frac{2000\ \text{J}}{1400\ \text{J}} = \frac{10}{7}$$

The Carnot efficiency is

$$e_{\text{Carnot}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}} = 30\%$$

Absolute temperature and ideal gas temperature

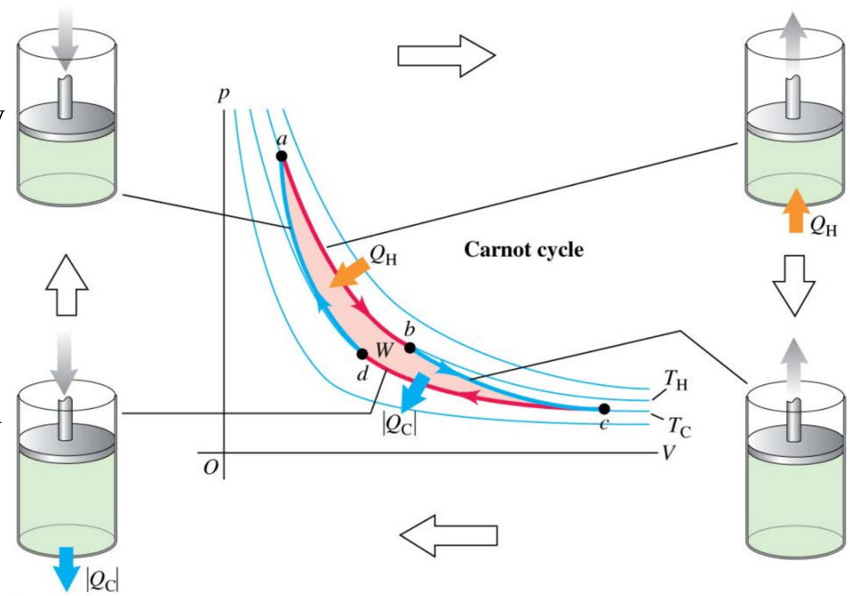
Previously we defined ideal gas temperature (as measured by a constant volume gas thermometer) by $pV = nRT$.

Here we will show that this is consistent with the definition of absolute temperature defined through a Carnot engine.

Suppose working substance is an ideal gas. Consist of 4 steps:

4. compressed adiabatically back to T_{H}

1. expands isothermally at T_{H}, absorbing heat Q_{H}



3. compressed isothermally at T_{C}, rejecting heat $|Q_{\mathrm{C}}|$

2. expands adiabatically until temperature drops to T_{C}

In steps (1) and (3),

$$\left.\begin{aligned} Q_{\mathrm{H}} &= W_{ab} = nRT_{\mathrm{H}} \ln \frac{V_b}{V_a} \\ Q_{\mathrm{C}} &= W_{cd} = nRT_{\mathrm{C}} \ln \frac{V_d}{V_c} \end{aligned}\right\} \Rightarrow \frac{Q_{\mathrm{H}}}{Q_{\mathrm{C}}} = \frac{T_{\mathrm{H}}}{T_{\mathrm{C}}} \frac{\ln(V_b/V_a)}{\ln(V_d/V_c)} = -\frac{T_{\mathrm{H}}}{T_{\mathrm{C}}} \frac{\ln(V_b/V_a)}{\ln(V_c/V_d)}$$

Need to eliminate the volumes. From steps (2) and (4)

$$\left.\begin{aligned} T_{\mathrm{H}} V_b^{\gamma-1} &= T_{\mathrm{C}} V_c^{\gamma-1} \\ T_{\mathrm{H}} V_a^{\gamma-1} &= T_{\mathrm{C}} V_d^{\gamma-1} \end{aligned}\right\} \Rightarrow \frac{V_b^{\gamma-1}}{V_a^{\gamma-1}} = \frac{V_c^{\gamma-1}}{V_d^{\gamma-1}} \quad \Rightarrow \quad \frac{V_b}{V_a} = \frac{V_c}{V_d}$$

Therefore

$$\frac{T_{\mathrm{H}}}{T_{\mathrm{C}}} = -\frac{Q_{\mathrm{H}}}{Q_{\mathrm{C}}} = \left|\frac{Q_{\mathrm{H}}}{Q_{\mathrm{C}}}\right|$$

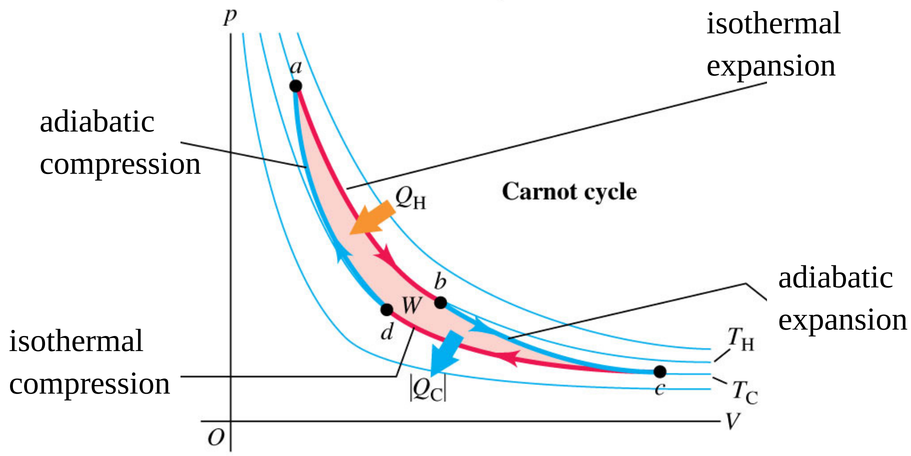
Here T_{H} and T_{C} are ideal gas temperatures, but expression is identical to the previous one in terms of absolute temperature. Since both scales set the water triple point temperature to be 273.16 K exactly, the ideal gas temperature is the same as the absolute temperature.

Exercise

Work out Example 20.3 P. 684 in your textbook on the Carnot cycle carefully. You can find a video solution here.

Suppose 0.200 mol of an ideal diatomic gas ($\gamma = 1.40$) undergoes a Carnot cycle between 227℃ and 27℃, starting at $p_a = 10.0 \times 10^5$ Pa at point a in the pV-diagram below.
The volume doubles during the isothermal expansion step $a \rightarrow b$.

(a) Find the pressure and volume at points a, b, c, and d.
(b) Find Q, W, and ΔU for each step and for the entire cycle.
(c) Find the efficiency.



Ans:

Process	***Q***	***W***	**ΔU**
$a \rightarrow b$	576 J	576 J	0
$b \rightarrow c$	0	832 J	−832 J
$c \rightarrow d$	−346 J	−346 J	0
$d \rightarrow a$	0	−832 J	832 J
Total	230 J	230 J	0

Entropy (optional, will not appear in final exam)

Thermodynamic definition: the entropy S is defined by

$$\Delta S = \int_a^b \frac{dQ}{T}$$

- ⚠ Like U, it is a state function, $\Delta S = S_b - S_a$
- ⚠ For a slow isothermal process, $\Delta S = \Delta Q/T$

Example (entropy as a measure of randomness/disorderness)

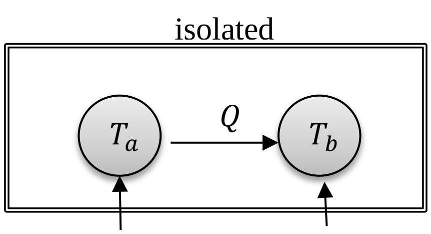
In changing 1 kg of ice at 0 °C into water at 0 °C, needs $Q = mL_f = 3.34 \times 10^5$ J. The associated entropy change is

$$\Delta S = \frac{Q}{T} = \frac{3.34 \times 10^5 \text{ J}}{273 \text{ K}} = 1.22 \times 10^3 \text{ J/K}$$

- ⚠ in this process the randomness of the system (ice molecules vs water molecules) increases, so is the entropy
- ⚠ In general, can interpret **entropy as a measure of the randomness of the thermodynamic system**

Example (entropy change in reversible/irreversible processes)

If the net result of a certain thermodynamic process is that an amount of heat $Q > 0$ flows from an object with temperature T_a to another object with temperature T_b without change in temperature.



$$\Delta S = \frac{-Q}{T_a} + \frac{Q}{T_b}$$

if $T_a = T_b$, isothermal heat flow, reversible, $\Delta S = 0$

if $T_a > T_b$, spontaneous, irreversible, $\Delta S > 0$

if $T_a < T_b$, forbidden by 2nd law, $\Delta S < 0$

Second law of thermodynamics in terms of entropy

The entropy of an *isolated* system never decreases: $\Delta S \geq 0$

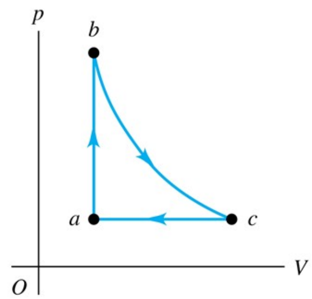
If $\Delta S = 0$, process is *reversible*.

If $\Delta S > 0$, process is *irreversible*.

Clicker Question:

Q20.2

An ideal gas is taken around the cycle shown in this *p*-*V* diagram, from *a* to *b* to *c* and back to *a*. Process $b \to c$ is *isothermal*. Which of the processes in this cycle could be *reversible*?



A. $a \to b$

B. $b \to c$

C. $c \to a$

D. two or more of A, B, and C

E. none of A, B, or C

Q20.7

A Carnot engine takes heat in from a reservoir at 400 K and discards heat to a reservoir at 300 K. If the engine does 12,000 J of work per cycle, how much heat does it take in per cycle?

A. 48,000 J

B. 24,000 J

C. 16,000 J

D. 9000 J

E. none of the above

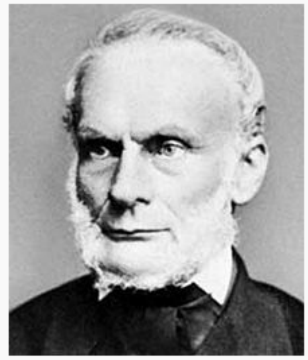
Ans: Q20.2) B, Q20.7) A

Rudolf Clausius

From Wikipedia, the free encyclopedia

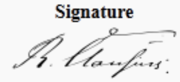
Rudolf Julius Emanuel Clausius (born **Rudolf Gottlieb**;[1] 2 January 1822 – 24 August 1888), was a German physicist and mathematician and is considered one of the central founders of the science of thermodynamics.[2] By his restatement of Sadi Carnot's principle known as the Carnot cycle, he put the theory of heat on a truer and sounder basis. His most important paper, *On the mechanical theory of heat*,[3] published in 1850, first stated the basic ideas of the second law of thermodynamics. In 1865 he introduced the concept of entropy.

Rudolf Clausius



Born	2 January 1822 Köslin (now Koszalin in Poland) in the Province of Pomerania in Prussia
Died	24 August 1888 (aged 66) Bonn
Nationality	German
Fields	Physics
Known for	Thermodynamics and originator of the concept of entropy

Signature



Life

Clausius was born in Köslin (now Koszalin in Poland) in the Province of Pomerania in Prussia. He started his education at the school of his father. After a few years, he went to the Gymnasium in Stettin (now Szczecin). Clausius graduated from the University of Berlin in 1844 where he studied mathematics and physics with, among others, Gustav Magnus, Johann Dirichlet and Jakob Steiner. He also studied history with Leopold von Ranke. During 1847, he got his doctorate from the University of Halle on optical effects in the Earth's atmosphere. He then became professor of physics at the Royal Artillery and Engineering School in Berlin and Privatdozent at the Berlin University. In 1855 he became professor at the ETH Zürich, the Swiss Federal Institute of Technology in Zürich, where he stayed until 1867. During that year, he moved to Würzburg and two years later, in 1869 to Bonn.

In 1870 Clausius organized an ambulance corps in the Franco-Prussian War. He was wounded in battle, leaving him with a lasting disability. He was awarded the Iron Cross for his services.

His wife, Adelheid Rimpham, died in childbirth in 1875, leaving him to raise their six children. He continued to teach, but had less time for research thereafter.

In 1886 he remarried Sophie Sack, and then had another child.

Two years later, on 24 August 1888, he died in Bonn, Germany.

Work

Clausius's PhD thesis concerning the refraction of light proposed that we see a blue sky during the day, and various shades of red at sunrise and sunset (among other phenomena) due to reflection and refraction of light. Later, Lord Rayleigh would show that it was in fact due to the scattering of light, but regardless, Clausius used a far more mathematical approach than some have used.

His most famous paper, "*Über die bewegende Kraft der Wärme*" ("*On the Moving Force of Heat and the Laws of Heat which may be Deduced Therefrom*")[4] was published in 1850, and dealt with the mechanical theory of heat. In this paper, he showed that there was a contradiction between Carnot's principle and the concept of conservation of energy. Clausius restated the two laws of thermodynamics to overcome this contradiction (the third law was developed by Walther Nernst, during the years 1906–1912). This paper made him famous among scientists.

Clausius' most famous statement of the second law of thermodynamics was published in German in 1854,[5] and in English in 1856.[6]

> Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

During 1857, Clausius contributed to the field of kinetic theory after refining August Krönig's very simple gas-kinetic model to include translational, rotational and vibrational molecular motions. In this same work he introduced the concept of 'Mean free path' of a particle.[7][8][9]

For more detail see http://en.wikipedia.org/wiki/Rudolf_Clausius