Lecture 10

Chemistry 163B

Refrigerators and Generalization of Ideal Gas Carnot

(*four steps to exactitude*)

E&R4th pp 125-129, 132-139 Raff pp. 159-164
E&R4th pp 86-91, 109-111

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**statements of the Second Law of Thermodynamics**

1. Macroscopic properties of an isolated system eventually assume constant values (e.g. pressure in two bulbs of gas becomes constant; two block of metal reach same T) [Andrews. p37]

2. It is impossible to construct a device that operates in cycles and that converts heat into work without producing some other change in the surroundings. *Kelvin’s Statement* [Raff p 157]: *Carnot Cycle*

3. It is impossible to have a natural process which produces no other effect than absorption of heat from a colder body and discharge of heat to a warmer body. *Clausius’s Statement, refrigerator*

4. In the neighborhood of any prescribed initial state there are states which cannot be reached by any adiabatic process
~ *Caratheodory’s statement* [Andrews p. 58]
perpetual motion and the 1st and 2nd Laws of thermodynamics

**cyclic machines:**

1**st** Law  \( \Delta U = 0 \)  \( q = -w_{sys} = w_{surr} \)

2**nd** Law  \( q_{in} > w_{surr} \)

It is impossible to construct a device that operates in cycles and that converts heat into work without producing some other change in the surroundings.  
*Kelvin’s Statement* [Raff p 157]; Carnot Cycle

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perpetual motion of the first kind  (produce work with no heat input)  
*Escher “Waterfall”*

cyclic machine  
(water ‘flows downhill’  
to pillar on left;  
‘round and ‘round)  
no energy input  
work on surroundings  

**VIOLATES 1**st **LAW**
**Remember Carnot Engine**

- does net work on surroundings

**BUT**

- extracts heat from surroundings at $T_U$
  \[ q_{U(I)} < 0 \]

- gives off heat to surroundings at $T_L$
  \[ q_{L(III)} > 0 \]

*Perpetual motion of the second kind* (produce work extracting heat from cooler source to run machine at warmer temperature)

**Brownian Ratchet**

Get work only if $T_1 > T_2$

roadmap for second law

1. Phenomenological statements (what is ALWAYS observed)
2. Ideal gas Carnot [reversible] cycle efficiency of heat → work
   (Carnot cycle transfers heat only at T_H and T_L)
3. Any cyclic engine operating between T_H and T_L must have an
   equal or lower efficiency than Carnot OR VIOLATE one of the
   phenomenological statements (observations)
4. Generalize Carnot to any reversible cycle (E&R fig 5.4)
5. Show that for this REVERSIBLE cycle
   \[ q_c + q_L \neq 0 \ (dq \text{ inexact differential}) \]
   \[ but \]
   \[ \frac{q_c}{T_H} + \frac{q_L}{T_L} = 0 \ (something \ special \ about \ \frac{dq_{rev}}{T}) \]
6. S, entropy and spontaneous changes

goals for lecture[s]

• Carnot in reverse: refrigerators and heat pumps
• Show that \( \varepsilon_{\text{ideal gas rev Carnot}} \geq \varepsilon_{\text{any other machine}} \) otherwise one of
  the phenomenological statements violated
• Not only for ideal gas but \( \varepsilon_{\text{ideal gas rev Carnot}} = \varepsilon_{\text{any other rev Carnot}} \)

• \( dS = \frac{dq_{\text{reversible}}}{T} \int dS = \oint \frac{dq_{\text{reversible}}}{T} = 0 \)
  and \( S \) is STATE FUNCTION
remember Carnot engine

- does net work on surroundings

and

- net heat $q_{U(I)} + q_{L(III)} = -w_{total}$

---

Carnot engine arithmetic *(for below table see handout)*

<table>
<thead>
<tr>
<th>ENGINE</th>
<th>q</th>
<th>$w_{net}$</th>
<th>$w_{sur}$</th>
<th>$w_{sur}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. isothermal</td>
<td>$+nRT_x \ln \frac{P_1}{P_2}$</td>
<td>$-nRT_x \ln \frac{P_1}{P_2}$</td>
<td>$+nRT_x \ln \frac{P_1}{P_2}$</td>
<td>heat in at $T_R$ work out</td>
</tr>
<tr>
<td>compression</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II adiabatic</td>
<td>0</td>
<td>$-nC_v(T_x - T_y)$</td>
<td>$-nC_v(T_x - T_y)$</td>
<td>work out</td>
</tr>
<tr>
<td>expansion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III isothermal</td>
<td>$nRT_x \ln \frac{P_2}{P_1}$</td>
<td>$-nRT_x \ln \frac{P_2}{P_1}$</td>
<td>$nRT_x \ln \frac{P_2}{P_1}$</td>
<td>heat lost at $T_L$ work in</td>
</tr>
<tr>
<td>compression</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV. adiabatic</td>
<td>0</td>
<td>$-nC_v(T_y - T_L)$</td>
<td>$-nC_v(T_y - T_L)$</td>
<td>work in</td>
</tr>
<tr>
<td>compression</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>net gain/cost</td>
<td>$Q_{in} = Q_{out} = q_c$</td>
<td>$(W_{net})<em>{sys}= (\text{in}+\text{W}</em>{1+\text{W}<em>{2}})</em>{sys}$</td>
<td>$(W_{net})<em>{sys}= (\text{in}+\text{W}</em>{1+\text{W}<em>{2}})</em>{sys}$</td>
<td>$\varepsilon = W_{net}/Q_{in}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-nR(T_y - T_L) \ln \frac{P_1}{P_2}$</td>
<td>$nR(T_y - T_L) \ln \frac{P_1}{P_2}$</td>
<td>$\varepsilon = (T_U - T_L)/T_U$</td>
</tr>
</tbody>
</table>
refrigerators and heat pumps: running the Carnot cycle in REVERSE

- it only makes ‘sense’ to talk about running a process in REVERSE for reversible processes (on a PV diagram there is no ‘reverse’ process for irreversible expansion against constant \( P_{ext} \))

- however the Carnot cycle is a combination of reversible processes

heat pumps and refrigerators (fig. 5.20 E&R 4th) 5.17 E&B 4th

Figure 5.20 Application of the principle of a reverse Carnot heat engine to refrigeration and household heating. The reverse Carnot heat engine can be used to induce heat flow from a cold reservoir to a hot reservoir with the input of work. The hot reservoir in both (a) and (b) is a room. The cold reservoir can be configured as the inside of a refrigerator or outside ambient air, earth, or water for a heat pump.
reverse Carnot cycle: a refrigerator

\[ q_U < 0 \Rightarrow \text{heat out at } T_U \]

\[ q_L > 0 \Rightarrow \text{heat in at } T_L \]

work done ON system

<table>
<thead>
<tr>
<th>Cyclic process</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Isothermal compression</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>II Adiabatic compression</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>III Isothermal expansion</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>IV Adiabatic expansion</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Coefficient of performance of refrigerator:

\[ \eta_r \equiv C_R = \frac{-W_{\text{surr, III}}}{W_{\text{total}}} = \frac{q_{\text{III}}}{W_{\text{total}}} = \frac{T_L}{T_U - T_L} \]

\[ q_{\text{III}} = -nRT_L \ln \frac{V_3}{V_4} \]

\[ W_{\text{total}} = q_{\text{III}} + W_{\text{sys}} = -\frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4} + \frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4} \]

\[ \eta_r = C_R = \frac{-\frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4}}{-\frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4} + \frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4}} = \frac{T_L}{T_U - T_L} \]

Carnot refrigerator arithmetic (just negatives of Carnot engine)

\[ q_L < 0 \Rightarrow \text{heat in at } T_L \]

Heat withdrawn from TL (ice box)

<table>
<thead>
<tr>
<th>REFRIGERATOR</th>
<th>( q )</th>
<th>( W_{\text{max}} )</th>
<th>( W_{\text{surr}} )</th>
<th>( \eta_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I adiabatic expansion ( T_L \rightarrow T_U )</td>
<td>0</td>
<td>(-\frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4} )</td>
<td>0</td>
<td>work done by system</td>
</tr>
<tr>
<td>II adiabatic compression ( T_U \rightarrow T_L )</td>
<td>0</td>
<td>( -\frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4} )</td>
<td>0</td>
<td>work done on system</td>
</tr>
<tr>
<td>III isothermal expansion ( T_L \rightarrow T_U )</td>
<td>(-\frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4} )</td>
<td>( +\frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4} )</td>
<td>( +\frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4} )</td>
<td>heat out at ( T_u ) (refrigeration) work on system</td>
</tr>
<tr>
<td>net gain/cost</td>
<td>( W_{\text{gain}} = W_{\text{tot}} + W_{\text{sys}} )</td>
<td>( q_{\text{III}} = -\frac{nRT_L}{T_U - T_L} \ln \frac{V_3}{V_4} )</td>
<td>( \eta_r = C_R = \frac{-W_{\text{surr, III}}}{W_{\text{total}}} = \frac{q_{\text{III}}}{W_{\text{total}}} = \frac{T_L}{T_U - T_L} )</td>
<td>eqn 5.69 ER4th 5.45 E&amp;R3rd</td>
</tr>
</tbody>
</table>
Refrigerators and Generalization of Carnot Cycle

Reverse Carnot cycle: a heat pump

\[ \eta_r = C_R = \frac{-q_{\text{from freeze}}}{w_{\text{total}}} = \frac{q_{\text{III}}}{w_{\text{total}}} = \frac{T_L}{T_U - T_L} \]

Equation 5.69 ER4th 5.45 E&R3rd

For a refrigerator performance is (heat in at TL/work total)

\[ \eta_{\text{hp}} = C_{\text{HP}} = \frac{q_{\text{given off to room}}}{w_{\text{total}}} = \frac{-q_{\text{I}}}{w_{\text{total}}} = \frac{T_U}{T_U - T_L} \]

Equation 5.68 ER4th 5.44 E&R3rd

Since refrigerators and heat pumps are just Carnot machines in reverse, the relationship for \( \epsilon = \frac{-w_{\text{total}}}{q_{\text{I}}} = \frac{(T_U - T_L)}{T_U} \) holds for these cycles. However only for “engines” does it represent the efficiency or “goodness of performance” (work total out/heat in).

For a refrigerator performance is (heat in at TL/work total)

For a heat pump performance is (heat out at TU/work total)
one more important FACTOID about Carnot machine

for complete reversible Carnot cycle:
\[ \oint dU = \Delta U = 0 \]
\[ \oint dH = \Delta H = 0 \]
\[ \oint dq_{rev} = q = \neq 0 \]
\[ \oint dw_{rev} = w = \neq 0 \]

BUT ALSO LET'S LOOK AT:
\[ \oint \frac{dq_{rev}}{T} \]

one more important FACTOID about Carnot machine

constant $T = T_U$
\[ \oint_{T = T_U} \frac{dq_{rev}}{T} = \frac{nRT}{P_U} \ln \frac{P}{P_U} \]

adiabatic
\[ \oint_{T = T_U} \frac{dq_{rev}}{T} = 0 \]

constant $T = T_L$
\[ \oint_{T = T_L} \frac{dq_{rev}}{T} = -\frac{nRT}{P_L} \ln \frac{P}{P_L} \]

adiabatic
\[ \oint_{T = T_L} \frac{dq_{rev}}{T} = 0 \]

have we uncovered a new state function entropy ($S$)??
\[ \Delta S = \int dS = \int \frac{dq_{rev}}{T} \]
does it just apply to ideal gas Carnot cycle??

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Our work on the (reversible) Carnot Cycle using an ideal gas as the ‘working substance’ lead to the relationship

$$\varepsilon = \frac{-W_{\text{total}}}{q_U} = \frac{T_U - T_L}{T_U}$$

However, the second law applies to machines with any ‘working substance’ and general cycles.

The following presentation shows that a (reversible) Carnot machine with ‘any working substance’ cannot have $$\varepsilon_{\text{rev any ws}} > \varepsilon_{\text{carnot ideal gas}}$$.

REVERSING the directions of the ideal gas and ‘any rev Carnot’ (e.g. Raff, pp 160-162) shows that $$\varepsilon_{\text{rev any ws}} = \varepsilon_{\text{carnot ideal gas}}$$.

One can also show (E&R4th, Fig 5.15, 5.43, Raff 162-164) that any Carnot machine has $$\oint dq_{\text{rev}}/T = 0$$ and that any reversible machine cycle can be expressed as a sum of Carnot cycles.

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**Carnot machine**

Carnot machine: cyclic, reversible, machine exchanging heat with environment at only two temperatures $$T_U, T_L$$

**Carnot engine**: ‘forward’ Carnot cycle

**Carnot heat pump**: ‘reverse’ Carnot cycle

$$\varepsilon = 1 - \frac{T_L}{T_U} = -\frac{w_{\text{total}}}{q_U}$$ applies to both forward and reverse Carnot cycles.
can $\varepsilon_x > \varepsilon_c$ for any Carnot machine $X$ vs ideal gas Carnot machine $C$ ??

(machine $X$: any ‘working substance” (not necessarily ideal gas)
exchanges heat at only two temperatures $T_U$ and $T_L$

the machine $X$ operates as a Carnot engine doing work, while
the machine $C$ operates as a reverse Carnot ideal gas engine
acting as a heat pump.
In this example the work done by $X$, $(w_t)_X$ is totally used by $C$: $(w_t)_C = -(w_t)_X$

CAN $\varepsilon_x > \varepsilon_{Carnot}$: worksheet for numerical example (all $w_x$ goes into $w_{Carnot}$)

TRY: $\varepsilon_x = 0.6 > \varepsilon_{Carnot} = 0.5$; specify heat into $x$ $(q_u)_x = 100 J$ and all $(w_{out})_x = (w_{in})_{Carnot}$

for each of the cyclic processes
Try: ε_x = 0.6 > ε_{Carnot} = 0.5; specify heat into x \((q_u)_x = 100 \text{ J}\) and all \((w_{out})_x = (w_n)_{Carnot}\)

\[
\begin{align*}
\epsilon &= \frac{w_l}{q_u}, \quad \Delta U = (q_u) + (q_l) + w_l = 0 \\
(\epsilon)_{total} &= -20 \text{ J} \text{ (into } T_U) \\
(\epsilon)_{total} &= +20 \text{ J} \text{ (out of } T_L)
\end{align*}
\]

For each of the cyclic processes

**Clausius Statement of Second Law** *(numerical example)*

We assumed an \(\epsilon_x > \epsilon_{Cig}\) for ideal gas Carnot and calculated

\[w_{total} = 0\]

\[\epsilon = \frac{w_l}{q_u}\]

\[\Delta U = (q_u) + (q_l) + w_l = 0\]

\[
\begin{align*}
(q_u)_{total} &= -20 \text{ J} \text{ (into } T_U) \\
(q_l)_{total} &= +20 \text{ J} \text{ (out of } T_L)
\end{align*}
\]

**BUT:** It is impossible to have a natural process which produces no other effect than absorption of heat from a colder body and discharge of heat to a warmer body. *Clausius’s Statement*

Specific example showed:

If second law holds \(\epsilon_x > \epsilon_{Cig}\) cannot be true

For \(x = \text{any Carnot ideal gas or not}\)
**Chemistry 163B Winter 2020**

**Refrigerators and Generalization of Carnot Cycle**

---

**general proof:** can εx > εc for Carnot machine X vs ideal gas Carnot machine C ???

---

![Diagram of Carnot cycle with conditions and equations]

\[
\begin{align*}
(q_u)_x > 0 & \quad (q_u)_c < 0 \\
(\epsilon_x) = -\frac{(w_i)_x}{(q_u)_x} & \quad (\epsilon_c) = -\frac{(w_i)_c}{(q_u)_c} \\
(q_l)_x + (q_u)_x + (w_i)_x &= 0 & \quad (q_l)_c + (q_u)_c + (w_i)_c &= 0 \\
(q_u)_\text{tot} - (q_u)_x - (q_u)_c - (w_i)_x - (w_i)_c &= 0 & \text{which will be < 0, for } \epsilon_x > \epsilon_c
\end{align*}
\]

---

**general proof:** can εx > εc for Carnot machine X vs ideal gas Carnot machine C ???

---

![Diagram of Carnot cycle with conditions and equations]

**So** \((q_u)_\text{tot} < 0\)

and

\((q_l)_\text{tot} = -(q_u)_\text{tot} > 0\)

with \(w_\text{tot} = (w_i)_x + (w_i)_c = 0\)

\(\epsilon_x > \epsilon_c\) is not a condition consistent with the Second Law

so any Carnot machine, ideal gas or not

\[
\epsilon_\text{any, not Carnot ideal gas} \leq \epsilon_\text{carnot ideal gas} = \frac{(T_U - T_L)}{T_U}
\]
HW#4 Prob. 23

23. The diagram below, where Carnot engine X and Carnot heat pump C are coupled, is similar to that used in lecture to illustrate that the efficiency of any Carnot engine, \( \varepsilon_x \), has to be the same as that of an ideal gas Carnot engine, \( \varepsilon_C \), when the engines operate between the same two temperatures. The diagram below differs in that now 33% (20 J) of the total work done by engine X is done on the surroundings, while 67% (40 J) is input into the Carnot refrigerator C.

\[ (w_{\text{to surr}})_X = -20 J \]
\[ (w_{\text{internal}})_X = -40 J \]
\[ (w_{\text{sys to surr}})_C = 20 J \]
\[ (w_{\text{internal to C}})_C = -40 J \]
\[ (w_{\text{total}})_C = +40 J \]
\[ (w_{\text{total}})_X = -60 J \]
\[ (q_{L})_X = 100 J \]
\[ (q_{U})_C = -80 J \]
\[ (q_{U})_X = -20 J \]
\[ (q_{L})_C = -40 J \]
\[ (q_{U})_X = +40 J \]
\[ (q_{L})_X = -40 J \]

Assume that as indicated \( \varepsilon_x = 0.6 \) and \( \varepsilon_C = 0.5 \).

For \( (q_{U})_X = 100 J \), \( (w_{\text{sys to surr}})_X = -20 J \), \( (w_{\text{internal}})_X = -40 J \), \( (w_{\text{total}})_X = -60 J \), and \( (q_{U})_C = -80 J \)

Calculate:

\[ (w_{\text{sys to surr}})_X = -20 J \]
\[ (w_{\text{internal}})_X = -40 J \]
\[ (w_{\text{total}})_X = -60 J \]
\[ (q_{L})_X = 100 J \]
\[ (q_{U})_C = -80 J \]

\[ (w_{\text{total}})_X = -60 J \]
\[ (q_{L})_X = 0.6 \]
\[ (q_{U})_C = 0.5 \]

TRY: \( \varepsilon_x = 0.6 > \varepsilon_C = 0.5 \); specify heat into X \( (q_{U})_X = 100 J \) and all \( (w_{\text{total}})_X = (w_{\text{total}})_C \)

ANOTHER CONSEQUENCE OF ASSUMING \( \varepsilon_X > \varepsilon_C \) (2nd Law Statement)
CAN $\varepsilon_x = 0.5 < \varepsilon_c = 0.6$ if $X$ is a some cyclic REVERSIBLE machine

NO: for reversible $X$ and reversible Carnot, WHY: can now run $X$ as heat pump $\varepsilon_x = 0.5$ heat pump and Carnot as machine $\varepsilon_c = 0.6$ engine

WHY: can now run $X$ as heat pump $\varepsilon_x = 0.5$ and Carnot as machine $\varepsilon_c = 0.6$ same violation as $\varepsilon_x > \varepsilon_c$

$\varepsilon_{Machine}$ must be less than or equal to $\varepsilon_{HeatPump}$

$\varepsilon_x > \varepsilon_c$ (no way!!; slides #21-#24); but can $\varepsilon_x < \varepsilon_c$ ($\varepsilon_x = 0.5 < \varepsilon_c = 0.6$) ??

$\varepsilon_x = 0.5 < \varepsilon_c = 0.6$ is OK (no violation)

if $X$ is machine and $C$ is heat pump real engine can be less efficient than reversible Carnot heat pump
moral of the story for machines exchanging heat at $T_U$ and $T_L$

- $\varepsilon_{\text{reversible Carnot gas}} = (1 - T_L/T_U)$
- $\varepsilon_{\text{reversible any working substance}}$ cannot be $>$ $\varepsilon_{\text{reversible Carnot ideal gas}}$ (slides 21-27)
- $\varepsilon_{\text{reversible any working substance}}$ cannot be $<$ $\varepsilon_{\text{reversible Carnot ideal gas}}$ (slide 29)
- $\varepsilon_{\text{reversible IN GENERAL}} = \varepsilon_{\text{reversible Carnot ideal gas}} = (1 - T_L/T_U)$
- $(\varepsilon_{\text{irreversible engine}} < \varepsilon_{\text{maximum}} = (1 - T_L/T_U)$ is OK (slide 30)

$\varepsilon_{\text{maximum}} = \varepsilon_{\text{reversible}} = (1 - T_L/T_U)$

generalization to arbitrary cycle (E&R Fig. 5.4, Raff Fig. 4.11)

WHAT about reversible cycle in general (maybe not only two T's)?

FIGURE 5.4
An arbitrary reversible cycle, indicated by the ellipse, can be approximated to any desired accuracy by a sequence of alternating adiabatic and isothermal segments.
a REALLY BIG RESULT: connecting $\varepsilon$ and entropy

have shown generally for any reversible CYCLIC engine operating between $T_U$ and $T_L$:

$$\varepsilon = \frac{-w_{\text{total}}}{q_U} = 1 - \frac{T_L}{T_U}$$

now

$$-w_{\text{total}} = q_U + q_L$$

so

$$\varepsilon = \frac{q_U + q_L}{q_U} = 1 + \frac{q_L}{q_U}$$

thus

$$1 + \frac{q_L}{q_U} = 1 - \frac{T_L}{T_U}$$

$$\frac{q_L}{T_L} + \frac{q_U}{T_U} = 0 \quad \text{FOR THE CYCLE}$$

(ANY REVERSIBLE cyclic process operating between $T_U$ and $T_L$)

the BOTTOM LINE

so generally for this reversible cycle

DEFINE:

$$dS = \frac{d q_{\text{reversible}}}{T}$$

$$\oint dS = \oint \frac{d q_{\text{reversible}}}{T} = 0$$

and $S$ is STATE FUNCTION
roadmap for second law

1. Phenomenological statements (what is ALWAYS observed)

2. Ideal gas Carnot [reversible] cycle efficiency of heat → work
   (Carnot cycle transfers heat only at $T_U$ and $T_L$)

3. Any cyclic engine operating between $T_U$ and $T_L$ must have an equal or lower efficiency than Carnot OR VIOLATE one of the phenomenological statements (observations)

4. Generalize Carnot to any reversible cycle (E&R fig 5.4)

5. Show that for this REVERSIBLE cycle
   
   $q_u + q_l \neq 0$ (dq inexact differential)
   
   but
   
   \[
   \frac{q_u}{T_U} + \frac{q_l}{T_L} = 0 \quad (\text{something special about } \frac{dq_{rev}}{T})
   \]

6. STATE FUNCTION $S$, entropy and spontaneous changes

(more to come)

did Sadi imagine his ideal gas Carnot Cycle?
Sadi Carnot’s Ingenious Reasoning of Ideal Heat Engine Reversible Cycles

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1. Introduction: Sadi Carnot’s Far-Reaching Treatise of Heat Engines Was Not Noticed at His Time and Even Not Fully Recognized Nowadays

Sadi Carnot laid ingenious foundations for the Second Law of Thermodynamics before the First Law of energy conservation was known and long before Thermodynamic concepts were established. Sadi Carnot may had not been aware of ingenuity of his reasoning, and we may have never known since he died at age 36 from cholera epidemic.
2. Sadi Carnot’s Ingenious Reasoning of Ideal Heat Engine Reversible Cycles

The operations which we have just described might have been performed in an inverse direction and order. There is nothing to prevent forming vapor with the caloric of the body B, and at the temperature of that body, compressing it in such a way as to make it acquire the temperature of the body A, finally condensing it by contact with this latter body, and continuing the compression to complete liquefaction.

The most importantly, Carnot introduced the reversible processes and cycles and, with ingenious reasoning, proved that maximum heat engine efficiency is achieved by any reversible cycle (thus all must have the same efficiency), i.e.:

\[ W = W_{\text{ad OUT}} = Q_{\text{IN}} \cdot f_c(T_h, T_L) \]

\[ \eta_c = \frac{W_{\text{ad OUT}}}{Q_{\text{IN}}} = f_c(T_h, T_L) \]

(Carnot’s function)\(^\text{rev} \)

---

Carnot vs Einstein ??? (Milivoje Kostic)

\[ \{Q_{\text{IN}}, Q_L, W_L\} \subseteq \{Q_{\text{IN}}, -Q_L, -W_L\} \]

Carnot

\[ \eta_c = \frac{W}{Q_{\text{IN}}} = f_c(T_h, T_L) \]

\[ \frac{Q(T_H)}{Q(T_L)} = f(T_H) \quad \text{at} \quad T_L = \frac{T_H}{T_0} \]

Carnot Ratio Equality

(by Carnot’s function)\(^\text{rev} \)

Einstein

\[ E = mc^2 \]

\[ \text{< Does not apply >} \]

Fig. 8: Significance of the Carnot’s reasoning of reversible cycles is in many ways comparable with the Einstein’s relativity theory in modern times. The Carnot Ratio Equality is much more important than what it appears at first. It is probably the most important equation in Thermodynamics and among the most important equations in natural sciences.
End of Lecture 10

(four steps to exactitude)