Lecture 10

Chemistry 163B Refrigerators and Generalization of Ideal Gas Carnot

(four steps to exactitude)

$E\&R_{4th}$ pp 125-129, 132-139 Raff pp. 159-164
$E\&R_{3rd}$ 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]

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perpetual motion and the 1^{st} and 2^{nd} 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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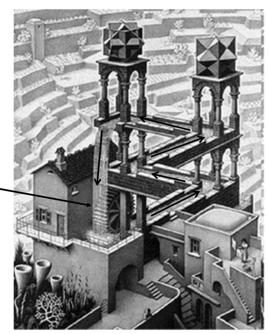
perpetual motion of the first kind (produce work with no heat input) Escher "Waterfall"

cyclic machine (water 'flows downhill' to pillar on left; 'round and 'round)

no energy input

work on surroundings

VIOLATES 1^{st} LAW



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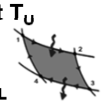
remember Carnot engine

- **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 $q_{L(III)} > 0$**



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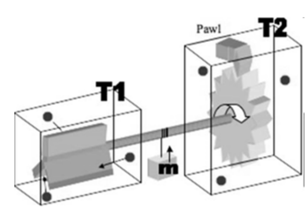
perpetual motion of the second kind (produce work extracting heat from cooler source to run machine at warmer temperature)

Brownian Ratchet



get work only if T1 > T2

https://en.wikipedia.org/wiki/Brownian_ratchet.

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Chemistry 163B Winter 2020
Refrigerators and Generalization of Carnot Cycle

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

  $q_U + q_L \neq 0$ (đq inexact differential)

  but

  $\frac{q_U}{T_U} + \frac{q_L}{T_L} = 0$ (*something* special about $\frac{đq_{rev}}{T}$)
- 6. S, entropy and spontaneous changes

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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 $\varepsilon_{\text{ideal gas rev Carnot}} = \varepsilon_{\text{any other rev Carnot}}$
- $dS \equiv \frac{đq_{reversible}}{T}$ $\oint dS = \oint \frac{đq_{reversible}}{T} = 0$

  and S is STATE FUNCTION

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remember Carnot engine

- **does net work on surroundings**

  and

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

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Carnot engine arithmetic <u>(for below table see handout)</u> ➡

ENGINE	q	w_{sys}	w_{surr}	
I. isothermal expansion	$+nRT_U \ln\frac{P_1}{P_2}$ 1.3	$-nRT_U \ln\frac{P_1}{P_2}$ 1.2	$+nRT_U \ln\frac{P_1}{P_2}$	heat in at T_H work out
II adiabatic expansion	0	$n\overline{C_V}(T_L - T_U)$ 2.4	$-n\overline{C_V}(T_L - T_U)$	work out
III. isothermal compression	$nRT_L \ln\frac{P_3}{P_4} = -nRT_L \ln\frac{P_1}{P_2}$ 3.3&T.3	$-nRT_L \ln\frac{P_3}{P_4} = nRT_L \ln\frac{P_1}{P_2}$ 3.2&T.3	$-nRT_L \ln\frac{P_1}{P_2}$	heat lost at T_L work in
IV. adiabatic compression	0	$n\overline{C_V}(T_U - T_L)$ 4.4	$-n\overline{C_V}(T_U - T_L)$	work in
net gain/cost	$q_{in} = q_I = q_U$ $+nRT_U \ln\frac{P_1}{P_2}$	$(w_{total})_{sys} = (w_I + w_{II} + w_{III} + w_{IV})_{sys} =$ $-nR(T_U - T_L)\ln\frac{P_1}{P_2}$	$(w_{total})_{surr} = (w_I + w_{II} + w_{III} + w_{IV})_{surr} = -(w_{total})_{sys}$ $nR(T_U - T_L)\ln\frac{P_1}{P_2}$	$\varepsilon = w_{surr}/q_{in}$ $\varepsilon = (T_U - T_L)/T_U$

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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**

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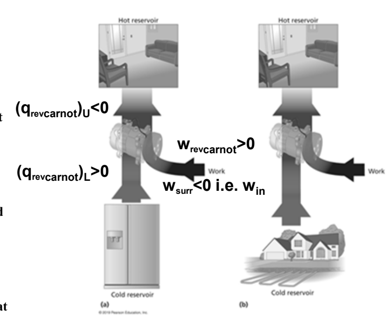
heat pumps and refrigerators (fig. 5.20 E&R$_{4th}$) 5.17 $_{ER3rd}$

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



refrigerator **heat pump**

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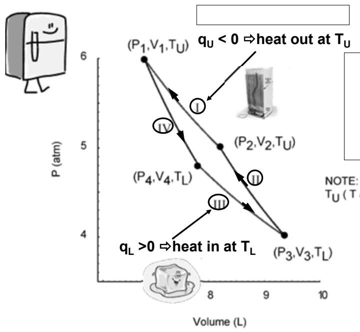
reverse Carnot cycle: a refrigerator



w_{sys}=-w_{surr} > 0
work done ON system

NOTE:
T_U (T *upper*) =T_H (T *higher* or T *hotter*)

cyclic process
IV adiabatic expansion
III isothermal expansion
II adiabatic compression
I isothermal compression

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Carnot refrigerator arithmetic (just negatives of Carnot engine)
for below table see handout

REFRIGERATOR	q	w_{sys}	q_{surr}	
IV. adiabatic expansion $T_H \to T_L$	0	$-n\overline{C}_V(T_U - T_L)$	0	work done by system
III. isothermal expansion at T_L $P_4 \to P_3$	$-nRT_L \ln\frac{P_3}{P_4} = nRT_L \ln\frac{P_1}{P_2}$	$+nRT_L \ln\frac{P_3}{P_4} = -nRT_L \ln\frac{P_1}{P_2}$	$-nRT_L \ln\frac{P_1}{P_2}$	work done by sys heat withdrawn from T_L (ice box)
II adiabatic compression $T_L \to T_H$	0	$-n\overline{C}_V(T_L - T_U)$	0	work on system
I. isothermal compression at T_H $P_2 \to P_1$	$-nRT_U \ln\frac{P_1}{P_2}$	$+nRT_U \ln\frac{P_1}{P_2}$	$+nRT_U \ln\frac{P_1}{P_2}$	heat out at T_H refrig "coils" work on system
net gain/cost		$w_{total}=w_I+w_{II}+w_{III}+w_{IV}=$ $+nR(T_U - T_L)\ln\frac{P_1}{P_2}$	$\lvert q_{out}\rvert = -q_{surr\_III}$ $+nRT_L \ln\frac{P_1}{P_2}$	$\eta_r \equiv C_R = \frac{-q_{surr\_III}}{w_{sys\,total}} = \frac{T_L}{T_U - T_L}$ eqn 5.69 E&R$_{4th}$ [5.45 E&R$_{3rd}$]

Coefficient of performance of refrigerator:

$$\eta_r \equiv C_R = \frac{-q_{surr\_III}}{w_{total}} = \frac{q_{III}}{w_{total}} = \boxed{\frac{T_L}{T_U - T_L}}$$

eqn 5.69 ER_{4th} 5.45 E&R3rd

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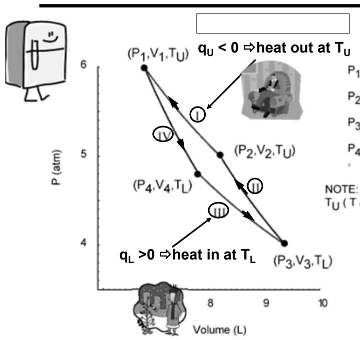
reverse Carnot cycle: a heat pump



w_{sys}=-w_{surr} > 0
work done ON system

P_1=6 atm, T_1=T_U=500K
P_2=5 atm, T_2=T_U=500K
P_3=4 atm, $q_{2\to3}$ = 0, T_3=T_L
P_4=4.8 atm, T_4=T_L, $q_{4\to1}$= 0

NOTE:
T_U (T *upper*) =T_H (T *higher* or T *hotter*)

cyclic process
IV adiabatic expansion
III isothermal expansion
II adiabatic compression
I isothermal compression

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"goodness of performance"

Since refrigerators and heat pumps are just Carnot machines in reverse, the relationship for ε=-w_{total}/q_I = (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$_{total}$)

$$\eta_r \equiv C_R = \frac{-q_{from\ freezer}}{w_{total}} = \frac{q_{III}}{w_{total}} = \frac{T_L}{T_U - T_L}$$

eqn 5.69 ER_{4th} 5.45 E&R3rd

HW5 #28† (E&R$_{4th}$ P5.33)

For a heat pump performance is (heat$_{out\ at\ TU}$/work$_{total}$)

$$\eta_{hp} \equiv C_{HP} = \frac{q_{given\ off\ to\ room}}{w_{total}} = \frac{-q_I}{w_{total}} = \frac{T_U}{T_U - T_L} \quad (>1)$$

eqn 5.68 ER_{4th} 5.44 E&R3rd

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one more important FACTOID about Carnot machine

for complete reversible Carnot cycle:

$$\oint dU = \Delta U = \boxed{0}$$
$$\oint dH = \Delta H = \boxed{0}$$
$$\oint đq_{rev} = q = \boxed{\neq 0}$$
$$\oint đw_{rev} = w = \boxed{\neq 0}$$

BUT ALSO LET'S LOOK AT:

$$\oint_{cycle} \frac{đq_{rev}}{T}$$

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one more important FACTOID about Carnot machine

constant $T = T_U$ $\quad \int_I \frac{đq_{rev}}{T} = \frac{nR\cancel{T_U}\ln\frac{P_1}{P_2}}{\cancel{T_U}}$

adibatic $\quad \int_{II} \frac{đq_{rev}}{T} = 0$

constant $T = T_L$ $\quad \int_{III} \frac{đq_{rev}}{T} = \frac{-nR\cancel{T_L}\ln\frac{P_1}{P_2}}{\cancel{T_L}}$

adibatic $\quad \int_{IV} \frac{đq_{rev}}{T} = 0$

$$\oint_{cycle} \frac{đq_{rev}}{T} = \boxed{0}$$

have we uncovered a new state function entropy (S) ??

$$\Delta S = \int dS = \int \frac{đq_{rev}}{T}$$

does it just apply to ideal gas Carnot cycle ???

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Refrigerators and Generalization of Carnot Cycle

Generalization of Ideal Gas Carnot Cycle

1. **Our work on the (reversible) Carnot Cycle using an ideal gas as the 'working substance" lead to the relationship**

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

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

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

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

4. **One can also show (E&R$_{4th}$ Fig 5.15** ***Fig 5.43$_{3rd}$, Raff 162-164*** **) that any Carnot machine has $\oint dq_{rev}/T = 0$ 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

$$\varepsilon = 1 - \frac{T_L}{T_U} = \frac{-w_{total}}{q_U}$$ **applies to both forward and reverse Carnot cycles**

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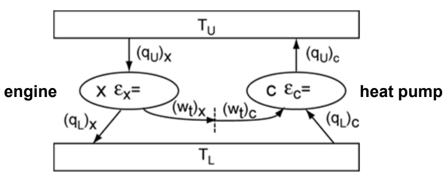
can $\varepsilon_x > \varepsilon_c$ for any Carnot machine X vs ideal gas Carnot machine C ???

(generalizing $\varepsilon_{rev}=1-T_L/T_U$ that was derived for reversible ideal gas Carnot cycle)

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:** $(w_t)_c = -(w_t)_x$

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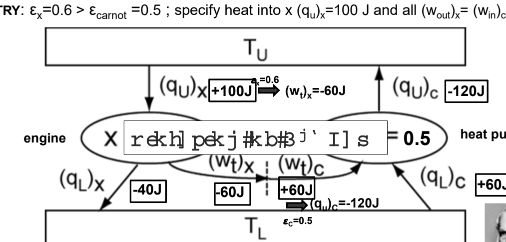
CAN $\varepsilon_x > \varepsilon_{Carnot}$: worksheet for numerical example (all w_x goes into w_{Carnot})

TRY: ε_x=0.6 > ε_{carnot} =0.5 ; specify heat into x $(q_u)_x$=100 J and all $(w_{out})_x$= $(w_{in})_{carnot}$



Clausius

$$\varepsilon = \frac{-w_t}{q_U} \qquad q_U = \frac{-w_t}{\varepsilon} \qquad w_t = -q_U\,\varepsilon \qquad \Delta U = q_U + q_L + w_t = 0$$

for each of the cyclic processes

w_{total}=0

$(q_U)_{total}$= -20J (into T_u)

$(q_L)_{total}$=+20J (out of T_L)

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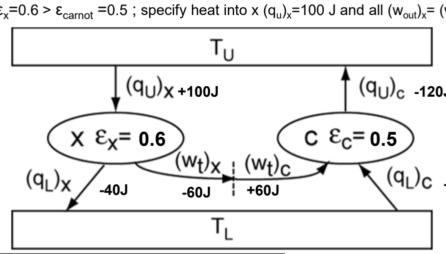
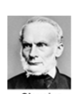
CAN $\varepsilon_x > \varepsilon_{Carnot}$: worksheet for numerical example (all w_x goes into w_{Carnot})

TRY: ε_x=0.6 > ε_{carnot} =0.5 ; specify heat into x $(q_u)_x$=100 J and all $(w_{out})_x$= $(w_{in})_{carnot}$





Clausius

$$\varepsilon = \frac{-w_t}{q_U} \qquad q_U = \frac{-w_t}{\varepsilon} \qquad w_t = -q_U\,\varepsilon \qquad \Delta U = q_U + q_L + w_t = 0$$

for each of the cyclic processes

w_{total}=0

$(q_U)_{total}$= -20J (into T_u)

$(q_L)_{total}$=+20J (out of T_L)

rekh] pekj#kb#B ʲ ` I] s

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Clausius Statement of Second Law (numerical example)

we assumed an $\varepsilon_x > \varepsilon_{Cig}$ for ideal gas Carnot and calculated

w_{total}=0

$(q_L)_{total}$=+20J (into 'combo engine' out of cold reservoir at T_{lower})

$(q_U)_{total}$=-20J (out of 'combo engine' into heat reservoir at T_{upper})

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 $\varepsilon_x > \varepsilon_{cig}$ cannot be true

for x= any Carnot ideal gas or not

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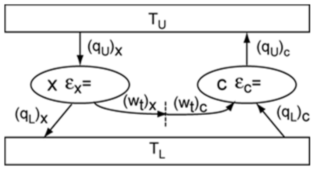
general proof: can $\varepsilon_x > \varepsilon_c$ for Carnot machine X vs ideal gas Carnot machine C ???



$(q_U)_x > 0$

$\varepsilon_x = \frac{-(w_t)_x}{(q_U)_x}$

$(w_t)_x = -(q_U)_x \varepsilon_x$

$(q_L)_x + (q_U)_x + (w_t)_x = 0$

$(q_U)_c < 0$

$\varepsilon_c = \frac{-(w_t)_c}{(q_U)_c} = \frac{(w_t)_x}{(q_U)_c}$

$(w_t)_x = (q_U)_c \varepsilon_c$

$(q_L)_c + (q_U)_c + (w_t)_c = 0$

to give $-(w_t)_x = (w_t)_c$, $\frac{-(q_U)_x}{(q_U)_c} = \frac{\varepsilon_c}{\varepsilon_x}$, and $(q_U)_c = -\frac{\varepsilon_x}{\varepsilon_c}(q_U)_x$

$(q_U)_{total} = (q_U)_x + (q_U)_c = (q_U)_x\left(1 - \frac{\varepsilon_x}{\varepsilon_c}\right)$ (which will be < 0, for $\varepsilon_x > \varepsilon_c$)

$(q_L)_{total} = (q_L)_x + (q_L)_c = (-(q_U)_x - (w_t)_x) + (-(q_U)_c + (w_t)_x) = -(q_U)_{total}$

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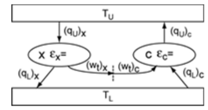
general proof: can $\varepsilon_x > \varepsilon_c$ for Carnot machine X vs ideal gas Carnot machine C ???



So $(q_U)_{total} < 0$

and

$(q_L)_{total} = -(q_U)_{total} > 0$

with $w_{total} = (w_t)_x + (w_t)_c = 0$

ok#s d]p o#pda#lnk^hai #===

q transferred $T_L \rightarrow T_U$ with no net work
violates Clausius statement of second law

ok#s d]p o#pda#okhqpekj#===

$\varepsilon_x > \varepsilon_c$ is not a condition consistent with the Second Law
so any Carnot machine, ideal gas or not

$$\varepsilon_{any\ carnot} \underset{so\ far}{\leq} \varepsilon_{carnot\ ideal\ gas} = (T_U - T_L)/T_U$$

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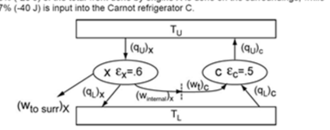
HW#4 Prob. 23

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, ε_X, has to be the same as that of an ideal gas Carnot engine, ε_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.



Assume that as indicated $\varepsilon_X = 0.6$ and $\varepsilon_c = 0.5$.
For $(q_U)_x = 100J$, $(w_{surr})_x = -20$ J, $(w_i)_x = -40$ J, $(w_t)_c = +40J$, and $(q_U)_c = -80J$
Calculate:
a. $(q_L)_x$
b. $(q_L)_c$
c. $(q_U)_{total} = (q_U)_x + (q_U)_c$
d. $(q_L)_{total} = (q_L)_x + (q_L)_c$
e. $w_{total} = (w_{surr})_x + (w_i)_x + (w_t)_c$
f. Considering the [correct] results for parts c, d, and e, how does the process with coupled Carnot engines X and C having $\varepsilon_X = 0.6$ and $\varepsilon_c = 0.5$ violate one of the statements of the Second Law of Thermodynamics

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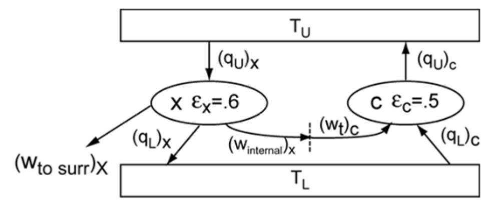
setup for (HW prob #23) ε_x efficiency greater than Carnot

TRY: $\varepsilon_x = 0.6 > \varepsilon_{carnot} = 0.5$; specify heat into x $(q_u)_x = 100$ J and all $(2/3)(w_{out})_x = (w_{in})_{carnot}$



$(q_U)_X = 100J \overset{\varepsilon_X = 0.6}{\Longrightarrow} (w_{total})_x = -60J$

$(w_{sys\ to\ surr})_x = -20J$ $(w_{internal\ to\ C})_X = -40J$

$(w_{total})_c = +40J \overset{\varepsilon_C = 0.5}{\Longrightarrow} (q_U)_c = -80J$

calc: $(q_L)_x$, $(q_L)_c$, $(q_L)_{total}$, $(q_U)_{total}$, $(w)_{total}$

ANOTHER CONSEQUENCE OF ASSUMING $\varepsilon_X > \varepsilon_C$ (2nd Law Statements)

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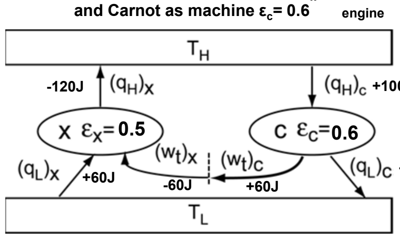
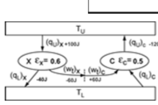
CAN $\varepsilon_x = 0.5 < \varepsilon_c = 0.6$ if X is a some cyclic REVERSIBLE machine

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





same calc as slides 21-23 same violation as $\varepsilon_x > \varepsilon_c$

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

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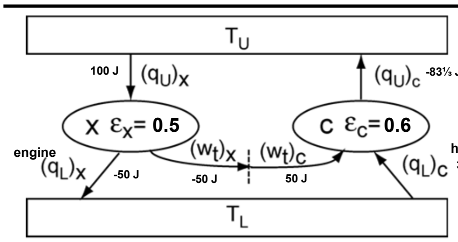
$\varepsilon_x > \varepsilon_C$ (no way !!; slides #21-#24); ***but can $\varepsilon_x < \varepsilon_C$ ($\varepsilon_x = 0.5 < \varepsilon_c = 0.6$) ??***



derivation a la slide #21 with input of $(q_u)_x = 100J$

gives $(q_u)_{total} = +16⅔$ (out of T_u)
$(q_L)_{total} = -16⅔$ (into T_L)
heat from hotter to cooler


Clausius

$\varepsilon_x = 0.5 < \varepsilon_c = 0.6$ is OK (no violation)
if X is machine and C is heat pump

(real engine can be less efficient than reversible Carnot heat pump)

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Chemistry 163B Winter 2020
Refrigerators and Generalization of Carnot Cycle

moral of the story for machines exchanging heat at T_U and T_L

- **$\varepsilon_{\text{reversible Carnot ideal gas}} = (1-T_L/T_U)$**
- **$\varepsilon_{\text{reversible any working substance}}$ 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)**
- **$\varepsilon_{\text{reversible IN GENERAL}} = \varepsilon_{\text{reversible Carnot ideal gas}} = (1-T_L/T_U)$**
- **$(\varepsilon_{\text{irreversible}})_{\text{engine}} < \varepsilon_{\text{maximum}} = (1-T_L/T_U)$ is OK (slide 30)**

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

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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) ?

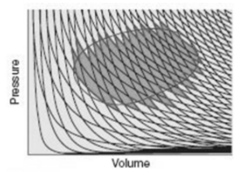
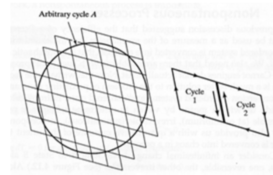


FIGURE 5.4
An arbitrary reversible cycle, indicated by the ellipse, can be approximated to any desired accuracy by a sequence of alternating adiabatic and isothermal segments.



sum of Carnot cycles

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a REALLY BIG RESULT: connecting ε and entropy

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

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

now

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

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)

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the BOTTOM LINE

so generally for this reversible cycle

DEFINE: $$dS \equiv \frac{đq_{reversible}}{T}$$

$$\oint dS = \oint \frac{đq_{reversible}}{T} = 0$$

and S is STATE FUNCTION

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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

$q_U + q_L \neq 0$ (đq inexact differential)

but

$\frac{q_U}{T_U} + \frac{q_L}{T_L} = 0$ (***something*** special about $\frac{đq_{rev}}{T}$)

✓ 6. **STATE FUNCTION S**, entropy and spontaneous changes

(more to come)

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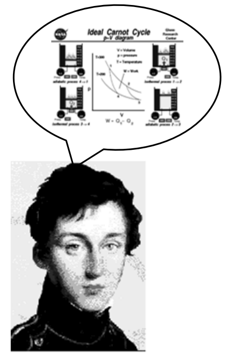
did Sadi imagine his ideal gas Carnot Cycle?



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Chemistry 163B Winter 2020
Refrigerators and Generalization of Carnot Cycle

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Sadi Carnot's Ingenious Reasoning of Ideal Heat Engine Reversible Cycles

MILIVOJE M. KOSTIC
Department of Mechanical Engineering
Northern Illinois University
DeKalb, IL 60115
U.S.A.
kostic@niu.edu; http://www.kostic.niu.edu

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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 Fist 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.

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2. Sadi Carnot's Ingenious Reasoning of Ideal Heat Engine Reversible Cycles

54 *MOTIVE POWER OF HEAT.*

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.:

"The motive power of heat is independent of the agents employed to realize it; its quantity is fired solely by the temperatures of the bodies between which is effected, finally, the transfer of the caloric." [1], i.e.:

$$W = W_{netOUT} = Q_{IN} \cdot f_c(T_H, T_L)$$

$$\eta_{Ct} = \left.\frac{W_{netOUT}}{Q_{IN}}\right|_{Max} = \left.\underbrace{f_c(T_H, T_L)}_{\text{Qualitative function}}\right|_{Rev.} \quad (1)$$

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Carnot vs Einstein ??? (Milivoje Kostic)

$$\{Q_H, Q_L, W_C\} \underset{\text{REVERSED}}{\overset{\text{If}}{\Leftrightarrow}} \{-Q_H, -Q_L, -W_C\}$$

Carnot

$$\eta_C = \frac{W}{Q_{IN}} = \left.\underbrace{f_c(T_H, T_L)}_{\text{Qualitative function}}\right|_{Rev.}$$

$$\frac{Q(T)}{Q(T_0)} = \left.\frac{f(T)}{f(T_0)}\right|_{f(T)=T} = \frac{T}{T_0} = \frac{Q}{Q_0}$$

Carnot Ratio Equality (by Carnot's followers)

versus $< ? >$

Einstein $\{E = mc^2\}$

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.

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End of Lecture 10

(four steps to exactitude)

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