Chemistry 163B Refrigerators and Generalization of Ideal Gas Carnot

(four steps to exactitude)

E&R pp 86-91 *[81-85]*$_{2nd}$, 109-111 *[102-104]*$_{2nd}$; Raff pp. 159-164

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]

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

$$q_U + q_L \neq 0 \quad (\text{đ}q \textit{ inexact differential})$$

but

$$\frac{q_U}{T_U} + \frac{q_L}{T_L} = 0 \quad (\textit{something special about } \frac{\text{đ}q_{rev}}{T})$$

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 $\varepsilon_{\text{ideal gas rev Carnot}} = \varepsilon_{\text{any other rev Carnot}}$
- $dS \equiv \frac{đq_{reversible}}{T} \qquad \oint dS = \oint \frac{đq_{reversible}}{T} = 0$ **and S is STATE FUNCTION**

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

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	$q_{in} = q_I$ $+nRT_U \ln\frac{P_1}{P_2}$		$w_{total}= w_I+w_{II}+w_{III}+w_{IV}=$ $nR(T_U - T_L)\ln\frac{P_1}{P_2}$	$\varepsilon = w_{surr}/q_{in}$ $\varepsilon = (T_U - T_L)/T_U$

- **does net work on surroundings**

and

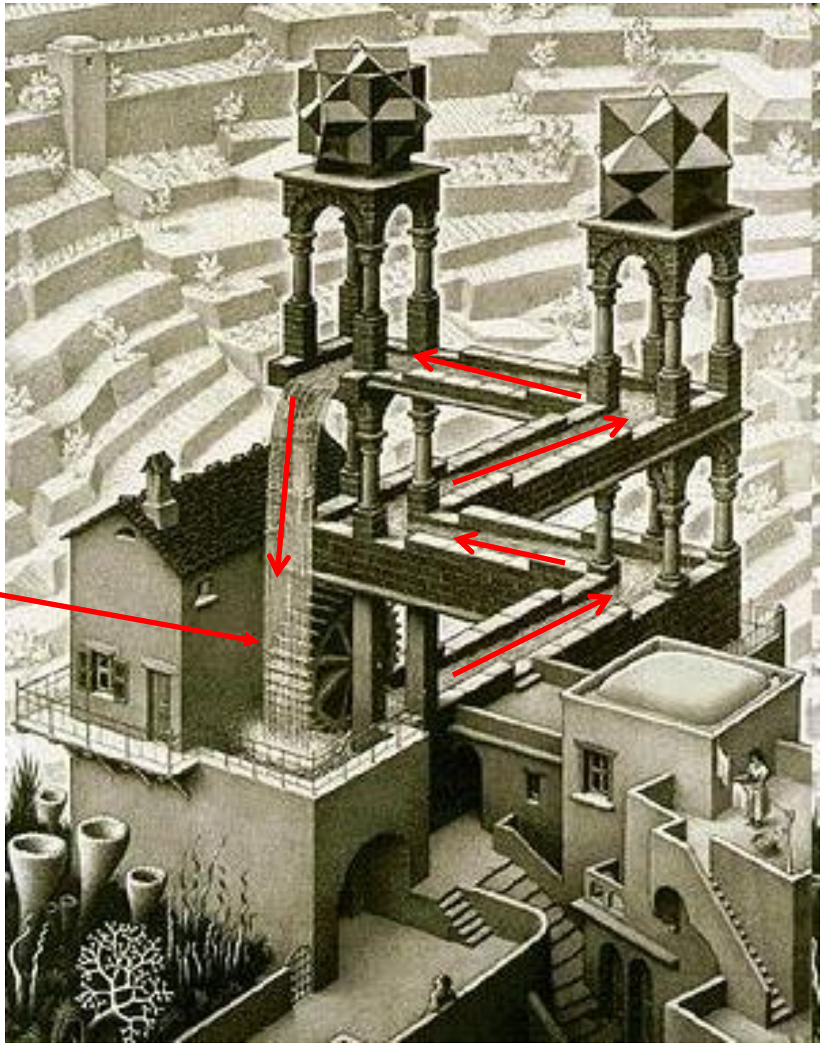
- **net heat $q_{U(I)} + q_{L(III)} = -w_{total}$**

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 1st LAW

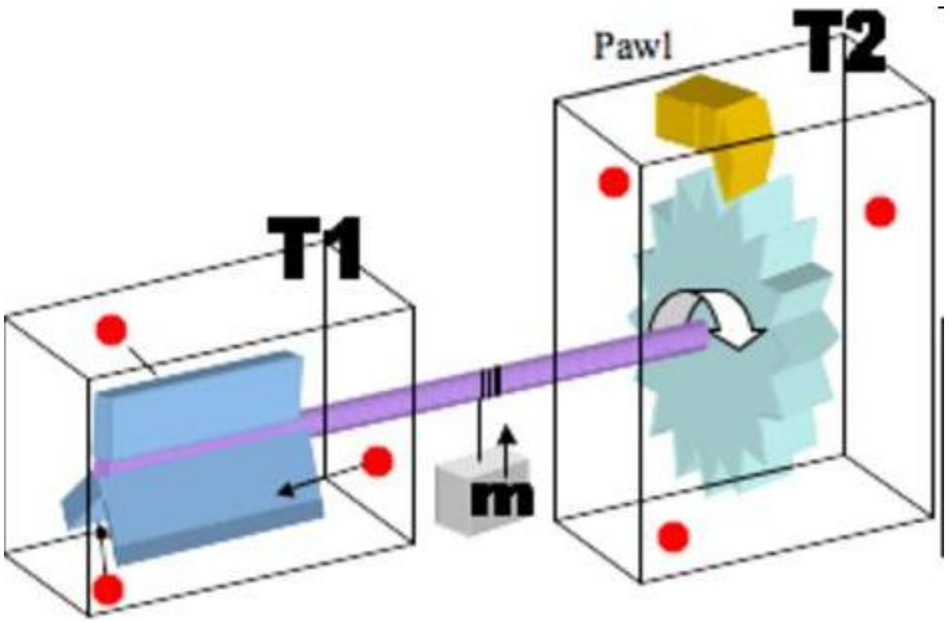
- **does net work on surroundings**

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 T1 > T2

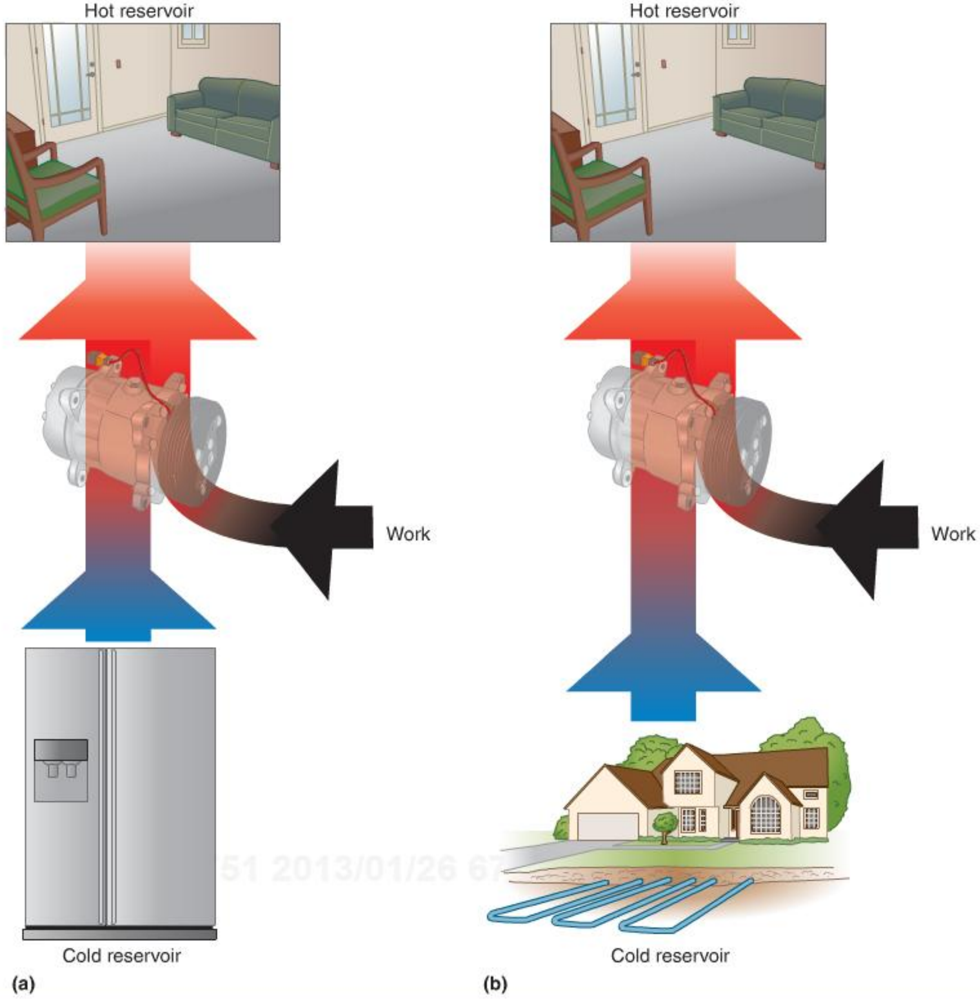
http://wapedia.mobi/en/Brownian_ratchet#1.

- **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 expansion against constant P_{ext})**

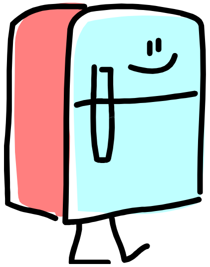
- **however the Carnot cycle is a combination of reversible processes**

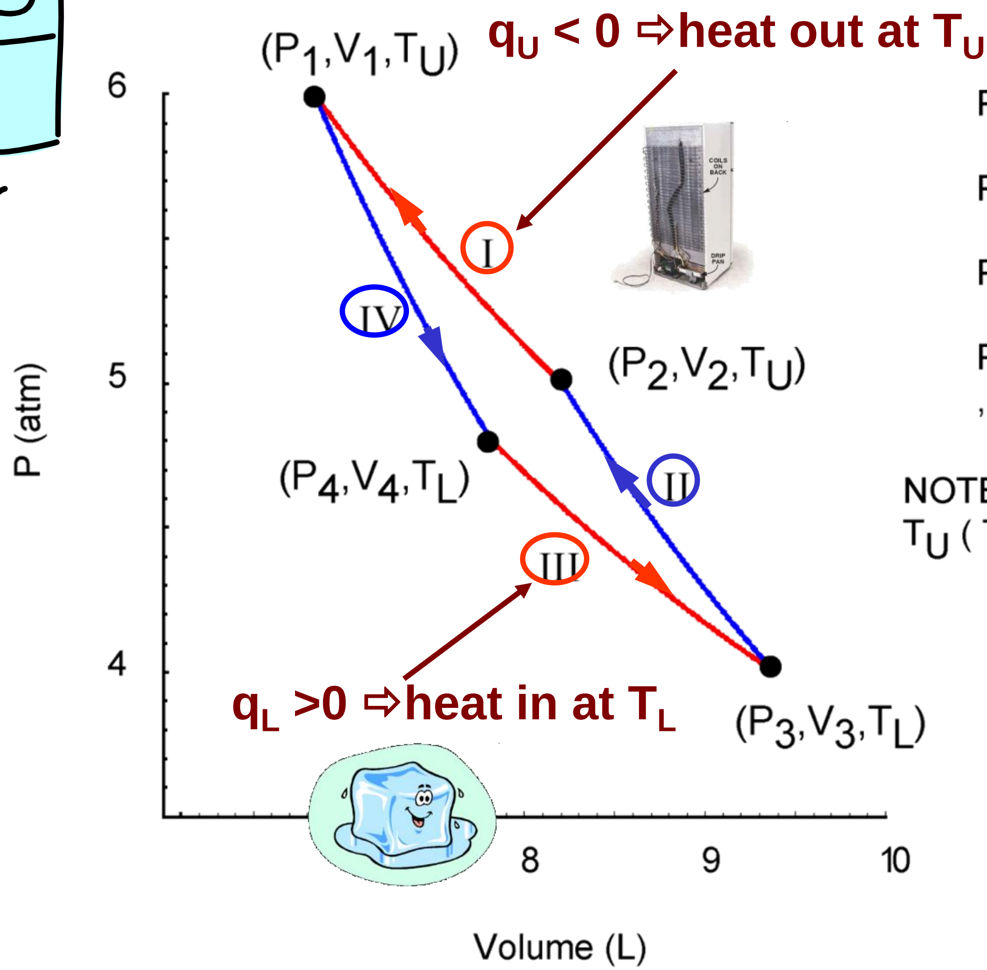
heat pumps and refrigerators (fig. 5.17 E&R) *3rd*

FIGURE 5.17
Reverse heat engines can be used to induce heat flow from a cold reservoir to a hot reservoir with the input of work. **(a)** Refrigerator: the cold reservoir is the interior of a refrigerator, and the hot reservoir is the room in which the refrigerator is located. **(b)** Heat pump: the cold reservoir is water-filled pipes buried in the ground, and the hot reservoir is the interior of the house to be heated. The relative widths of the two paths entering the hot reservoir show that a small amount of work input can move a larger amount of heat from the cold to the hot reservoir. In both cases, the engine is a compressor.



reverse Carnot cycle: a refrigerator





$w_{sys}=-w_{surr} > 0$

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, $q_{2\rightarrow3}$ = 0, $T_3=T_L$

P_4=4.8 atm, $T_4=T_L$, $q_{4\rightarrow1}$= 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

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

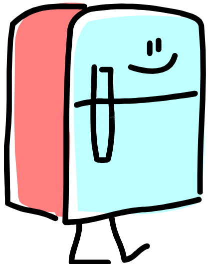
REFRIGERATOR	q	w_{sys}	q_{surr}	
IV. adiabatic expansion $T_H \longrightarrow T_L$	0	$-n\overline{C}_V(T_U - T_L)$	0	work done by system
III. isothermal expansion at T_L $P_4 \longrightarrow P_3$	$-nRT_L \ln \frac{P_3}{P_4}$	$+nRT_L \ln \frac{P_3}{P_4} = -nRT_L \ln \frac{P_1}{P_2}$	$-nRT_L \ln \frac{P_1}{P_2}$	work done by sys heat withdrawn from T_L (ice box)
II adiabatic compression $T_L \longrightarrow T_H$	0	$-n\overline{C}_V(T_L - T_U)$	0	work on system
I. isothermal compression at T_H $P_2 \longrightarrow P_1$	$-nRT_U \ln \frac{P_1}{P_2}$	$+nRT_U \ln \frac{P_1}{P_2}$	$+nRT_U \ln \frac{P_1}{P_2}$	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 5.45 E&R

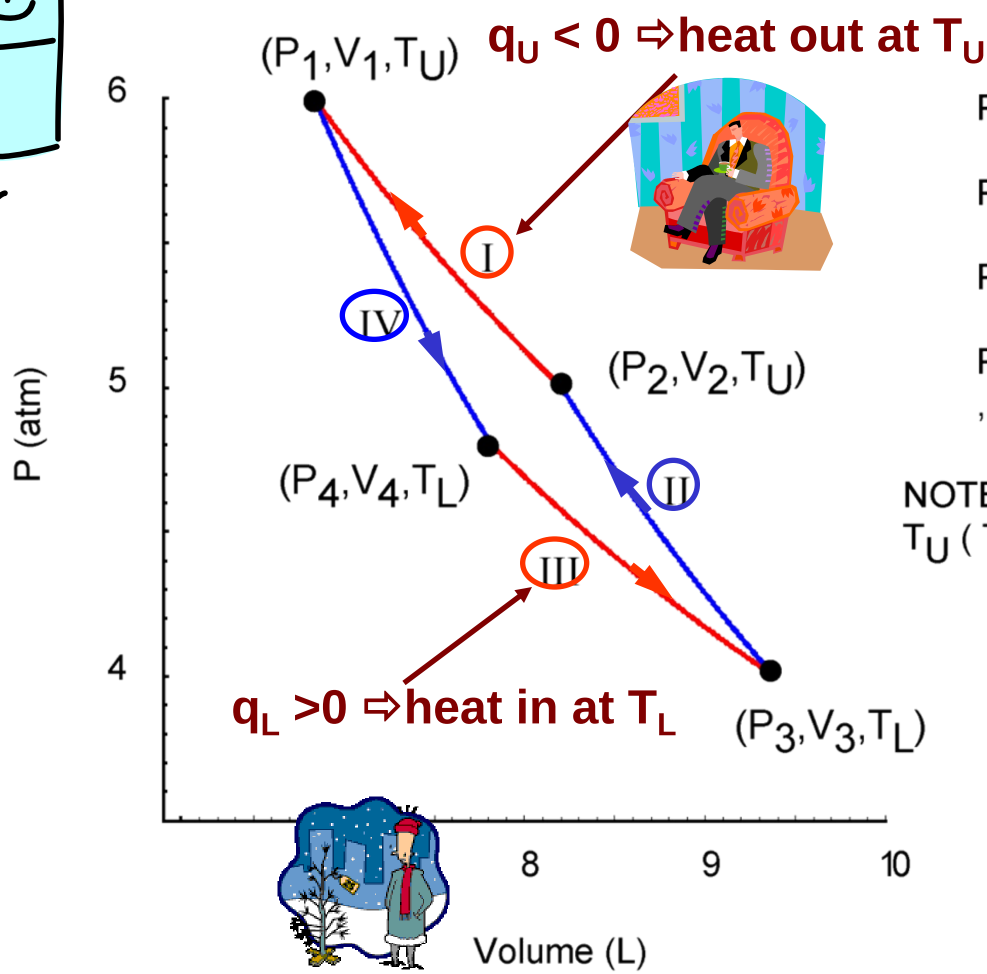
Coefficient of performance of refrigerator:

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

E&R eqn 5.45

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, $q_{2\rightarrow 3} = 0$, $T_3 = T_L$

P_4=4.8 atm, $T_4 = T_L$, $q_{4\rightarrow 1} = 0$

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

"goodness of performance"

Since refrigerators and heat pumps are just Carnot machines in reverse, the relationship for $\varepsilon = -w_{total}/q_I = (T_U - T_L)/T_U$ 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 ($heat_{in\ at\ TL}/work_{total}$)

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

E&R eqn 5.45

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

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

E&R eqn 5.44

(> 1)

for complete reversible Carnot cycle:

$\oint dU = \quad \Delta U = 0$

$\oint dH = \quad \Delta H = 0$

$\oint đq_{rev} = \quad q = \neq 0$

$\oint đw_{rev} = \quad w = \neq 0$

BUT ALSO LET'S LOOK AT:

$$\oint_{cycle} \frac{đq_{rev}}{T}$$

one more important FACTOID about Carnot machine

$$\int_{I} \frac{đq_{rev}}{T} = \frac{nRT_U \ln \frac{P_1}{P_2}}{T_U}$$

$$\int_{II} \frac{đq_{rev}}{T} = 0 \; (adiabatic)$$

$$\int_{III} \frac{đq_{rev}}{T} = \frac{-nRT_L \ln \frac{P_1}{P_2}}{T_L}$$

$$\int_{IV} \frac{đq_{rev}}{T} = 0 \; (adiabatic)$$

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

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 ???

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 $\mathcal{E}_{rev\ any\ ws} > \mathcal{E}_{carnot\ ideal\ gas}$.**

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

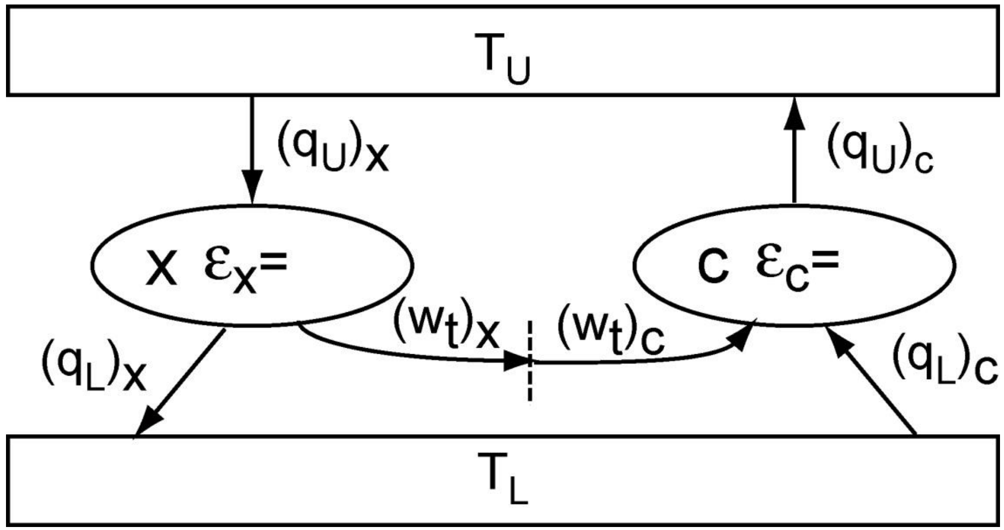
4. **One can also show (E&R Fig 5.4,** *Raff 162-164* **) that any Carnot machine has $\oint dq_{rev}/T = 0$ and that any reversible machine cycle can be expressed as a sum of Carnot cycles.**

Carnot machine: <u>cyclic</u>, <u>reversible</u>, machine exchanging heat with environment at only two temperatures T_U, T_L

Carnot engine: ‘forward’ Carnot cycle

Carnot heat pump: ‘reverse’ Carnot cycle

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

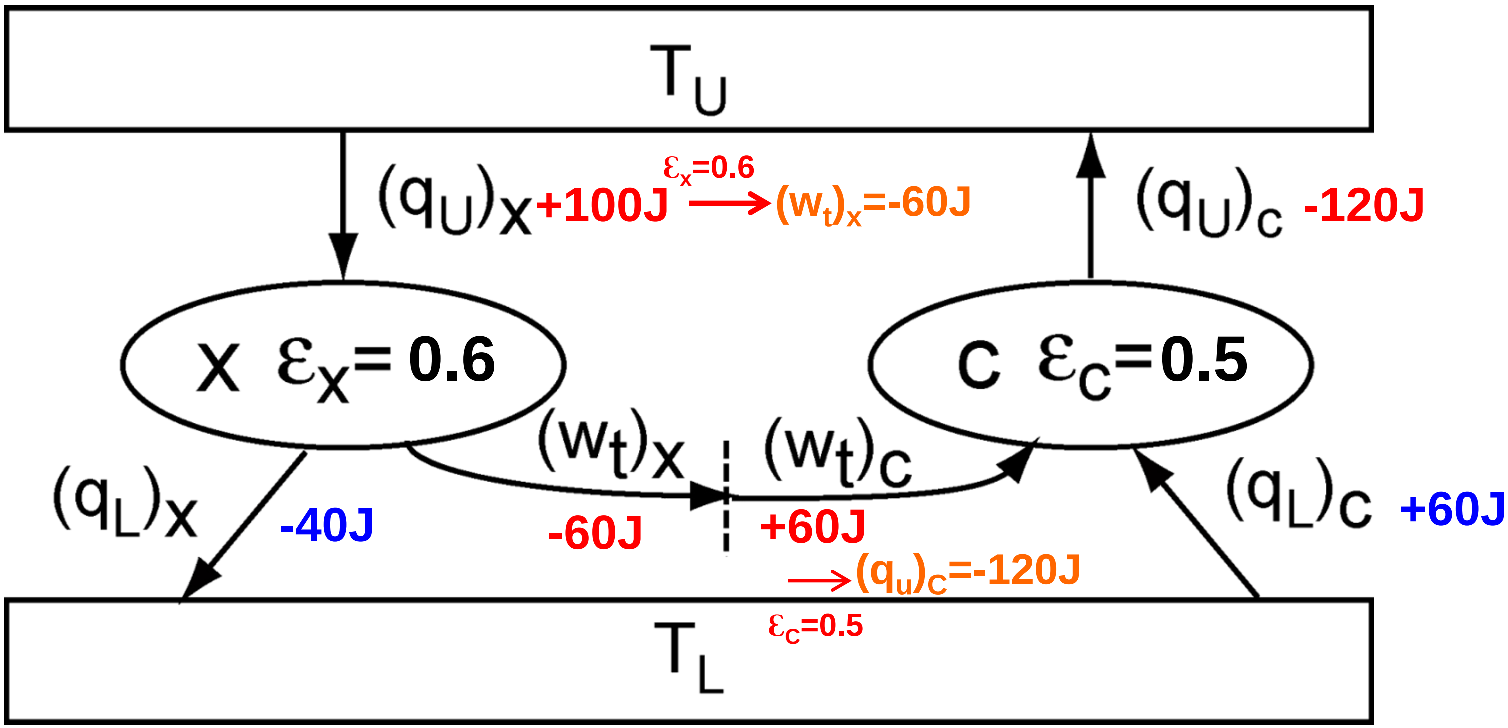


the machine X operates as a Carnot engine doing work, while the machine C operates as a reverse Carnot ideal gas engine acting as a heat pump.

The work **done by X**, $(w_t)_x$ is **used by C:**

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

?? $\varepsilon_x > \varepsilon_{Carnot}$: worksheet for **numerical example** (all w_x goes into w_C)



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

$$w_t = -\, q_U\, \varepsilon$$

w_{total}=0

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

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

Clausius Statement of Second Law *(numerical example)*

we assumed an $\varepsilon_x > \varepsilon_C$ for ideal gas Carnot and calculated

w_{total}=0

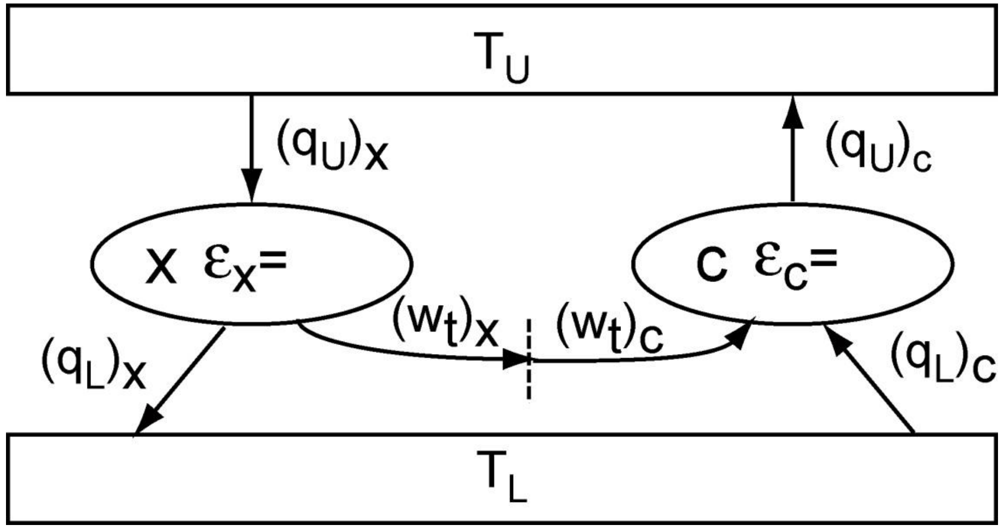
$(q_L)_{total}$=+20J (into 'combo engine' out of cold reservoir at T_{lower})

$(q_U)_{total}$=-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*

if second law holds $\varepsilon_x > \varepsilon_c$ cannot be true

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



$$(q_U)_x > 0 \qquad (q_U)_c < 0$$

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

$$(w_t)_x = -(q_U)_x \varepsilon_x \qquad (w_t)_x = (q_U)_c \varepsilon_c$$

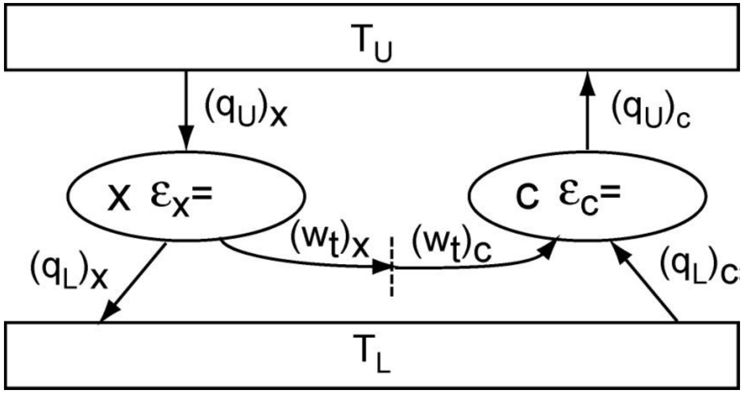
$$(q_L)_x + (q_U)_x + (w_t)_x = 0 \qquad (q_L)_c + (q_U)_c + (w_t)_c = 0$$

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 $\varepsilon_x > \varepsilon_c$

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

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

so what's the problem ???

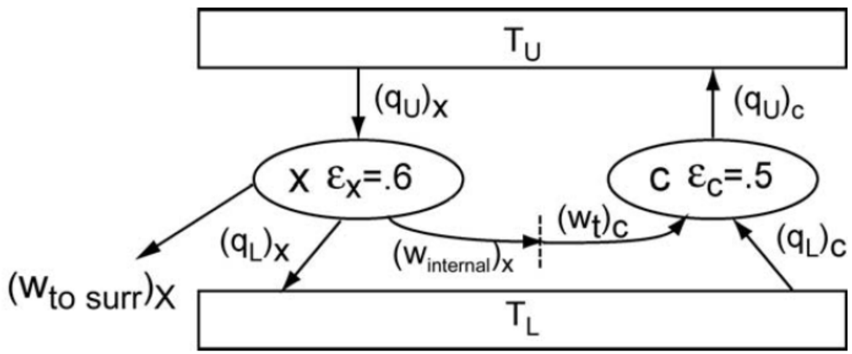
q transferred $T_L \rightarrow T_U$ with no net work
violates Clausius statement of second law

so what's the solution ???

$\varepsilon_x > \varepsilon_c$ is not a condition consistent with the Second Law

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 ε_X = 0.6 and ε_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. $(q_L)_C$

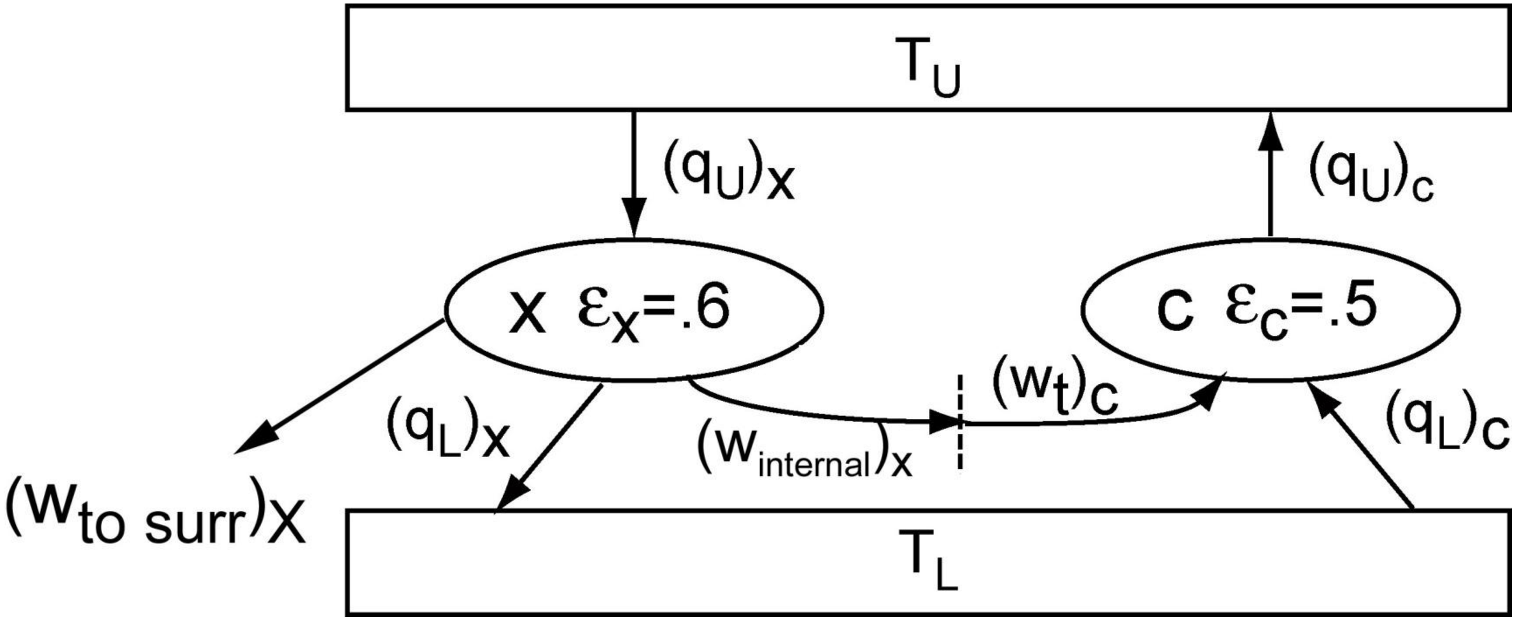
c. $(q_U)_{total} = (q_U)_X + (q_U)_C$

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 ε_X = 0.6 and ε_C=0.5 violate one of the statements of the Second Law of Thermodynamics

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



$(q_U)_x = 100\text{J} \xrightarrow{\varepsilon_x = 0.6} (w_{total})_x = -60\text{J}$

$(w_{total})_c = +40\text{J} \xrightarrow{\varepsilon_c = 0.5} (q_U)_c = -80\text{J}$

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

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)

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

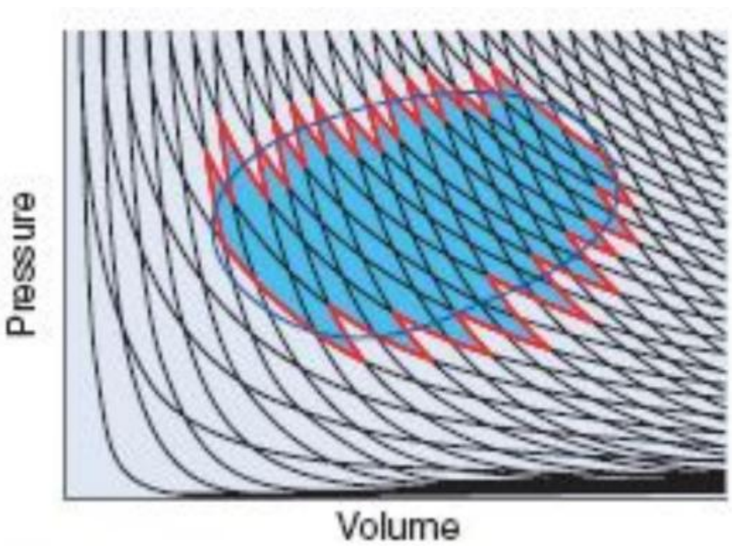
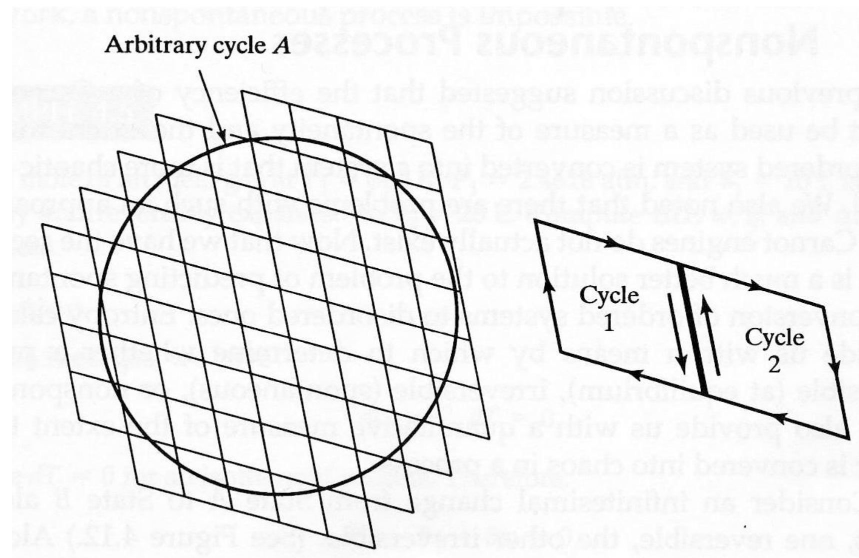


FIGURE 5.4

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 ε and entropy

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

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

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

now *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: $$dS \equiv \frac{đq_{reversible}}{T}$$

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

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

$$q_U + q_L \neq 0 \quad (\text{đ}q \text{ inexact differential})$$

but

$$\frac{q_U}{T_U} + \frac{q_L}{T_L} = 0 \quad (\textit{something special about } \frac{\text{đ}q_{rev}}{T})$$

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

(more to come)