Chemistry 163B Winter 2012
Refrigerators and Generalization of Carnot Cycle

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

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statements of the Second Law of Thermodynamics

1. Macroscopic properties of an <u>isolated system</u> 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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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

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

   but

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

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 $\varepsilon_{\text{ideal gas rev Carnot}} = \varepsilon_{\text{any other rev Carnot}}$
- $dS \equiv \dfrac{\text{đ}q_{reversible}}{T} \quad \oint dS = \oint \dfrac{\text{đ}q_{reversible}}{T} = 0$ and S is STATE FUNCTION

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

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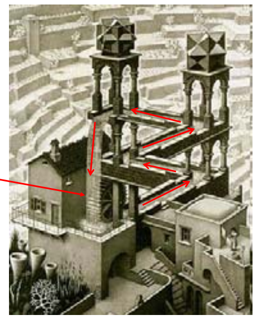
perpetual motion of the first kind (produce work with no heat input)
Escher "Waterfall"

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

no energy input

work on surroundings

VIOLATES 1st LAW



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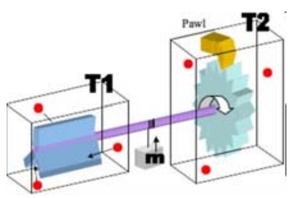
perpetual motion of the second kind (produce work extracting heat from cooler source to run machine at warmer temperature)

Brownian Ratchet



get work only if T1 > T2

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

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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 expansion against constant P_{ext})**

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

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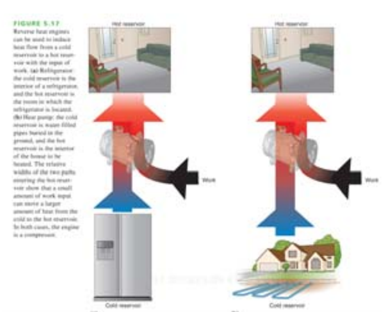
heat pumps and refrigerators (fig. 5.17 E&R) $_{3rd}$



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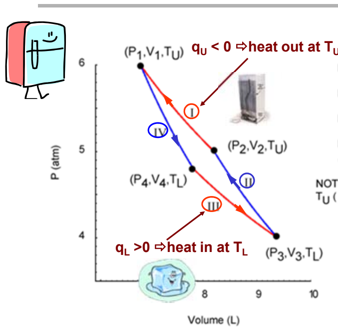
reverse Carnot cycle: a refrigerator



$w_{sys} = -w_{surr} > 0$
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, $q_{2\to3}$ = 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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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	$-n\bar{C}_V(T_U - T_L)$	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	$-n\bar{C}_V(T_L - T_U)$	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		$w_{total}=w_I+w_{II}+w_{III}+w_{IV}= +nR(T_U - T_L)\ln\frac{P_1}{P_2}$	$\lvert q_{out}\rvert = -q_{surr\_III}$ $+nRT_L \ln\frac{P_1}{P_2}$	$\eta_r = C_R = \frac{-q_{surr\_III}}{w_{sys\,total}} = \frac{T_L}{T_U - T_L}$ eqn 5.45 E&R

Coefficient of performance of refrigerator:

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

E&R eqn 5.45

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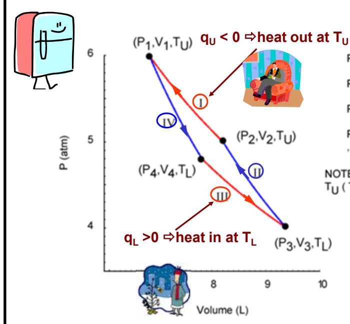
reverse Carnot cycle: a heat pump



$w_{sys}=-w_{surr} > 0$
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, $q_{2\rightarrow3}$ = 0, $T_3=T_L$

P_4=4.8 atm, $T_4=T_L$, $q_{4\rightarrow1}$= 0

NOTE:
T_U (T *upper*) $\equiv T_H$ (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 $\varepsilon=-w_{total}/q_I = (T_U-T_L)/T_U$ 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 ($heat_{in\ at\ TL}/work_{total}$)

$$\eta_r \equiv C_R = \frac{-q_{from\ freezer}}{w_{total}} = \frac{q_{III}}{w_{total}} = \frac{T_L}{T_U - T_L} \qquad \text{E\&R eqn 5.45}$$

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

$$\eta_{hp} \equiv C_{HP} = \frac{q_{given\ off\ to\ room}}{w_{total}} = \frac{-q_I}{w_{total}} = \frac{T_U}{T_U - T_L} \qquad \text{E\&R eqn 5.44}$$

(> 1)

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one more important FACTOID about Carnot machine

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:

$$\oint_{cycle} \frac{đq_{rev}}{T}$$

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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 ???

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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 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.**

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Carnot machine

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

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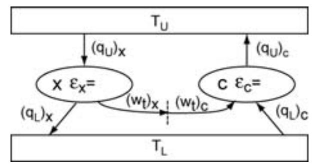
can $\varepsilon_x > \varepsilon_c$ for any Carnot machine X vs ideal gas Carnot machine C ???



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

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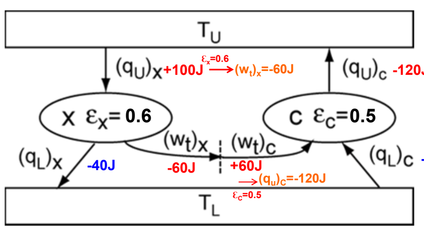
*?? $\varepsilon_x > \varepsilon_{Carnot}$: worksheet for **numerical example** (all w_x goes into w_C)*



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

$w_{total}=0$

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

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

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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

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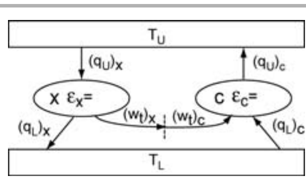
***general proof:** can $\varepsilon_x > \varepsilon_c$ for Carnot machine X vs ideal gas Carnot machine C ???*



$(q_U)_x > 0$

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

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

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

$(q_U)_c < 0$

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

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

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

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

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

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

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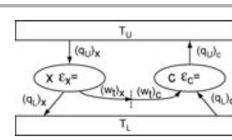
***general proof:** can $\varepsilon_x > \varepsilon_c$ for Carnot machine X vs ideal gas Carnot machine C ???*



So $(q_U)_{total} < 0$
and
$(q_L)_{total} = -(q_U)_{total} > 0$
with $w_{total}=(w_t)_x + (w_t)_c=0$

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

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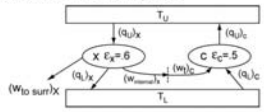
HW#4 Prob. 23

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, $(w_i)_c = +40J$, 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. $w_{total} = (w_{surr})_x + (w_i)_x + (w_i)_c$
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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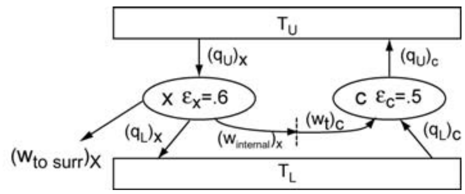
setup for (HW prob #23) ε_x efficiency greater than Carnot



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

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

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

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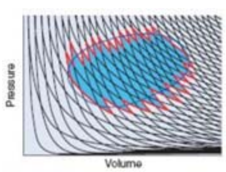
generalization to arbitrary cycle (E&R Fig. 5.4, Raff Fig. 4.11)



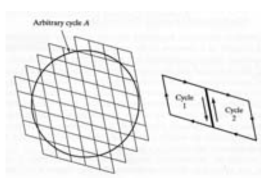


FIGURE 5.4
An arbitrary reversible cycle, indicated by the ellipse, can be approximated to any desired accuracy by a sequence of alternating adiabatic and isothermal segments.

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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

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

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

(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

$$q_U + q_L \neq 0 \quad (đq \textit{ inexact differential})$$

but

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

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

(more to come)

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