Chemistry 163B Refrigerators and Generalization of Ideal Gas Carnot

(four steps to exactitude) E&R pp 86-91, 109-111 Raff pp. 159-164

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statements of the Second Law of Thermodynamics

- 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]
- 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
- 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
- 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 <code>[reversible]</code> cycle efficiency of heat \rightarrow 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

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

6. S, entropy and spontaneous changes

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goals for lecture[s]

- Carnot in reverse: refrigerators and heat pumps
- Show that $\epsilon_{\text{ideal gas rev Carnot}} \geq \epsilon_{\text{any other machine}}$ otherwise one of the phenomenological statements violated
- Not only for ideal gas but $\epsilon_{\mbox{\tiny ideal gas rev Carnot}}\!=\;\epsilon_{\mbox{\tiny any other rev Carnot}}$
- $dS \equiv \frac{dq_{reversible}}{T}$ $\oint dS = \oint \frac{dq_{reversible}}{T} = 0$ and S is STATE FUNCTION

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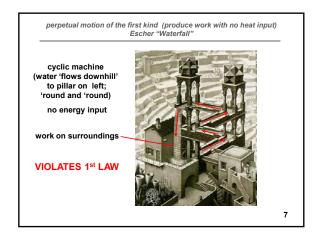
ENGINE	q	West	Waun	
I. isothermal expansion	$+nRT_v \ln \frac{P_v}{P_z}$ 1.3	$-nRT_{z} \ln \frac{P_{z}}{P_{z}}$ 1.2	$+ nR T_v \ln \frac{P_v}{P_v}$	heat in at T _H work out
II adiabatic expansion	0	$n\overline{C_V}(T_L-T_V)$ 2.4	$-n\overline{C_{_{\mathrm{F}}}}(T_{_{\downarrow}}-T_{_{\mathrm{F}}})$	work out
III. isothermal compression	$\begin{split} nR \; T_{\scriptscriptstyle L} \; & \ln \frac{P_{\scriptscriptstyle L}}{P_{\scriptscriptstyle L}} = \\ -nR \; T_{\scriptscriptstyle L} \; & \ln \frac{P_{\scriptscriptstyle L}}{P_{\scriptscriptstyle L}} \end{split}$	$\begin{split} &-nRT_{\pm}\ln\frac{P_{\pm}}{P_{\pm}}\\ &=nRT_{\pm}\ln\frac{P_{\pm}}{P_{\pm}}\\ \end{split}$	$-nRT_{\perp}\ln\frac{P_{\rm t}}{P_{\rm b}}$	heat lost at T work in
IV. adiabatic compression	0	$n\overline{C_V}(T_{\Gamma}-T_L)$ 4.4	$-n\overline{C_v}(T_v - T_k)$	work in
net gain/cost	$\begin{aligned} \mathbf{q}_{\mathrm{in}} &\equiv \mathbf{q}_{\mathrm{l}} \\ &+ nR \; T_{\mathrm{p}} \; \ln \frac{P_{\mathrm{s}}}{P_{\mathrm{s}}} \end{aligned}$		$w_{\text{total}} = w_i + w_{ii} + w_{ii} + w_{N} = nR(T_v - T_L) \ln \frac{P_i}{P_v}$	$\varepsilon = w_{sum}/q_m$ $\varepsilon = (T_U - T_L)/T_m$

remember Carnot engine

· does net work on surroundings

and

• net heat $\mathbf{q}_{\mathrm{U(I)}}$ + $\mathbf{q}_{\mathrm{L(III)}}$ = - $\mathbf{w}_{\mathrm{total}}$



• does net work on surroundings but • extracts heat from surroundings at T $q_{U(I)} < 0$ • gives off heat to surroundings at T $q_{L(III)} > 0$

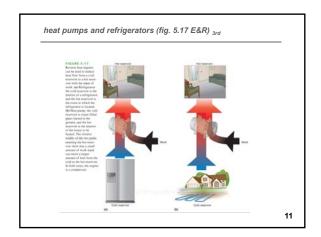
perpetual motion of the second kind (produce work extracting heat from cooler source to run machine at warmer temperature)

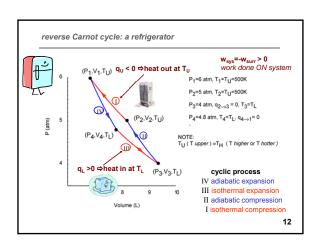
Brownian Ratchet

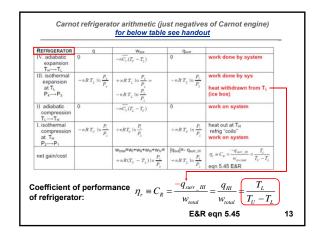
Pawline Trouble Trouble

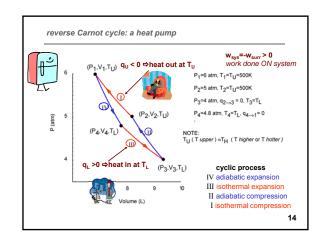
refrigerators and heat pumps: running the Carnot cycle in REVERSE

- 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









"goodness of performance"

Since refrigerators and heat pumps are just Carnot machines in reverse, the relationship for $\mathcal{E}=w_{total}/q_1=(T_U^T T_U^T T_U$ 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 $_{\rm in~at~TL}/{\rm work}_{\rm total})$

$$\eta_r \equiv C_R = \frac{-q_{from freezer}}{w_{total}} = \frac{q_{III}}{w_{total}} = \frac{T_L}{T_U - T_L}$$
E&R eqn 5.45
$$HW#6 P28 (E&RP5.33)$$

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

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

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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:

$$\oint_{cycle} \frac{d\overline{q}_{rev}}{T}$$

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one more important FACTOID about Carnot machine

$$\int_{II}^{\underline{d}\underline{q}_{rev}} \frac{aRT_v \ln \frac{P_1}{P_2}}{T_v} = 0 \text{ (adiabatic)}$$

$$\int_{II}^{\underline{d}\underline{q}_{rev}} \frac{dq_{rev}}{T} = 0 \text{ (adiabatic)}$$

$$\int_{III}^{\underline{d}\underline{q}_{rev}} \frac{dq_{rev}}{T} = \frac{-nRT_v \ln \frac{P_1}{P_2}}{T_v}$$

$$\int_{III}^{\underline{d}\underline{q}_{rev}} \frac{dq_{rev}}{T} = 0 \text{ (adiabatic)}$$

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

$$\Delta S = \int \! dS = \int \! \frac{dq_{\rm rev}}{T}$$
 does it just apply to ideal gas Carnot cycle ???

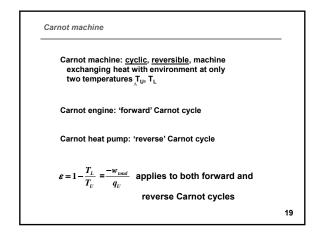
Generalization of Ideal Gas Carnot Cycle

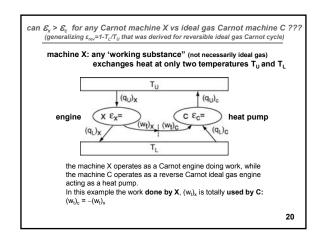
1. Our work on the (reversible) Carnot Cycle using an ideal gas as the 'working substance" lead to the relationship

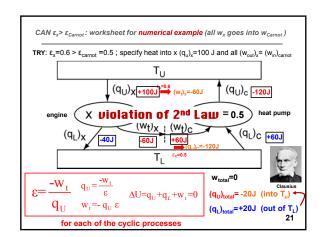
$$\epsilon = \frac{-w_{total}}{q_U} = \frac{T_U - T_L}{T_U}$$

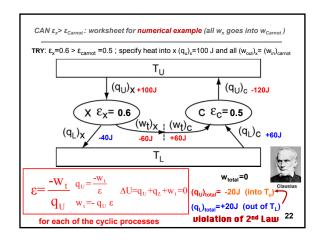
However, the second law applies to machines with any 'working substance' and general cycles.

- 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 $\mathcal{G}_{rev\ any\ ws} = \mathcal{E}_{carnot\ ideal\ gas}$
- One can also show (E&R Fig 5.4, Raff 162-164) that any Carnot machine has ∮ dq_{rev}/T =0 and that any reversible machine cycle can be expressed as a sum of Carnot cycles.

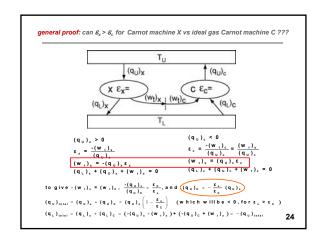


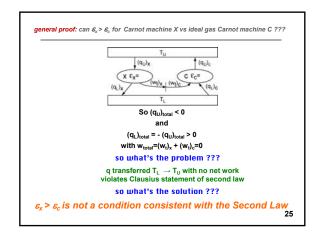


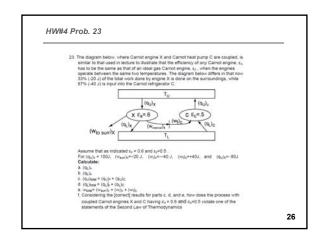


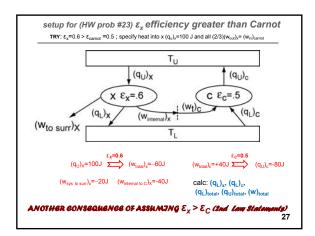


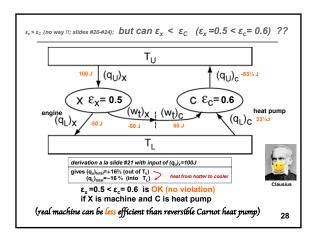
We assumed an $\epsilon_{\rm x} > \epsilon_{\rm c}$ for ideal gas Carnot and calculated ${\rm w_{total}} = 0$ $({\rm q_L})_{\rm total} = +20 {\rm J} \quad ({\rm into 'combo \ engine'} \quad {\rm out \ of \ cold\ reservoir \ at \ T_{lower}})$ $({\rm q_U})_{\rm total} = -20 {\rm J} \quad ({\rm out \ of 'combo \ engine'} \quad {\rm into \ heat \ reservoir \ at \ T_{upper}})$ ${\rm BUT: \ It \ is \ impossible \ to \ have \ a \ natural \ process} \quad {\rm which \ produces \ no \ other \ effect \ than \ absorption \ of \ heat \ from \ a \ colder \ body \ and \ discharge \ of \ heat \ to \ a \ warmer \ body. \ {\it Clausius's \ Statement}$ ${\it if \ second \ law \ holds \ \epsilon_{\rm x} > \epsilon_{\rm c} \ cannot \ be \ true}$

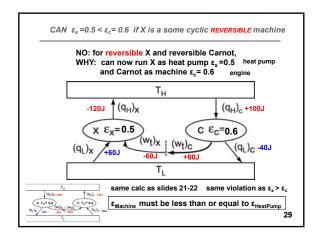


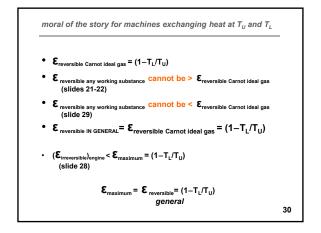


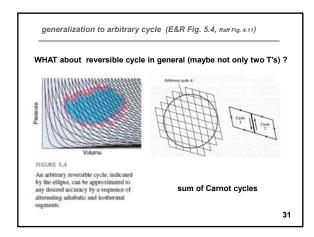


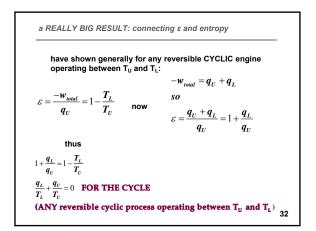












so generally for this reversible cycle $DEFINE: \qquad dS \equiv \frac{dq_{reversible}}{T}$ $\oint dS = \oint \frac{dq_{reversible}}{T} = 0$ and S is STATE FUNCTION

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)

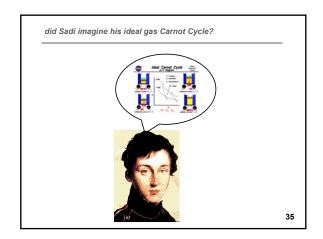
✓ 5. Show that for this REVERSIBLE cycle

q_v + q_L ≠ 0 (āq inexact differential)

but

q_v + q_L = 0 (something special about dq_r / T)

✓ 6. STATE FUNCTION S, entropy and spontaneous changes (more to come)



Againe, Periogil, June 11-13, 2008

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

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

4 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 T_0 , and at the temperature of that body, compressing it in such a way as to make it scapier the temperature of the body T_0 , finally condeming 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 fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of the caloric."
[1], i.e.:

$$\begin{split} W &= W_{neOUT} = Q_{IN} \cdot f_e(T_H, T_L) \\ \eta_{Cl} &= \frac{W_{neOUT}}{Q_{IN}} \bigg|_{Mass} = \frac{f_e(T_H, T_L)}{Q_{oullature Annihilation}} \bigg|_{Rev.} \end{split} \tag{1}$$

