Chemistry 163B
Lecture 09

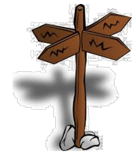
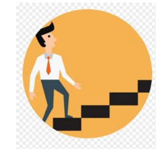
Carnot Arithmetic

Challenged Penmanship

Notes

see handout: Carnot Arithmetic

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

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

but

$$\frac{q_U}{T_U} + \frac{q_L}{T_L} = 0 \quad (\textit{something } \textbf{VERY VERY special about } \frac{\text{đq}_{rev}}{T}; \quad \oint \frac{\text{đq}_{rev}}{T} = !!!)$$

6. S, entropy and spontaneous changes

from lecture on 2nd Law and probability (disorder)

- Disorder, **W**, did not change during an adiabatic reversible expansion (q_{rev} =0)
- Disorder, **W**, increased in isothermal reversible expansion (q_{rev} >0)
- Disorder, **W**, increased with T increase ($q>0$)
- Disorder, **W**, decreased with T decrease ($q<0$)
- As $T \rightarrow 0$, $\mathbf{W} \rightarrow 1$

statements of the Second Law of Thermodynamics (roadmap #1)

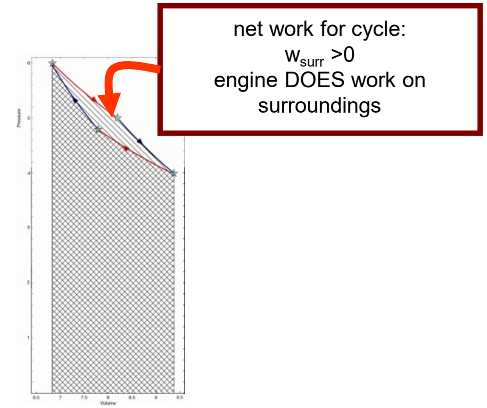
1. Macroscopic properties of an isolated system eventually assume constant values (e.g. pressure in two bulbs of gas becomes constant; two block of metal reach same T) [*Andrews. p37]*

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*

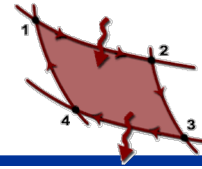
4. In the neighborhood of any prescribed initial state there are states which cannot be reached by any adiabatic process
   ~ *Caratheodory's statement [Andrews p. 58]*

goals of Carnot arithmetic (step 2 of roadmap)



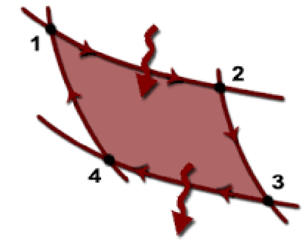
1. Carnot cycle is "engine" that produces work from heat
2. Define efficiency:
   efficiency=(**net work** done **by** machine)/(**heat** energy **input** to machine)
3. Today, arithmetic manipulations of 1st Law results from ideal gas Carnot cycle (HW2 #10) to show that this efficiency depends only on the two temperatures at which heat is transferred to and from surroundings (the T_U of step 1 and T_L of step 3; the non-adiabatic paths)
4. Although for [reversible] Carnot cycle $\oint đq_{rev} \overset{\text{WILL}}{\neq} 0$ but $\oint \frac{đq_{rev}}{T} \overset{\text{WILL}}{=} 0$

from Carnot cycle



https://www.learnthermo.com/T1-tutorial/ch09/lesson-A/pg03.php

for system in complete cycle:
$\Delta U=0$; $q>0$; $w<0$ (work DONE on surr) **(Prob #10e)**



$q > 0$ (q_{in}) at higher T_H; $q < 0$ (q_{out}) at lower T_L

efficiency= $-w/q_{1\rightarrow 2}$
(how much total [net] **work out** (-sign) for **heat in** $1\rightarrow 2$)

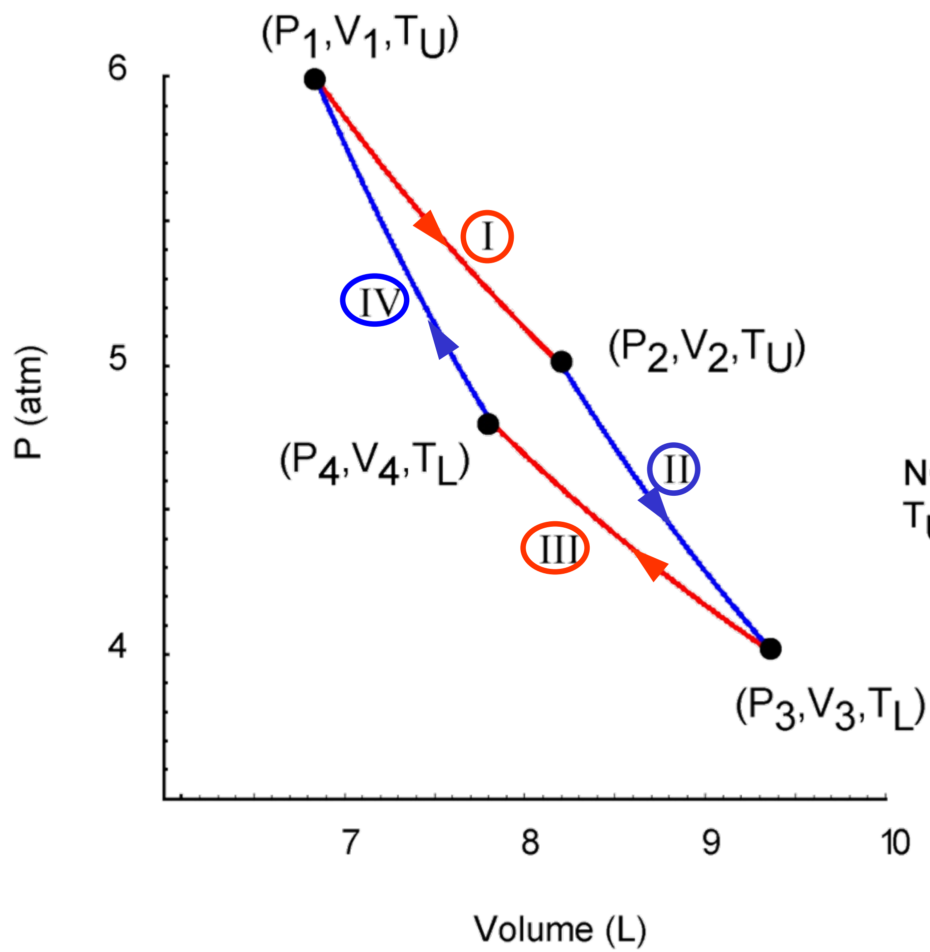
efficiency will depend on T_U and T_L

HW4 prob #22 ε is εfficiency

$$\varepsilon = \frac{T_H - T_C}{T_H} \quad or \quad \varepsilon = \frac{T_U - T_L}{T_U}$$

H=HOT C=COLD or U=UPPER L=LOWER

Problem HW2 #10 ***(see handout "Carnot Cycle Arithmetic)***



in prob #10

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

I isothermal expansion

II adiabatic expansion

III isothermal compression

IV adiabatic compression

- get $w_{I} + w_{II} + w_{III} + w_{IV} = w_{total}$
- get $q_{I} = q_{input}$

Summary

(see handout "Summary of Heat and Work for the Carnot Cycle Engines, Refrigerators, Heat Pumps")

general expressions for $(P_1,T_U) \xrightarrow{I} (P_2,T_U) \xrightarrow{II} (P_3,T_L) \xrightarrow{III} (P_4,T_L) \xrightarrow{IV} (P_1,T_U)$

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

Step I Isothermal expansion, T_U, $V_1 \rightarrow V_2$:

$$\Delta U_I = 0 \qquad (1.1)$$

$$w_I = -nRT_U \ln\frac{V_2}{V_1} = nRT_U \ln\frac{P_2}{P_1} \qquad (1.2)$$

$$q_I = -w_I = nRT_U \ln\frac{V_2}{V_1} = nRT_U \ln\frac{P_1}{P_2} \qquad (1.3)$$

step II: adiabatic reversible compression $T_U \rightarrow T_L$

$$V_3 = V_2 \left(\frac{T_U}{T_L}\right)^{\frac{\overline{C_V}}{R}} \qquad V_3 = V_2 \left(\frac{P_2}{P_3}\right)^{\frac{\overline{C_V}}{\overline{C_P}}} \qquad (2.1)$$

$$T_L = T_U \left(\frac{V_2}{V_3}\right)^{\frac{R}{\overline{C_V}}} \qquad T_L = T_U \left(\frac{P_3}{P_2}\right)^{\frac{R}{\overline{C_P}}} \qquad (2.2)$$

$$P_3 = P_2 \left(\frac{V_3}{V_2}\right)^{\frac{\overline{C_P}}{\overline{C_V}}} \qquad P_3 = P_2 \left(\frac{T_L}{T_U}\right)^{\frac{\overline{C_P}}{R}} \qquad (2.3)$$

P,V,T relationships
for adiabatic reversible
process

$$q_{II} = 0; \qquad w_{II} = \Delta U \qquad (2.4)$$

$$\Delta U_{II} = n\overline{C_V}\Delta T = n\overline{C_V}(T_L - T_U)$$

$$w_{II} = \Delta U_{II} = n\overline{C_V}T_U\left(\left(\frac{V_2}{V_3}\right)^{\frac{R}{\overline{C_V}}} - 1\right) = n\overline{C_V}T_U\left(\left(\frac{P_3}{P_2}\right)^{\frac{R}{\overline{C_P}}} - 1\right) \qquad (2.5)$$

Step III: isothermal reversible compression at T_L

$$\Delta U_{III} = 0 \tag{3.1}$$

$$w_{III} = -nRT_L \ln\frac{V_4}{V_3} = nRT_L \ln\frac{P_4}{P_3} \tag{3.2}$$

$$q_{III} = -w_{III} = nRT_L \ln\frac{V_4}{V_3} = nRT_L \ln\frac{P_3}{P_4} \tag{3.3}$$

Step IV: adiabatic reversible compression ($T_L \rightarrow T_U$)

$$V_4 = V_1 \left(\frac{T_U}{T_L}\right)^{\frac{\overline{C_V}}{R}} \qquad V_4 = V_1 \left(\frac{P_1}{P_4}\right)^{\frac{\overline{C_V}}{\overline{C_P}}} \qquad (4.1)$$

$$T_L = T_U \left(\frac{V_1}{V_4}\right)^{\frac{R}{\overline{C_V}}} \qquad T_L = T_U \left(\frac{P_4}{P_1}\right)^{\frac{R}{\overline{C_P}}} \qquad (4.2)$$

$$P_4 = P_1 \left(\frac{V_1}{V_4}\right)^{\frac{\overline{C_P}}{\overline{C_V}}} \qquad P_4 = P_1 \left(\frac{T_L}{T_U}\right)^{\frac{\overline{C_P}}{R}} \qquad (4.3)$$

P,V,T relationships for adiabatic reversible process

$$q_{IV} = 0; \qquad w_{IV} = \Delta U_{IV} \qquad (4.4)$$

$$\Delta U_{IV} = n\overline{C_V}\Delta T = n\overline{C_V}(T_U - T_L)$$

$$w_{IV} = \Delta U_{IV} = n\overline{C_V}T_U \left(1 - \left(\frac{V_1}{V_4}\right)^{\frac{R}{\overline{C_V}}}\right) = n\overline{C_V}T_U \left(1 - \left(\frac{P_4}{P_1}\right)^{\frac{R}{\overline{C_P}}}\right) \qquad (4.5)$$

note: w_{IV}=–w_{II} *the two adiabatic steps have opposite work out ↔ work in*

$$\Delta U_{II} = n\overline{C_V}(T_L - T_U) = w_{II} \quad \longleftrightarrow \quad w_{IV} = n\overline{C_V}(T_U - T_L) = \Delta U_{IV}$$

$$w_{II} = n\overline{C_V}T_U\left(\left(\frac{P_3}{P_2}\right)^{\frac{R}{\overline{\overline{C_P}}}} - 1\right) = n\overline{C_V}T_U\left(\left(\frac{4}{5}\right)^{\frac{R}{\overline{\overline{C_P}}}} - 1\right) = n\overline{C_V}T_U\left((.8)^{\frac{R}{\overline{\overline{C_P}}}} - 1\right)$$

$$\updownarrow \qquad\qquad\qquad\qquad \updownarrow$$

$$w_{IV} = n\overline{C_V}T_U\left(1 - \left(\frac{P_4}{P_1}\right)^{\frac{R}{\overline{\overline{C_P}}}}\right) = n\overline{C_V}T_U\left(1 - \left(\frac{4.8}{6}\right)^{\frac{R}{\overline{\overline{C_P}}}}\right) = n\overline{C_V}T_U\left(1 - (.8)^{\frac{R}{\overline{\overline{C_P}}}}\right)$$

and now for the TOTAL cycle (T_U and T_L; and P_1 and P_2 given)

$w_{total} = w_I + w_{II} + w_{III} + w_{IV}$

$w_{II} = -w_{IV} \Rightarrow w_{total} = w_I + w_{III}$

$$w_I = nRT_U \ln\frac{P_2}{P_1}$$

$$w_{III} = nRT_L \ln\frac{P_4}{P_3} \quad with \quad P_3 = P_2\left(\frac{T_L}{T_U}\right)^{\frac{\bar{C}_P}{R}} \quad and \ P_4 = P_1\left(\frac{T_L}{T_U}\right)^{\frac{\bar{C}_P}{R}}$$

$$w_{III} = nRT_L \ln\left(\frac{P_1\left(\frac{T_L}{T_U}\right)^{\frac{\bar{C}_P}{R}}}{P_2\left(\frac{T_L}{T_U}\right)^{\frac{\bar{C}_P}{R}}}\right) = nRT_L \ln\left(\frac{P_1}{P_2}\right) = -nRT_L \ln\left(\frac{P_2}{P_1}\right)$$

$$w_{total} = nR\left(T_U - T_L\right)\ln\frac{P_2}{P_1}$$

and NOW EFFICIENCY ε

efficiency: $\varepsilon = \dfrac{\text{(total work done ON SURROUNDINGS)}}{\text{(heat INPUT)}}$

only $q_I \equiv q_{UPPER}$

q_{III} is wasted heat lost to surroundings at T_L as thermal pollution

$$\varepsilon = \frac{-w_{total}}{q_I}$$

$$w_{total} = nR\left(T_U - T_L\right)\ln\frac{P_2}{P_1}$$

$$q_I = -w_I = nRT_U \ln\frac{P_1}{P_2} = -nRT_U \ln\frac{P_2}{P_1}$$

and

$$\varepsilon = \frac{-nR\left(T_U - T_L\right)\ln\frac{P_2}{P_1}}{-nRT_U \ln\frac{P_2}{P_1}}$$

$$\varepsilon = \frac{\left(T_U - T_L\right)}{T_U} = 1 - \frac{T_L}{T_U}$$

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some limits on efficiency of ideal engine

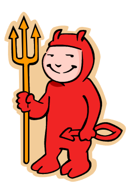
$$\varepsilon = \frac{(T_U - T_L)}{T_U} = 1 - \frac{T_L}{T_U}$$

$$\lim_{T_L \to T_U} \varepsilon = \mathbf{0}$$

must have q in at higher and q out at lower T

$$\lim_{T_L \to 0} \varepsilon =$$

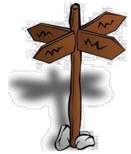
or **1**

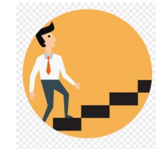


$$\lim_{T_U \to \infty} \varepsilon =$$

perfect efficiency at finite temperatures only for T_{LOWER} = 0 K

roadmap for second law



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

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but

$$\frac{q_U}{T_U} + \frac{q_L}{T_L} = 0 \quad \left(\textit{something}\ \textbf{VERY VERY special about } \frac{\text{đq}_{rev}}{T}; \quad \oint \frac{\text{đq}_{rev}}{T} = !!!\right)$$

6. S, entropy and spontaneous changes

End of Lecture 9

Two bodies 500 molecules each
one at $T_A = .63 \times T_f$,
the other at $T_B = 1.37 \times T_f$

$.63\ T_f$	$1.37\ T_f$

~ microstates
$\approx 10^{556}$
$= 10^{202} \times 10^{354}$

(relative)
ORDER

bring into thermal contact

STAY COLD-HOT ??

spontaneous

or

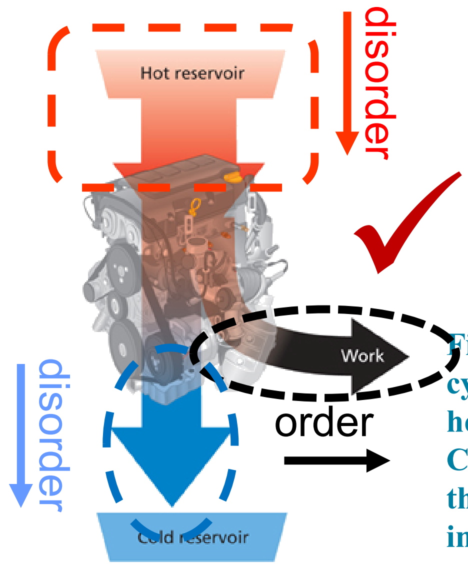
EQUILIBRIUM ??

$T_E = T_f$

(relative)
DISORDER

$\approx 10^{594}$

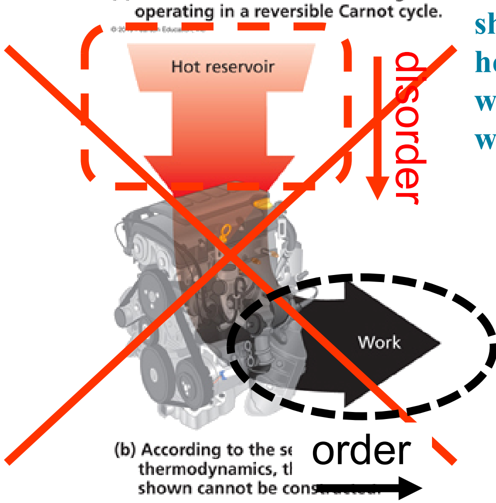
E&R$_{4th}$ fig 5.14 p. 127 *[fig 5.3, p. 89]$_{E\&R3rd}$*



(a) Schematic model of the heat engine operating in a reversible Carnot cycle.

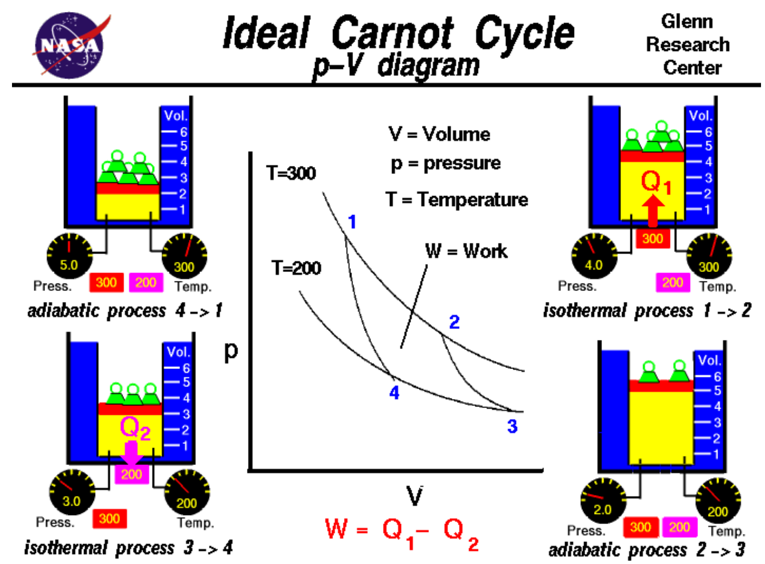
These considerations on the efficiency of reversible heat engines led to the Kelvin–Planck formulation of the **second law of thermodynamics:**

> It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equal amount of work by the system on the surroundings.



(b) According to the se... thermodynamics, tl... shown cannot be cons...

Figure 5.14 Carnot heat engine cycle. (a) A schematic model of a heat engine operating in a reversible Carnot cycle. (b) The second law of thermodynamics asserts that it is impossible to construct a heat engine as shown that operates using a single heat reservoir and converts the heat withdrawn from the reservoir into work with 100% efficiency as shown



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Two bodies 500 molecules each
one at $T_A = .63 \times T_f$,
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$.63\ T_f$	$1.37\ T_f$

$\approx 10^{556} = 10^{202} \times 10^{354}$

(relative)
ORDER

(keep) transferring heat from colder body to warmer body

will not occur spontaneously (requires work a la refrigerator)

Two bodies 500 molecules each at T_f,

$T_E = T_f$

(relative)
DISORDER
$\approx 10^{594}$