Chemistry 163B Winter 2014
notes for Carnot Arithmetic and Efficiency

Chemistry 163B

Carnot Arithmetic

Challenged Penmanship

Notes

see handout: Carnot Arithmetic

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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. S, entropy and spontaneous changes

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from lecture on 2nd Law and probability (disorder)

(*something special about* $\frac{đq_{rev}}{T}$)

- 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 → 0, **W** →1

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

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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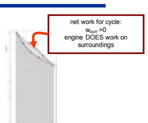
goals of Carnot arithmetic (step 2 of roadmap)



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 $\oint đq_{rev} \neq 0$

   $\oint \frac{đq_{rev}}{T} \overset{WILL}{=} 0$

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from Carnot cycle

for system in complete cycle:
ΔU=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= $-w/q_{1\to 2}$
(how much net **work out** (-sign) for **heat in** 1→2)

efficiency will depend on T_U and T_L

HW5 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

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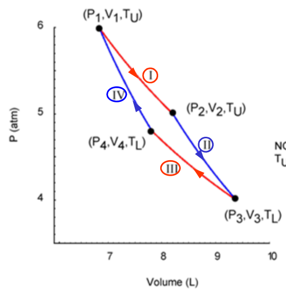
Problem HW2 #10 (see handout "Carnot Cycle Arithmetic)



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

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let's go

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

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

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

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isothermal expansion at T_U (see handout "Carnot Cycle Arithmetic)

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

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

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

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

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

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

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

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

P,V,T relationships for adiabatic reversible process

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

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

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

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Step III: isothermal reversible compression at T_L

$$\Delta U_{III} = 0 \qquad (3.1)$$

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

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

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

$$V_4 = V_1\left(\frac{T_U}{T_L}\right)^{\frac{\bar{C}_V}{R}} \qquad V_4 = V_1\left(\frac{P_1}{P_4}\right)^{\frac{\bar{C}_V}{\bar{C}_P}} \qquad (4.1)$$

$$T_L = T_U\left(\frac{V_1}{V_4}\right)^{\frac{R}{\bar{C}_V}} \qquad T_L = T_U\left(\frac{P_4}{P_1}\right)^{\frac{R}{\bar{C}_P}} \qquad (4.2)$$

P,V,T relationships for adiabatic reversible process

$$P_4 = P_1\left(\frac{V_1}{V_4}\right)^{\frac{\bar{C}_P}{\bar{C}_V}} \qquad P_4 = P_1\left(\frac{T_L}{T_U}\right)^{\frac{\bar{C}_P}{R}} \qquad (4.3)$$

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

$$\Delta U_{IV} = n\bar{C}_V \Delta T = n\bar{C}_V (T_U - T_L)$$

$$w_{IV} = \Delta U_{IV} = n\bar{C}_V T_U\left[1-\left(\frac{V_1}{V_4}\right)^{\frac{R}{\bar{C}_V}}\right] = n\bar{C}_V T_U\left[1-\left(\frac{P_4}{P_1}\right)^{\frac{R}{\bar{C}_P}}\right] \qquad (4.5)$$

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

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

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

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

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

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

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

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and NOW EFFICIENCY ε

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

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

only q_I; q_{III} is wasted heat lost to surroundings as thermal pollution

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

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

and

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

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

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

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
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IV. adiabatic compression	0	$n\bar{C}_V(T_U - T_L)$ 4.4	$-n\bar{C}_V(T_U - T_L)$	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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some limits on efficiency of ideal engine

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

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

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

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take home messages (lecture 8) and statements of 2nd Law (Andrews)

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

.63 T_f	1.37 T_f

~ microstates

≈10^{556}= 10^{202}×10^{354} (relative) **ORDER**

bring into thermal contact

STAY COLD-HOT ??

spontaneous

or

EQUILIBRIUM ??

T_E= T_f

(relative) **DISORDER** ≈10^{594}

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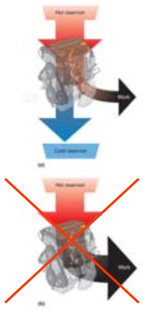
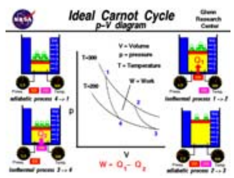
E&R fig 5.3, p. 89



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.

FIGURE 5.3 (a) A schematic model of the heat engine operating in a reversible Carnot cycle. The relative widths of the two paths leaving the hot reservoir show the partitioning between work and heat injected into the cold reservoir. (b) The second law of thermodynamics asserts that it is impossible to construct a heat engine 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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take home messages (lecture 8) and statements of 2nd Law (Clausius)

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

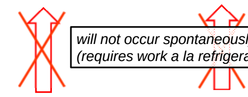
.63 T_f	1.37 T_f

~ microstates

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

(relative) **ORDER**

(keep) transferring heat from warm side to cold side



will not occur spontaneously (requires work a la refrigerator)

$T_E = T_f$

(relative) **DISORDER**

$\approx 10^{594}$

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End of Lecture 9

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