Chemistry 163B Winter 2020
Lecture 9- Carnot Arithmetic and Efficiency

Chemistry 163B
Lecture 09

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 $\oint$ đq $\neq 0$)
   but
   $\frac{q_U}{T_U} + \frac{q_L}{T_L} = 0$ (***something*** **VERY VERY special about** $\frac{đq_{rev}}{T}$; $\oint \frac{đq_{rev}}{T} =$ **!!!**)
6. S, entropy and spontaneous changes

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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 → 0, **W** →1

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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]

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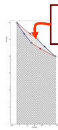
goals of Carnot arithmetic (step 2 of roadmap)



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

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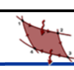
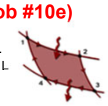
from Carnot cycle



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

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= $-w/q_{1\to2}$
(how much total [net] **work out** (-sign) for **heat in** 1→2)

efficiency will depend on T_U and T_L

HW4 prob #22 ε is εfficiency

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

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

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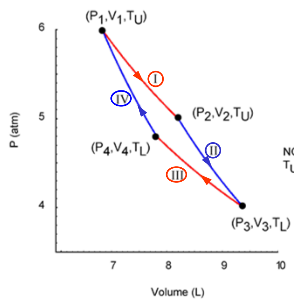
Problem HW2 #10 (see handout "Carnot Cycle Arithmetic)



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

let's go

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

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

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

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

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

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

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

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

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

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

P,V,T relationships for adiabatic reversible process

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

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

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

Step III: isothermal reversible compression at T_L

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

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

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

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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,V,T relationships for adiabatic reversible process

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

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

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

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

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

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

$$w_{II} = n\overline{C}_V T_U\left[\left(\frac{P_3}{P_2}\right)^{\frac{R}{\overline{C}_P}} - 1\right] = n\overline{C}_V T_U\left[\left(\frac{4}{5}\right)^{\frac{R}{\overline{C}_P}} - 1\right] = n\overline{C}_V T_U\left[(.8)^{\frac{R}{\overline{C}_P}} - 1\right]$$

$$w_{IV} = n\overline{C}_V T_U\left[1-\left(\frac{P_4}{P_1}\right)^{\frac{R}{\overline{C}_P}}\right] = n\overline{C}_V T_U\left[1-\left(\frac{4.8}{6}\right)^{\frac{R}{\overline{C}_P}}\right] = n\overline{C}_V T_U\left[1-(.8)^{\frac{R}{\overline{C}_P}}\right]$$

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

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

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

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

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

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

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

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and NOW EFFICIENCY ε

efficiency: ε = (total work done **ON SURROUNDINGS**) / (heat **INPUT**)

only $q_I \equiv q_{UPPER}$
q_{III} is wasted heat lost to surroundings at T_L as thermal pollution

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

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

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

and

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

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

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Summary

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

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

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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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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 $\oint$ đq $\neq 0$)

but

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

6. S, entropy and spontaneous changes

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End of Lecture 9

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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)
Q T F G T

bring into thermal contact

STAY COLD-HOT ??

spontaneous

or

EQUILIBRIUM ??

T_E= T_f

(relative)
DISORDER
≈10^{594}

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

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.

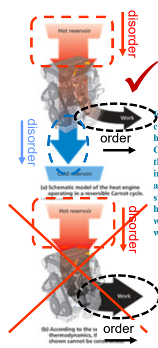
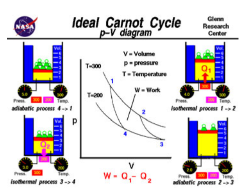


Figure 5.14 Carnot heat engine cycle. (a) A schematic model of a heat engine operating in a reversible Carnot cycle. (b) The second law of thermodynamics asserts that it is impossible to construct a heat engine as shown that operates using a single heat reservoir and converts the heat withdrawn from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



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

~ microstates

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

≈10^{556}=
10^{202}×10^{354}
(relative)
Q T F G T

(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
≈10^{594}

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