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

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

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

*but*

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

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 → 0, **W** →1

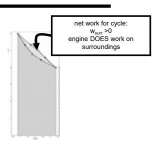


***statements of the Second Law of Thermodynamics (roadmap #1)***

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)***



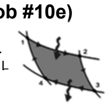

1. Carnot cycle is "engine" that produces work from heat
2. Define efficiency:
efficiency=(**net work** done **by** machine)/(**heat** energy **input** to machine)
3. Today, arithmetic manipulations of 1st Law results from ideal gas Carnot cycle (HW2 #10) to show that this efficiency depends only on 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→2)

efficiency will depend on $T_U$ and $T_L$

HW4 prob #22 $\varepsilon$ is $\varepsilon$fficiency

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

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

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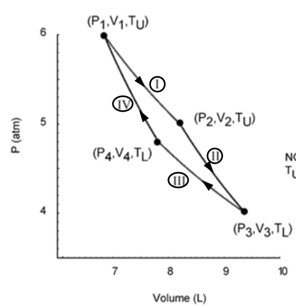
***Problem HW2 #10 (see handout "Carnot Cycle Arithmetic)***




***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, $q_{2\rightarrow 3}$ = 0, $T_3$=$T_L$

$P_4$=4.8 atm, $T_4$=$T_L$, $q_{4\rightarrow 1}$= 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, $T_U$, $V_1 \rightarrow V_2$:

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

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

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



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

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

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

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

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 ($T_L \to T_U$)*

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

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

P,V,T relationships for adiabatic reversible process

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

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

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

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

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

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

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

↕ ↕

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

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

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

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

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

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

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

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

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### *and NOW EFFICIENCY ε*

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

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

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

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

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

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

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### *some limits on efficiency of ideal engine*

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

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

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

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

*or* $\boxed{1}$

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

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

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

*but*

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

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 TFGT

bring into thermal contact

STAY COLD-HOT ??

or

EQUILIBRIUM ??

*spontaneous*

$T_E$= $T_f$

(relative) DISORDER ≈$10^{594}$

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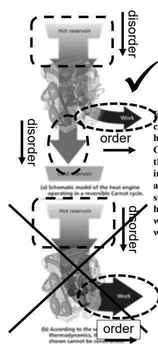
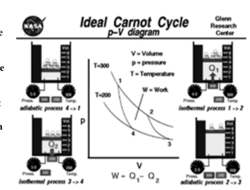
***E&R$_{4th}$ fig 5.14 p. 127*** *[fig 5.3, p. 89]$_{E\&R3rd}$*




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)***

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 TFGT

(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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