Details on the Carnot Cycle

The isothermal expansion \((a\rightarrow b)\) and compression \((c\rightarrow d)\):

\[
\Delta U_{\text{isothermal}} = 0 \quad \text{ (T is constant and } U(T) \text{ is a function of } T \text{ only for an Ideal Gas.)}
\]

\[
|Q_H| = W_{ab} = nRT_H \ln \left( \frac{V_b}{V_a} \right) \quad \text{(a}\rightarrow b : \text{isothermal expansion)}
\]

\[
|Q_C| = |W_{cd}| = \left| nRT_C \ln \left( \frac{V_d}{V_c} \right) \right| = nRT_C \ln \left( \frac{V_c}{V_d} \right) \quad (V_c > V_d)
\]

\[
(c\rightarrow d : \text{isothermal compression})
\]
Details on the Carnot Cycle

The adiabatic expansion \((b \rightarrow c)\) and compression \((d \rightarrow a)\):

\[
Q_{\text{adiabatic}} = 0 \quad \text{(by definition)}
\]

From Section 19.8, we learned that \(TV^{\gamma-1} = \text{const}\) for adiabatic processes.

\[
T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1} \quad (b \rightarrow c: \text{adiabatic expansion})
\]

\[
T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1} \quad (d \rightarrow a: \text{adiabatic compression})
\]

Dividing these two equations gives,

\[
\frac{V_b}{V_a} = \frac{V_c}{V_d}
\]
Efficiency of the Carnot Cycle

From definition, we have

\[ e = 1 - \frac{|Q_c|}{|Q_H|} \]

Using our results for \( Q_C \) and \( Q_H \) from the isothermal processes,

\[ e = 1 - \frac{nRT_C \ln(V_c/V_d)}{nRT_H \ln(V_b/V_a)} = 1 - \frac{T_C \ln(V_c/V_d)}{T_H \ln(V_b/V_a)} \]

From the adiabatic processes, we have \( V_b/V_a = V_c/V_d \)

\[ \ln\left(\frac{V_c}{V_d}\right) \frac{\ln(V_c/V_d)}{\ln(V_b/V_a)} = 1 \]

\[ e \equiv 1 - \frac{|Q_c|}{|Q_H|} = 1 - \frac{T_C}{T_H} \quad (T \text{ must be in K}) \]

(Carnot Cycle only)
Efficiency of the Carnot Cycle

\[ e_{\text{carnot}} = 1 - \frac{T_C}{T_H} \]  
(Carnot Cycle)

General Comments:

- Higher efficiency if either \( T_C \) is lower and/or \( T_H \) is higher.
- For any *realistic* thermal process, the cold reservoir is far above absolute zero and \( T_C > 0 \).
- Thus, a *realistic* e  is *strictly less* than 1! (No 100\% efficient heat engine)
- *Realistic* heat engines must take in energy from the high \( T \) reservoir for the work that it produces AND some heat energy must be *released* back to the lower \( T \) reservoir.  
  (Kelvin-Planck’s Statement)
Entropy

Recall from a Carnot Cycle, we have derived the following relationship:

\[ \frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \quad \Rightarrow \quad \frac{|Q_H|}{T_H} + \frac{-|Q_C|}{T_C} = 0 \]

Formally, we can rewrite this as,

\[ \sum_{\text{cycle}} \frac{Q}{T} = 0 \quad \text{(We have absorbed the explicit sign back into the variable } Q.) \]

where \( Q \) represents the heat absorbed/released along the isotherm at temp \( T \).
Entropy

Any reversible cycles can be approximated as a series of Carnot cycles!
Entropy

This suggests that the following generalization to be true for any reversible processes,

\[ \oint \frac{dQ_r}{T} = 0 \]

where, 
\( dQ_r \) is the infinitesimal heat absorbed/released by the system at an infinitesimal *reversible* step at temp \( T \).

\[ \oint \text{ denotes the integration evaluated over one complete cycle.} \]
Entropy

We have seen this property previously,

$$\oint \ dU = 0$$  

Changes in the internal energy $U$ over a closed cycle is zero!

This is a consequence of the fact that $U$ is a *state variable* and $dU$ for any processes depends on the initial and final states only.

Thus the result  

$$\oint \frac{dQ}{T} = 0$$  

indicates that there is another state variable $S$ such that,

$$dS \equiv \frac{dQ}{T}$$  

and

$$\oint dS = 0$$

This new state variable $S$ is called the *entropy* of the system.
Entropy: Disorder

Recall that the 2nd Law of Thermodynamics is a statement on nature’s preferential direction for systems to move toward the state of disorder. Let see how Entropy is a quantitative measure of disorder.

From our previous derivation, the quantity $\frac{dQ}{T}$ was from the isothermal branch of the infinitesimal Carnot cycle. Let look at an isothermal expansion of an ideal gas microscopically:

Intuitively, as the gas expands into a bigger volume, the degree of randomness for the system increases since molecules now have more choices (spaces) for them to move around. One can associate the increase in randomness to the ratio:

$$\frac{\Delta V}{V} \quad \text{or} \quad \frac{dV}{V}$$

($T$ stays the same $\rightarrow$ avg. $KE$ stays the same)
Entropy: Disorder

Since this is an isothermal process, we have the following relation from the 1st Law:

\[ dQ = dW = PdV = \frac{nRT}{V}dV \]

\[ \text{(dU = 0)} \]

\[ \Rightarrow \quad \frac{1}{nR} \frac{dQ}{T} = \frac{dV}{V} \]

So, the newly introduced macroscopic variable \( S \) (entropy),

\[ dS \equiv \frac{dQ}{T} \quad \quad [S] = J/K \]

is directly proportion to the degree of disorder of the system.

\( dS \) is an infinitesimal entropy change for a reversible process at temperature \( T \).

For any finite reversible process, the total entropy change \( \Delta S \) is,

\[ \Delta S = \int_{i}^{f} \frac{dQ}{T} \]
2\textsuperscript{nd} Law (Quantitative Form)

\[ \Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{env}} \geq 0 \]
\[ (\Delta S_{\text{tot}} = 0 \text{ reversible;} \quad \Delta S_{\text{tot}} > 0 \text{ irreversible}) \]

“The total entropy (disorder) of an isolated system in any processes can never decrease.”

“Nature always tends toward the macrostate with the highest $S$ (disorder) [most probable (later)] in any processes.”
Entropy Changes for Different Processes

1. General *Reversible* Processes:

\[ \Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T} \]

Note: \( S \) is a *state variable*, \( \Delta S \) is the *same* for all processes (including *irreversible* ones) with the same initial and final states!

**NOTE:** in most applications, it is the change in entropy \( \Delta S \) which one typically needs to calculate and not \( S \) itself.
Entropy Changes for Different Processes

2. Reversible Cycles:

\[ \Delta S_{cycle} = \oint_{cycle} ds = \oint_{cycle} \frac{dQ_r}{T} = 0 \]

3. Any Reversible Processes for an Idea Gas:

\((T_i, V_i) \rightarrow (T_f, V_f)\)  

(Note: Thru the Ideal Gas Law, \(P\) is fixed for a given pair of \(T\) & \(V\).)

1st Law gives,

\[ dU = dQ_r - dW \]
\[ dQ_r = dU + dW = nC_v \, dT + P \, dV \]
\[ dQ_r = nC_v \, dT + \frac{nRT}{V} \, dV \]
Entropy Changes for Different Processes

Dividing $T$ on both sides and integrating,

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \int_i^f \left( \frac{nC_v dT}{T} + nR \frac{dV}{V} \right)$$

We have,

$$\Delta S = nC_v \ln \left( \frac{T_f}{T_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right)$$
Entropy: Disorder
(General Reversible Process)

In our derivation of $\Delta S$ for an ideal gas through a general reversible process, we have the following relation,

$$dS = \frac{dQ_r}{T} = \frac{nC_v dT}{T} + nR \frac{dV}{V}$$

**Thermal agitations**

$$\frac{dT}{T} \uparrow \Rightarrow S \uparrow$$

**Availability of space**

$$\frac{dV}{V} \uparrow \Rightarrow S \uparrow$$
Entropy Changes for Different Processes

4. Calorimetric Changes:

\[ dQ = mc \, dT \]

\[ \Delta S = \int_i^f \frac{dQ}{T} = \int_i^f \frac{mc \, dT}{T} \]

If \( c \) is constant within temperature range, \( \Delta S = mc \ln \left( \frac{T_f}{T_i} \right) \)

If \( c(T) \) is a function of \( T \), \( \Delta S = m \int_i^f \frac{c(T) \, dT}{T} \)
Entropy Changes for Different Processes

5. During Phase Changes (or other isothermal Processes):

\[ \Delta S = \int \frac{dQ}{T} = \frac{1}{T} \int dQ \]  

(T stays constant during a phase change.)

\[ \Delta S = \frac{Q}{T} = \frac{mL}{T} \]
Entropy Changes for Different Processes

6. Irreversible Processes:

Although for a given irreversible process, we cannot write \( dS = \frac{dQ_r}{T} \), \( \Delta S \) between a well defined initial state \( a \) and final state \( b \) can still be calculated using a surrogate reversible process connecting \( a \) and \( b \). (\( S \) is a state variable!)

Example 20.8: (adiabatic free expansion of an ideal gas)

Initial State \( a: (V, T) \)   Final State \( b: (2V, T) \)

Since \( Q=W=0, \Delta U=0 \).
For an ideal gas, this means that \( \Delta T=0 \) also.

Although \( Q=0 \), but \( \Delta S \) is not zero!
**ΔS in a Adiabatic Free Expansion**

**Important point:** Since \( S \) is a *state variable*, \( ΔS \) is the *same* for any processes connecting the same initial \( a \) and final \( b \) states.

In this case, since \( T \) does not change, we can use an *surrogate* isothermal process to take the ideal gas from state \( a \ (V,T) \) to state \( b \ (2V,T) \) to calculate \( ΔS \).

Applying our general formula,

\[
ΔS = nC_v \ln \left( \frac{T_f}{T_i} \right) + nR \ln \left( \frac{V_f}{V_i} \right)
\]

we have,

\[
ΔS = nC_v \ln \left( \frac{T}{T} \right) + nR \ln \left( \frac{2V}{V} \right) = nR \ln 2 = 5.76 \text{J} / \text{K} \quad (n=1)
\]
2\textsuperscript{nd} Law (Quantitative Form)

\[ \Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{env}} \geq 0 \]

\[ (\Delta S_{\text{tot}} = 0 \quad \text{reversible}; \quad \Delta S_{\text{tot}} > 0 \quad \text{irreversible}) \]

“The total entropy (disorder) of an isolated system in any processes can never decrease.”

“Nature always tends toward the macrostate with the highest \( S \) (disorder) [most probable] in any processes.”
2\textsuperscript{nd} Law ($\Delta S > 0$ & Clausius Statement)

Clausius Statement: Heat can’t spontaneously transfer from $T_C$ to $T_H$.

We will prove this by contradiction using $\Delta S_{\text{tot}} > 0$.

Assume the contrary:

\[
\Delta S_H = \frac{+|Q|}{T_H} \quad \text{(heat absorbed into $T_H$)}
\]

\[
\Delta S_C = \frac{-|Q|}{T_C} \quad \text{(heat released by $T_C$)}
\]

(with the explicit signs, $|Q|$ is taken to be +.)

\[
\Delta S_{\text{tot}} = \frac{+|Q|}{T_H} + \frac{-|Q|}{T_C}
\]

\[
\Delta S_{\text{tot}} = |Q| \left( \frac{1}{T_H} - \frac{1}{T_C} \right) \quad (T_H > T_L)
\]

\[
< 0
\]

Not Possible!

(violated $\Delta S_{\text{tot}} > 0$)
2nd Law ($\Delta S > 0$ & Kelvin-Planck Statement)

Kelvin-Planck Statement: No heat engine can convert heat from $T_H$ completely into $W$.

We will prove this by contradiction again using the $\Delta S_{\text{tot}} > 0$.

Assume the contrary,

- $\Delta S_{\text{engine}} = 0$ (engine operates in a cycle)
- $\Delta S_H = \frac{-|Q_H|}{T_H}$
- $\Delta S_C = 0$ (no heat exchange)

So, $\Delta S_{\text{tot}} = \Delta S_{\text{engine}} + \Delta S_H + \Delta S_C = \frac{-|Q_H|}{T_H} < 0$

Not Possible! (again violated $\Delta S_{\text{tot}} > 0$)
2nd Law ($\Delta S > 0$ & Carnot Theorem)

For any reversible heat engines,

$$\Delta S_{\text{engine}} = 0$$

$$\Delta S_{\text{env}} = \frac{+|Q_C|}{T_C} - \frac{|Q_H|}{T_H}$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{engine}} + \Delta S_{\text{env}} = \frac{|Q_C|}{T_C} - \frac{|Q_H|}{T_H} \geq 0$$

$$\frac{|Q_C|}{T_C} \geq \frac{|Q_H|}{T_H} \quad \text{or} \quad \frac{|Q_C|}{|Q_H|} \geq \frac{T_C}{T_H}$$
Consider the efficiency of a heat engine in general,

\[ e \equiv 1 - \frac{|Q_C|}{|Q_H|} \]

Applying the inequality from the previous slide,

\[ \frac{|Q_C|}{|Q_H|} \geq \frac{T_C}{T_H} \]

we get

\[ e \equiv 1 - \frac{|Q_C|}{|Q_H|} \leq 1 - \frac{T_C}{T_H} \]

Recall that the efficiency of a Carnot Cycle is given by

\[ e_{\text{carnot}} = 1 - \frac{T_C}{T_H} \]

This gives our desired result, \( e \leq e_{\text{carnot}} \). Carnot engine is the most efficient!

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Extra:engines
Example: $\Delta S$ for some Reversible Processes in an Ideal Gas

One mole of monatomic gas doubles its volume. Calculate the entropy change if the expansion is done through i) a reversible isobaric process, ii) a reversible adiabatic process, and iii) a reversible isothermal process.

link to solution