How to please the rulers of NPL-213
– *the geese*

(Entropy and the 2\textsuperscript{nd} Law of Thermodynamics)

Physics 116 2017

Tues. 3/21, Thurs 3/23
# Review

## Equation Sheet:

<table>
<thead>
<tr>
<th>Name</th>
<th>What is held constant?</th>
<th>Work done by gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobaric</td>
<td>Pressure</td>
<td>(=P(V_f - V_i))</td>
</tr>
<tr>
<td>Isovolumetric (or Isochoric)</td>
<td>Volume</td>
<td>(=0)</td>
</tr>
<tr>
<td>Isothermal</td>
<td>Temperature</td>
<td>(=nRT\ln \left(\frac{V_f}{V_i}\right))</td>
</tr>
<tr>
<td>Adiabatic</td>
<td>No heating or cooling</td>
<td>(-\Delta U)</td>
</tr>
<tr>
<td>Cyclic</td>
<td>(\Delta U=0) between initial and final states</td>
<td>area enclosed by cycle on P-V diagram</td>
</tr>
</tbody>
</table>

### 1st Law of Thermodynamics:

\[
\Delta U = Q - W \quad \text{(assuming positive work is work done by the gas)}
\]

\[
\Delta U = Q + W \quad \text{(assuming positive work is work on the gas)}
\]

Your equation sheet is written all in terms of work done BY the gas, i.e., work done by a gas is positive when the gas expands, since \(V_f > V_i\)
“Now, in the second law of thermodynamics . . .”
Possible outcomes

All the same – **multiplicity** of 2
One different – **multiplicity** of 6

The outcome with the highest multiplicity is the one that is most likely to happen.
Inventing a possibility rule

- molecular ensembles will spontaneously tend to evolve from configurations of lower multiplicity to configurations of greater multiplicity (toward greater disorder)
- We never see it go the other direction in nature.
- This defines the arrow of time.
Entropy is a measure of multiplicity. Increasing entropy defines the direction of time.
2nd Law: Entropy statement

No process can exist with a net effect of causing the entropy of the universe to decrease.
Laws of Thermodynamics

In order for an engine to do work

• 1st Law:
  “There ain’t no such thing as a free lunch...” , by the conservation of energy you need to provide energy to the engine. Heat engines get the energy from burning fuel.

• 2nd Law:
  No process can exist with a net effect of causing the entropy of the universe to decrease.

How can we make sense of these laws of nature? Why do we need both to describe nature? Is conservation of energy sufficient?
<table>
<thead>
<tr>
<th>Event 1</th>
<th>Event 2</th>
<th>Event 3</th>
<th>Event 4</th>
<th>Event 5</th>
<th>Event 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two touching blocks $T_1=280K$ and $T_2=320K$ come to thermal equilibrium in perfect thermal isolation from their surroundings. Each has a heat capacity $C_p=200$ J/K.</td>
<td>Two touching blocks are at the same initial temperature of 300K. Block 1 cools to $T_1=280K$ and thereby warms Block 2 to $T_2=320K$ in perfect thermal isolation from their surroundings. Each has a heat capacity $C_p=200$ J/K.</td>
<td>Ice cube (m=0.1 kg) melts in kitchen (which can be treated as a hot reservoir that transfers heat to ice) that is 300K. Lf(ice) = 3.34 x105 J/K</td>
<td>Puddle of 0°C water forms into an ice cube (m=0.1 kg) in a kitchen, thereby transferring heat to the hot reservoir that is 300K. Lf(ice) = 3.34 x105 J/K</td>
<td>Sun(1) Transfers 58 MJ of thermal energy to the earth(2) $T_{sun}=5800$ K $T_{earth}=290$ K</td>
<td>Earth(2) Transfers 58 MJ of thermal energy to Sun(1) $T_{sun}=5800$ K $T_{earth}=290$ K</td>
</tr>
</tbody>
</table>

**Final Temps**

<table>
<thead>
<tr>
<th>$T_1$</th>
<th>$T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>300 K</td>
</tr>
<tr>
<td>280 K</td>
<td>320 K</td>
</tr>
<tr>
<td>273 K</td>
<td>300 K</td>
</tr>
<tr>
<td>273 K</td>
<td>300 K</td>
</tr>
<tr>
<td>5800 K</td>
<td>290 K</td>
</tr>
<tr>
<td>5800 K</td>
<td>290 K</td>
</tr>
</tbody>
</table>

**Energy Conserved?**

<table>
<thead>
<tr>
<th>Q</th>
<th>$\Sigma Q$</th>
<th>$\Delta S_1$</th>
<th>$\Delta S_2$</th>
<th>$\Sigma(\Delta S)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_1$</td>
<td>+4 kJ</td>
<td>-4 kJ</td>
<td>3.34 x10^4 J</td>
<td>-3.34 x 10^4 J</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>-4 kJ</td>
<td>+4 kJ</td>
<td>-3.34 x10^4 J</td>
<td>3.34 x10^4 J</td>
</tr>
<tr>
<td>$\Sigma(\Delta S)$</td>
<td>+0.9 J/K</td>
<td>-0.9 J/K</td>
<td>+11 J/K</td>
<td>-11 J/K</td>
</tr>
</tbody>
</table>
Quantifying entropy

• Consider isothermal processes

• Transferring heat at a low temperature increases disorder relatively more than transferring that same amount of heat at a high temperature since

$$\Delta S_{isotherm} = \frac{Q}{T}$$

• Entropy can be thought of as “energy spreading”. This is more noticeable at low temps than at high temps.

\[
\begin{align*}
TdS &= dQ \\
\frac{dQ}{T} &= dS \\
\int dS &= \int \frac{dQ}{T}
\end{align*}
\]

\[
\begin{align*}
\Delta S_{isobar, isovol} &= \int_{Ti}^{Tf} \frac{nc_{p,v}dT}{T} = nc_{p,v} \ln \left( \frac{T_f}{T_i} \right) \\
\Delta S_{isotherm} &= \frac{Q}{T} \\
\Delta S_{phase change} &= \frac{Q}{T} = \frac{mL}{T}
\end{align*}
\]
Quantifying entropy

- Consider isothermal processes
- Transferring heat at a low temperature increases disorder relatively more than transferring that same amount of heat at a high temperature. (consider adding 1000 KJ of heat to an ice cube vs. Sun)
- Entropy can be thought of as “energy spreading”. This is more noticeable at low temps than at high temps.
- $\Delta S$ must be greater at cold reservoir than at hot reservoir to be a “possible” engine

How can we understand bullets 2+3? Why must the last bullet point be true? What are the algebraic signs of $\Delta S_{\text{cold}}$ and $\Delta S_{\text{hot}}$? Let’s break this down a bit.

$\sum \Delta S > 0$  \[ \Delta S_{\text{engine}} + \Delta S_{\text{cold}} + \Delta S_{\text{hot}} > 0 \]
We take heat energy from a hot reservoir and deposit it directly to a cold reservoir ($Q_c = Q_h$).

Is this isothermal process allowed by the 1\textsuperscript{st} law (energy conservation) and 2\textsuperscript{nd} law (entropy of the universe cannot decrease)?

What if we place an ideal engine in between the reservoirs that converts some of $Q$ into work?

Which $Q$ changes: $Q$ into the cold reservoir ($Q_c$), or $Q$ out of the hot reservoir ($Q_h$)?

How does this $Q$ change?

Quantifying entropy

\[ \Delta S_{isotherm} = \frac{Q}{T} \]

\[ \Delta S_{cold} = \frac{+Q_c}{T_{cold}} \]

\[ \Delta S_{hot} = \frac{-Q_h}{T_{hot}} \]
Quantifying entropy

\[ \Delta S_{\text{isothermal}} = \frac{Q}{T} \]

\[ \Delta S_{\text{cold}} = \frac{+Q_c}{T_{\text{cold}}} \quad \Delta S_{\text{hot}} = \frac{-Q_h}{T_{\text{hot}}} \]

• We take heat energy from a hot reservoir and deposit it directly to a cold reservoir \((Q_c = Q_h)\).

• Is this *isothermal process* allowed by the 1\(^{\text{st}}\) law (energy conservation) and 2\(^{\text{nd}}\) law (entropy of the universe cannot decrease)?

• What if we place an ideal engine in between the reservoirs that converts some of \(Q\) into work?

• Which \(Q\) changes: \(Q\) into the cold reservoir \((Q_c)\), or \(Q\) out of the hot reservoir \((Q_h)\)?

• How does this \(Q\) change?
Quantifying entropy

\[ \Delta S_{iso\text{therm}} = \frac{Q}{T} \]

\[ \Delta S_{cold} = \frac{+Q_c}{T_{cold}} \quad \Delta S_{hot} = \frac{-Q_h}{T_{hot}} \]

- We take heat energy from a hot reservoir and deposit it directly to a cold reservoir \((Q_c = Q_h)\).
- Is this \textit{isothermal process} allowed by the 1\textsuperscript{st} law (energy conservation) and 2\textsuperscript{nd} law (entropy of the universe cannot decrease)?
- What if we place an ideal engine in between the reservoirs that converts some of \(Q\) into work?
- Which \(Q\) changes: \(Q\) into the cold reservoir \((Q_c)\), or \(Q\) out of the hot reservoir \((Q_h)\)?
- How does this \(Q\) change?
Heat Engine
involves both heating and cooling

1\textsuperscript{st} Law of Thermo
(Energy conservation
for full engine cycle
implies $\Delta U=0$):

$W = Q_h - Q_c$

2\textsuperscript{nd} Law of Thermo:
Entropy of universe
can't decrease

$\Delta S_{universe} \geq 0$

$\Delta S_{isotherm} = \frac{Q}{T}$

$\Delta S_{hot} = -\frac{Q_h}{T_h}$

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

$\Delta S_{cold} = \frac{+Q_c}{T_c}$

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = \Delta S_{engine} + \Delta S_{hot} + \Delta S_{cold}$
Most efficient (ideal) engine

- Carnot Cycle involves two isothermal processes ($Q_{\text{hot}}$ for expansion and $Q_{\text{cold}}$ for compression) and two adiabatic processes (no heat exchange, $Q = 0$)
- Carnot Cycle net change in entropy is zero which means it’s reversible.
- A reversible cycle or process means it can run forward or backward.
- An ice cube melting on a room temperature table is not a reversible process

\[
\begin{align*}
\Delta U &= 0 \\
Q_{\text{hot}} &= W_{\text{by gas}} \\
Q_{\text{cold}} &= W_{\text{by gas}} \\
\Delta U &= 0 \\
Q &= 0
\end{align*}
\]
**Ideal Carnot Cycle**

*p-V diagram*

**NASA Glenn Research Center**

**adiabatic process** 4 → 1

**isothermal process** 3 → 4

**isothermal process** 1 → 2

**adiabatic process** 2 → 3

\[ W = Q_1 - Q_2 \]

- **V** = Volume
- **p** = pressure
- **T** = Temperature

**Diagram Notes:**
- Lines 1 and 2 represent the adiabatic process.
- Lines 3 and 4 represent the isothermal process.
- Points 1, 2, 3, and 4 correspond to different states of the system.
- The Carnot cycle consists of two isothermal and two adiabatic processes.
Real (non-reversible) Engines

**Otto Cycle Engine** (automotive engine)
[~50% efficient cycle for real engine numbers—doesn’t include power loss during transfer to wheels.]

![Otto Cycle Diagram](https://commons.wikimedia.org/wiki/File:P-V_Otto_cycle.svg)

1-0: Air released to atmosphere
0-1: Air intake into cylinder
1-2: Adiabatic compression of air by piston
2-3: Ignition of air-fuel mixture (very fast – volume constant for an instant)
3-4: Adiabatic expansion after ignition
4-1: Heat rejected from air after expansion

**Stirling Engine** – high efficiency but low power to weight ratio, ~50% efficiency reached

**Steam Engine** ~40% efficient for steam turbine plants

[Image 7x63 to 696x382]


Demo time! Steam engines and efficiency
• The efficiency of an engine is the ratio of the work it does to the amount of energy it takes in:

$$\varepsilon_{real} = \frac{W}{Q_{hot}} = 1 - \frac{Q_{cold}}{Q_{hot}}$$

Since for a full engine cycle: $W = Q_{hot} - Q_{cold}$ (full engine cycle means $T_f = T_i$ and $\Delta U=0$)

• If the engine is a Carnot engine, this efficiency is the maximum possible allowed by the 2\textsuperscript{nd} law. It can be expressed as:

$$\varepsilon_{ideal/carnot} = 1 - \frac{T_{cold}}{T_{hot}}$$

• This is because the net change in entropy of the reservoirs must be zero for a reversible process (Carnot cycle):

$$\sum \Delta S = \frac{Q_c}{T_c} - \frac{Q_h}{T_h} = 0 \Rightarrow \frac{Q_c}{T_c} = \frac{Q_h}{T_h}$$

So:

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

Where $Q_h$ and $Q_c$ are positive numbers, the heat flow direction was taken into account already with the minus sign in the equation.
2\textsuperscript{nd} Law: Heat Engine statement

• In order for a heat engine to be possible, the entropy of the universe must either be unchanged or increased:

\[
\Delta S_{\text{universe}} \geq 0
\]

\[
\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0
\]

\[
\Delta S_{\text{engine}} + \Delta S_{\text{hot}} + \Delta S_{\text{cold}} \geq 0 \rightarrow \text{But } \Delta S_{\text{engine}} = 0 \text{ for an ideal, reversible engine}
\]

\[
\Delta S_{\text{hot}} + \Delta S_{\text{cold}} \geq 0
\]

• This means that the amount of entropy change at the cold reservoir must be larger than the amount of entropy change at the hot reservoir

\textbf{Entropy change at cold reservoir: } \Delta S_{\text{cold}} = \frac{+Q_c}{T_c} \quad \rightarrow \quad \frac{+Q_c}{T_c} + \frac{-Q_h}{T_h} \geq 0

\textbf{Entropy change at hot reservoir: } \Delta S_{\text{hot}} = \frac{-Q_h}{T_h}

• Consequently, there must always be some amount of energy that is taken into the engine through heating that cannot be converted to work, and must be deposited in a cold reservoir.
Laws of Thermodynamics

In order for an engine to do work

• **1\(^{st}\) Law:**
  “There ain’t no such thing as a free lunch...” , by the conservation of energy you need to provide energy to the engine. Heat engines get the energy from burning fuel.

• **2\(^{nd}\) Law:**
  “...and you can’t break even.”
  All of the energy that is transferred to the engine through heating is not available to do work. The percentage that does work is called the *efficiency* of the engine.
a) Which of the engines, A through F, are allowable by the 1st law of thermodynamics? Please explain your reasoning.
b) Of those that are allowable by the 1st law (that you selected in part a), which ones are also allowable by the 2nd law of thermodynamics? Please explain your reasoning.
c) What are the efficiencies of the engines allowed by both the 1\textsuperscript{st} and 2\textsuperscript{nd} laws?

\[ \varepsilon_{\text{real}} = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} \]

\[ \varepsilon_{\text{real}} = \frac{W}{Q_h} = \frac{800 \text{ J}}{2000 \text{ J}} = 0.4 = 40\% \]

\[ \varepsilon_{\text{real}} = \frac{W}{Q_h} = \frac{300 \text{ J}}{800 \text{ J}} = 0.38 = 38\% \]
c) What are the efficiencies of the engines allowed by both the 1\textsuperscript{st} and 2\textsuperscript{nd} laws?

\[ \epsilon_{\text{real}} = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} \]

\[ \epsilon_{\text{Carnot}} = 1 - \frac{T_c}{T_h} \]

\[ \epsilon_{\text{real}} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{1200\, J}{2000\, J} = 0.4 \]

\[ \epsilon_{\text{real}} = 1 - \frac{500\, J}{800\, J} = 0.38 \]