## Physics 5D - Lecture 8 - Dec 2, 2013 Thermodynamics of Earth and Cosmos; Overview of the Course

Reminder: the Final Exam is next Wednesday December II, 4:00-7:00 pm, here in Thimann Lec 3. You can bring with you two sheets of paper with any formulas or other notes you like. A PracticeFinalExam is at http://physics.ucsc.edu/~joel/Phys5D

The Physics Department has elected to use the new eCommons Evaluations System to collect end of the quarter instructor evaluations from students in our courses. All students in our courses will have access to the evaluation tool in eCommons, whether or not the instructor used an eCommons site for course work. Students will receive an email from the department when the evaluation survey is available. The email will provide information regarding the evaluation as well as a link to the evaluation in eCommons. Students can click the link, login to eCommons and find the evaluation to take and submit. Alternately, students can login to ecommons.ucsc.edu and click the Evaluation System tool to see current available evaluations.

## 20-8 Heat Death of the Universe

If we look at the universe as a whole, it seems inevitable that, as more and more energy is converted to unavailable forms, the total entropy $S$ will increase and the ability to do work anywhere will gradually decrease. This is called the "heat death of the universe". It was a popular theme in the late 19th century, after physicists had discovered the 2nd Law of Thermodynamics.

Lord Kelvin calculated that the sun could only shine for about 20 million years, based on the idea that its energy came from gravitational contraction. He got a similar value for the age of the earth, assuming that its internal heat today is left over from its initial molten state. Both calculations disagreed with geological arguments indicating far greater ages.

Lord Kelvin didn't know about nuclear energy. The heat of the earth comes partly from radioactivity, which was discovered in the 1890s. In the 1930s physicists showed that the sun is powered by nuclear fusion, which releases energy as four hydrogen nuclei

William Thomson, Lord Kelvin

(protons) are converted to a tightly bound helium nucleus (2 protons and 2 neutrons). Ernest Rutherford was the physicist who coined the names alpha, beta, and gamma radioactivity. He used alpha rays (helium nuclei) to discover the atomic nucleus. Using radioactive dating, Rutherford easily found rocks that were far older than Kelvin thought possible.

## Heat Death of the Universe?

According to the modern theory of the origin and evolution of the universe, most of the entropy is actually in the photons and neutrinos in the heat radiation of the Big Bang. There is also a lot of entropy associated with supermassive black holes, because their entropy scales as the square of their mass. Stars contribute only relatively small additional entropy, and they are nowhere near burning out. The stars in our Milky Way galaxy will actually get brighter for more than a trillion years, a hundred times longer than the present age of the universe (13.8 billion years).

## Thermodynamics of the Earth

The sun provides $1350 \mathrm{~W} / \mathrm{m}^{2}$ at the earth's distance, so multiplying this by the earth's cross sectional area, the solar power received by the earth is

$$
P=\pi R^{2}\left(1350 \mathrm{~W} / \mathrm{m}^{2}\right)=\pi\left(6.4 \times 10^{6} \mathrm{~m}\right)^{2}\left(1350 \mathrm{~W} / \mathrm{m}^{2}\right)=1.7 \times 10^{17} \mathrm{~W}
$$

While the earth receives solar radiation only on the side facing the sun, the atmosphere warms the entire earth so it emits heat radiation into space over its entire area.

As you found in solving problem 1 on Homework 5, setting Power $=\sigma A T^{4}$ where $\sigma=5.67 \times 10^{-8} \mathrm{~W} \mathrm{~m}^{-2} \mathrm{~K}^{-4}$ is the Stefan-Boltzmann constant and $A=$ surface area of the earth $=4 \pi R^{2}$, the resulting temperature is $T=5^{\circ} \mathrm{C}$. The average temperature of the entire earth is larger, about $15{ }^{\circ} \mathrm{C}$, partly because of greenhouse gases.

If an ideal thermally conductive absorber were the same size and distance from the Sun as the Earth is, it would have a temperature of about $5{ }^{\circ} \mathrm{C}$. However, since the Earth reflects about $30 \%$ of the incoming sunlight, the planet's effective temperature is about $-18^{\circ} \mathrm{C}$, about $33^{\circ} \mathrm{C}$ below the actual average surface temperature of about $14^{\circ} \mathrm{C}$. The mechanism that produces this difference between the actual surface temperature and the effective temperature is due to the atmosphere and is known as the greenhouse effect.
Solar radiation at the short wavelengths of visible light passes through the atmosphere to warm the earth's surface, which then emits this energy at the longer wavelengths of infrared thermal radiation. Infrared radiation is absorbed by greenhouse gases, which in turn re-radiate much of the energy to the surface and lower atmosphere. The mechanism is named after the effect of solar radiation passing through glass and warming a greenhouse, but the way it retains heat is fundamentally different, since a greenhouse works mainly by reducing airflow, isolating the warm air inside the structure so that heat is not lost by convection.


The sun was much cooler long ago, but earth had a much higher concentration of greenhouse gases then.


Astronomers at UCSC have proposed that our distant descendants could keep the earth's climate balmy by steadily moving earth farther from the sun. This could be done using a comet about 100 miles across to borrow kinetic energy from Jupiter and give it to Earth once every 100,000 years or so.

We have a more critical problem of getting through the next several decades -- your lifetimes -- when we must moderate our increasing use of Earth's resources and in particular decrease our production of $\mathrm{CO}_{2}$ and other greenhouse gases.

The fact that people in California use half the U.S. national average electricity per capita shows that we can greatly reduce energy use by being smart.

## U.S. Per Capita Electricity Use by State and DC in 2010

| Ranking | State | Population (thousands) | kWh (millions) | kWh per capita | 26 | Ohio | 11,537 | 154,445 | 13,388 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | Wyoming | 564 | 15,475 | 27,457 | 27 | Delaware | 898 | 11,587 | 12,904 |
| 2 | Kentucky | 4,339 | 93,686 | 21,590 | 28 | Minnesota | 5,304 | 68,126 | 12,845 |
| 3 | District of Columbia | 602 | 11,972 | 19,896 | 29 | Nevada | 2,701 | 33,748 | 12,497 |
| 4 | North Dakota | 673 | 13,100 | 19,477 | 30 | Florida | 18,801 | 232,735 | 12,379 |
| 5 | Louisiana | 4,533 | 85,461 | 18,852 |  | United States | 308,746 | 3,749,985 | 12,146 |
| 6 | South Carclina | 4,625 | 82,809 | 17,903 | 31 | Wisconsin | 5,687 | 69,147 | 12,159 |
| 7 | Alabama | 4,780 | 82,654 | 17,293 | 32 | Oregon | 3,831 | 46,269 | 12,077 |
| 8 | West Virginia | 1,853 | 32,039 | 17,290 | 33 | Pennsylvania | 12,702 | 149,36B | 11,759 |
| 9 | Mississippi | 2,967 | 49,829 | 16,793 | 34 | Arizona | 6,392 | 72,836 | 11,395 |
| 10 | Arkansas | 2,916 | 48,167 | 16,519 | 35 | Maryland | 5,774 | 65,489 | 11,343 |
| 11 | Indiana | 6,484 | 105,782 | 16,315 | 36 | Illinois | 12,831 | 144,378 | 11,253 |
| 12 | Nebraska | 1,826 | 29,757 | 16,293 | 37 | New Mexico | 2,059 | 22,113 | 10,739 |
| 13 | Tennessee | 6,346 | 102,281 | 16,117 | 38 | Michigan | 9,884 | 103,941 | 10,516 |
| 14 | Oklahoma | 3.751 | 58,399 | 15.568 | 39 | Colorado | 5,029 | 52,099 | 10,359 |
| 14 | Okanoma | 3,751 | 50,399 | 15,560 | 40 | Utah | 2,764 | 27,932 | 10,106 |
| 15 | lowa | 3,046 | 45,841 | 15,048 | 41 | New Jersey | 8,792 | 78,999 | 8,985 |
| 16 | Georgia | 9,688 | 141,226 | 14,578 | 42 | Vermont | 626 | 5,620 | 8,982 |
| 17 | Virginia | 8,001 | 115,928 | 14,489 | 43 | Maine | 1,328 | 11,552 | 8,696 |
| 18 | Idaho | 1,588 | 22,690 | 14,475 | 44 | Massachusetts | 6,548 | 56,252 | 8,591 |
| 19 | Missouri | 5,989 | 85,913 | 14,345 | 45 | Connecticut | 3,574 | 30,432 | 8,514 |
| 20 | North Carolina | 9,535 | 136,595 | 14,325 | 46 | New Hampshire | 1,316 | 10,909 | 8,286 |
| 21 | Kansas | 2,853 | 40,695 | 14.263 | 47 | Alaska | 710 | 5,648 | 7,952 |
| 22 | Texas | 25,146 | 356,536 | 14,179 | 48 | New York | 19,378 | 144,693 | 7,467 |
| 23 | Montana | 989 | 13,844 | 13,992 | 49 | Rhode Island | 1,053 | 7,825 | 7,434 |
| 24 | South Dakota | 814 | 11,330 | 13,916 | 50 | Hawail | 1,360 | 10,016 | 7,363 |
| 25 | Washington | 6,725 | 91,166 | 13,557 | 51 | California | 37,254 | 250,384 | 6,721 |


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| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

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| $\cdots$ | 2011 Integrated Energy Policy |
| $\cdots$ | Investment Plan for the Alternate Fuels Program (AB 118) |
| \# | Appliance Efficiency Regulations, 2011 Rulemaking |
| - ${ }^{\text {d }}$ | Appliance Efficiency Regulations, Battery Chargers |
| - ${ }^{\text {d }}$ | Alternative and Renewable Fuels and Vehicles Program (AB 118) |
| $\cdots$ | Power Source Disclosure (AB 162) |
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## Physics 5D - Overview of the Course

Two objects placed in thermal contact will eventually come to the same temperature. When they do, we say they are in thermal equilibrium. The zeroth law of thermodynamics says that if two objects are each in equilibrium with a third object, they are also in thermal equilibrium with each other.

Linear expansion occurs when an object is heated: $\ell=\ell_{0}(1+\alpha \Delta T)$
Volume expansion is similar $\Delta V=\beta V_{0} \Delta T$. Typically, $\boldsymbol{\beta} \approx \mathbf{3} \boldsymbol{\alpha}$.
Water behaves differently from most other liquids and solids-its minimum volume occurs when its temperature is $4^{\circ} \mathrm{C}$. As it cools further, it expands, as anyone who leaves a bottle of water in the freezer to cool and then forgets about it can testify.

The ideal gas law is $\boldsymbol{P V}=\boldsymbol{n} \boldsymbol{R} \boldsymbol{T}=\boldsymbol{N} \boldsymbol{k} \boldsymbol{T}$ where $\boldsymbol{n}$ is the number of moles and $R=8.314 \mathrm{~J} / \mathrm{mol} \mathrm{K}$, and where $N$ is the number of molecules and Boltzmann's constant $k=1.38 \times 10^{-23} \mathrm{~J} / \mathrm{K}$. At STP ( $P=1 \mathrm{~atm}, T=273 \mathrm{~K}$ ) one mole of an ideal gas has a volume of

$$
V=R T / P=(8.314 \mathrm{~J} / \mathrm{mol} \mathrm{~K})(273 \mathrm{~K}) /\left(1.013 \times 10^{5} \mathrm{~N} / \mathrm{m}^{2}\right)=22.4 \mathrm{~L}
$$

A PT diagram is called a phase diagram; it shows all three phases of matter. The solid-liquid transition is melting or freezing; the liquid-vapor one is boiling or condensing; and the solid-vapor one is sublimation.

$$
\begin{aligned}
& P_{\text {tp }}=4.58 \text { torr }=0.0604 \mathrm{~atm} \\
& T_{\text {tp }}=273.16 \mathrm{~K}
\end{aligned}
$$




The force exerted on the wall by the collision of one molecule is

$$
F=\frac{\Delta(m v)}{\Delta t}=\frac{2 m v_{x}}{2 \ell / v_{x}}=\frac{m v_{x}^{2}}{\ell} .
$$

Then the force due to all $N$ molecules colliding with that wall is

$$
F=\frac{m}{\ell} N \overline{v_{x}^{2}} .
$$

The averages of the squares of the speeds in all three directions are equal: $\overline{\mathrm{v}_{\mathrm{x}}{ }^{2}}=\overline{\mathrm{v}_{\mathrm{y}}{ }^{2}}=\overline{\mathrm{v}_{\mathrm{z}}{ }^{2}}=\overline{\mathrm{v}^{2}} / 3$

So the pressure is: $\boldsymbol{P}=\boldsymbol{F} / \mathrm{A}$, or $P=\frac{1}{3} \frac{N m \overline{v^{2}}}{V}$.

## The Ideal Gas Law and the Molecular Interpretation of Temperature

Rewriting, $P V=\frac{2}{3} N\left(\frac{1}{2} m \overline{v^{2}}\right)$, so $\bar{K}=\frac{1}{2} m \overline{v^{2}}=\frac{3}{2} k T$.
The average translational kinetic energy of the molecules in an ideal gas is directly proportional to the temperature of the gas.

We can now calculate the average speed of molecules in a gas as a function of temperature:

Maxwell distribution of speeds


## Real Gases and Changes of Phase

The curves here represent the behavior of the gas at different temperatures. The cooler it gets, the further the gas is from ideal.


In curve D, the gas becomes liquid; it begins condensing at (b) and is entirely liquid at (a). The point (c) is called the critical point.

Below the critical temperature, the gas can liquefy if the pressure is sufficient; above it, no amount of pressure will suffice.

## Van der Waals Equation of State

We assume that some fraction $b$ of the volume is unavailable due to the finite size of the molecules. We also expect that the pressure will be reduced by a factor proportional to the square of the density, due to particle interactions. This gives the Van der Waals equation of state; the constants $a$ and $b$ are found experimentally for each gas:


$$
\left(P+\frac{a}{(V / n)^{2}}\right)\left(\frac{V}{n}-b\right)=R T
$$

## Mean Free Path

The mean free path can be calculated, given the average speed, the density of the gas, the size of the molecules, and the relative speed of the colliding molecules. The result, now including the motion of all the particles, is

$$
\ell_{\mathrm{M}}=\frac{1}{4 \pi \sqrt{2} r^{2}(N / V)}
$$



The experiment below found the mechanical equivalent of heat by using the falling weight to heat the water:


$$
\begin{gathered}
4.186 \mathrm{~J}=1 \mathrm{cal} \\
4.186 \mathrm{~kJ}=1 \mathrm{kcal}
\end{gathered}
$$

## Unit of heat: calorie (cal)

1 cal is the amount of heat necessary to raise the temperature of 1 g of water by 1 Celsius degree.

The calories on our food labels are kilocalories (kcal or Calories), the heat necessary to raise 1 kg of water by 1 Celsius degree.

## Internal Energy

## Temperature: measures molecules' average kinetic energy

Internal energy: total thermal energy of all the molecules. Internal energy of an ideal monatomic gas: $E_{\text {int }}=N\left(\frac{1}{2} m \overline{v^{2}}\right)$.

But since we know the average kinetic energy in terms of the temperature, we can write: $E_{\text {int }}=\frac{3}{2} N k T$.

Free expansion is an adiabatic process: when the valve is opened, the gas expands with no change in its internal energy: $W=0, Q=0$, so $\Delta E_{\text {int }}=$ $0 \Rightarrow$ for an ideal gas $\Delta T=0$.


## The First Law of Thermodynamics

The change in internal energy of a closed system will be equal to the energy added to the system minus the work done by the system on its surroundings:

$$
\Delta E_{\mathrm{int}}=Q-W
$$

The work done in moving a piston by an infinitesimal displacement is

$$
d W=\overrightarrow{\mathbf{F}} \cdot d \vec{\ell}=P A d \ell=P d V
$$

For an isothermal process, $P=n R T / V$. Integrating to find the work done in taking the gas from point A to point $\mathrm{B}^{p^{1}}$ gives:

$$
W=\int_{V_{A}}^{V_{\mathrm{B}}} P d V=n R T \int_{V_{\mathrm{A}}}^{V_{\mathrm{B}}} \frac{d V}{V}=n R T \ln \frac{V_{\mathrm{B}}}{V_{\mathrm{A}}} .
$$



## Specific Heat $Q=m c \Delta T$.

The amount of heat required to change the temperature of a material is proportional to the mass and to the temperature change.

The specific heat, $c$, is characteristic of the material. Water has one of the highest specific heats of common substances, $\boldsymbol{c}=1 \mathrm{cal} / \mathrm{g}$.

## Latent Heat $Q=m L$.

Energy is required for a material to change phase,


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## TABLE 19-3 Simple Thermodynamic Processes and the First Law

| Process | What is constant: | The first law predicts: |
| :--- | :--- | :--- |
| Isothermal | $T=$ constant | $\Delta T=0$ makes $\Delta E_{\text {int }}=0$, so $Q=W$ |
| Isobaric | $P=$ constant | $Q=\Delta E_{\text {int }}+W=\Delta E_{\text {int }}+P \Delta V$ |
| Isovolumetric | $V=$ constant | $\Delta V=0$ makes $W=0$, so $Q=\Delta E_{\text {int }}$ |
| Adiabatic | $Q=0$ | $\Delta E_{\text {int }}=-W$ |

For gases, the specific heat depends on the process-the isobaric molar specific heat $C_{P}$ is different from the isovolumetric one $C_{V}$. For a monatomic ideal gas $\Delta E_{\text {int }}=\frac{3}{2} n R \Delta T=n C_{V} \Delta T$, so $C_{V}=\frac{3}{2} R$.
TABLE 19-4 Specific Heats of Gases at $15^{\circ} \mathrm{C}$

| Gas | Specific heats (kcal/kg•K) |  | Molar specific heats ( $\mathrm{cal} / \mathrm{mol} \cdot \mathrm{K}$ ) |  | $\begin{gathered} C_{P}-C_{V} \\ (\mathrm{cal} / \mathrm{mol} \cdot \mathrm{~K}) \end{gathered}$ | $\gamma=\frac{C_{P}}{C_{V}}$ | Note that$C_{P}-C_{V}=R$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $c_{V}$ | $c_{P}$ | $C_{V}$ | $C_{P}$ |  |  |  |
| Monatomic ${ }^{\text {a }}$ |  |  |  |  |  |  |  |
| He | 0.75 | 1.15 | 2.98 | 4.97 | 1.99 | 1.67 | where the gas constant |
| Ne | 0.148 | 0.246 | 2.98 | 4.97 | 1.99 | 1.67 |  |
| Diatomic |  |  |  |  |  |  |  |
| $\mathrm{N}_{2}$ | 0.177 | 0.248 | 4.96 | 6.95 | 1.99 | 1.40 | $R=1.99 \mathrm{cal} / \mathrm{mol} \cdot \mathrm{K}$ |
| $\mathrm{O}_{2}$ | 0.155 | 0.218 | 5.03 | 7.03 | 2.00 | 1.40 |  |
| Triatomic |  |  |  |  |  |  |  |
| $\mathrm{CO}_{2}$ | 0.153 | 0.199 | 6.80 | 8.83 | 2.03 | 1.30 |  |
| $\mathrm{H}_{2} \mathrm{O}\left(100^{\circ} \mathrm{C}\right)$ | 0.350 | 0.482 | 6.20 | 8.20 | 2.00 | 1.32 |  |

## Molar Specific Heats for Gases

1st Law: $\Delta E_{\mathrm{int}}=Q-W$; ideal gas: $P \Delta V+V \Delta P=R \Delta T$ for one mole ( $n=1$ ). In a constant-volume process, no work is done, so $Q_{V}=\Delta E_{\text {int }}=C_{\mathrm{V}} \Delta T$.
At constant pressure, $Q_{P}=C_{P} \Delta T=\Delta E_{\text {int }}+P \Delta V$.
Comparing these two processes for one mole of a monatomic gas when $\Delta T$ is the same gives
$Q_{P}=C_{\mathrm{P}} \Delta T=C_{\mathrm{V}} \Delta T+R \Delta T$, so dividing by $\Delta T$ gives

$$
C_{P}-C_{V}=R
$$

which is consistent with the measured values (note that $R=1.99 \mathrm{cal} / \mathrm{mol}-\mathrm{K}$ ). Then $\gamma=C_{\mathrm{P}} / C_{\mathrm{V}}$ is approximately $5 / 3=1.67$ for monatomic gases, $7 / 5=1.4$ for diatomic gases, and 9/7 = 1.3 for triatomic gases.

## Molar Specific Heats for Gases

Each mode of vibration or rotation is called a degree of freedom. The equipartition theorem states that the total internal energy is shared equally among the active degrees of freedom, each accounting for $1 / 2 k T$. At $T \approx 200-700 \mathrm{~K}$, rotations are active and add $k T$ for diatomic gases so $C_{v}=5 / 2 k T$ so $\gamma=7 / 5=1.4$; rotations add $2 k T$ for triatomic gases so $C_{V}=7 / 2 k T$ and $\gamma=9 / 7$.


## Adiabatic Expansion of a Gas

For an adiabatic expansion, $d E_{\text {int }}=-P d V$, since there is no heat transfer, and here $d E_{\text {int }}=n C_{V} d T$. From the ideal gas law, $P d V+V d P=n R d T$. Then $d E_{\text {int }}=-P d V=n C_{V} d T=n C_{V}(P d V+V d P) / n R$. Thus $-R P d V=C_{V}(P d V+V d P),\left(C_{V}+R\right) P d V+C_{V} V d P=0$, and dividing by $C_{V} P V$ gives $\left(C_{P} / C_{V}\right) P d V+V d P=0$.
We define: $\quad \gamma=\frac{C_{P}}{C_{V}}$. Integration then gives
the result for adiabatic expansion of an ideal gas:

$$
P V^{\gamma}=\text { constant. }
$$

## Heat Transfer by Radiation

$$
\frac{\Delta Q}{\Delta t}=\epsilon \sigma A T^{4}
$$

The constant $\sigma$ is called the Stefan-Boltzmann constant:

$$
\sigma=5.67 \times 10^{-8} \mathrm{~W} / \mathrm{m}^{2} \cdot \mathrm{~K}^{4}
$$

The emissivity $\epsilon$ is a number between 0 and 1 characterizing the surface; black objects have an emissivity near 1 , while shiny ones have an emissivity near 0 . It is the same for absorption; a good emitter is also a good absorber.

Heat conduction can be visualized as occurring through molecular collisions.

The heat flow per unit time is given by:

$$
\frac{\Delta Q}{\Delta t}=k A \frac{T_{1}-T_{2}}{\ell} .
$$



The constant $k$ is called the thermal conductivity.
Building materials are measured using $R$-values rather than thermal conductivity: $R=\ell / k$. Here, $\ell$ is the thickness of the material.

Convection occurs when heat flows by the mass movement of molecules from one place to another. It may be natural or forced; both these examples are natural convection:


## The Second Law of Thermodynamics

Clausius version: Heat can flow spontaneously from a hot object to a cold object; it will not flow spontaneously from a cold object to a hot object.

Kelvin-Planck version: No device is possible whose sole effect is to transform a given amount of heat completely into work.

Entropy version: The entropy of an isolated system is constant in reversible processes and increases in irreversible ones.

## Heat Engines

We consider only engines that run in a repeating cycle; the change in internal energy over a cycle is zero, since the system returns to its initial state.

The high-temperature reservoir transfers an amount of heat $Q_{\mathrm{H}}$ to the engine, where part of it is transformed into work $W$ and the rest, $Q_{\mathrm{L}}$, is exhausted to the lower temperature reservoir. Thus $W=Q_{\mathrm{H}}-Q_{\mathrm{L}}$. Note that all three of these quantities are positive.


The efficiency of the heat engine is the ratio of the work done to the heat input:

$$
e=\frac{W}{Q_{\mathrm{H}}} .
$$

Using conservation of energy to eliminate $W$, we find:

$$
\begin{aligned}
e & =\frac{W}{Q_{\mathrm{H}}} \\
& =\frac{Q_{\mathrm{H}}-Q_{\mathrm{L}}}{Q_{\mathrm{H}}}=1-\frac{Q_{\mathrm{L}}}{Q_{\mathrm{H}}} .
\end{aligned}
$$

The Carnot cycle consists of:

- Isothermal expansion ab
- Adiabatic expansion bc
- Isothermal compression cd
- Adiabatic compression da

The area enclosed in the $P-V$
 diagram is the work $W$ done in the cycle since $\mathrm{d} W=P \mathrm{~d} V$.

We can alternatively draw the Carnot cycle in a T-S diagram. The area in the $T-S$ diagram is the heat $Q$ transferred since $\mathrm{d} Q=T \mathrm{~d} S$. It is also the work done $W$, by energy conservation.


## Proof that for a Carnot cycle

 with an ideal gas $\quad \frac{Q_{\mathrm{L}}}{Q_{\mathrm{H}}}=\frac{T_{\mathrm{L}}}{T_{\mathrm{H}}}$.In the isothermal processes

$$
Q_{\mathrm{H}}=W_{\mathrm{ab}}=n R T_{\mathrm{H}} \ln \frac{V_{\mathrm{b}}}{V_{\mathrm{a}}}
$$

and $Q_{\mathrm{L}}=n R T_{\mathrm{L}} \ln \frac{V_{\mathrm{c}}}{V_{\mathrm{d}}}$.

$\boldsymbol{P} \boldsymbol{V}^{\gamma}=$ constant and $P V / T=$ constant $\Rightarrow \frac{V_{\mathrm{b}}}{V_{\mathrm{a}}}=\frac{V_{\mathrm{c}}}{V_{\mathrm{d}}}$.
Substituting into the expressions above for $Q_{H}, Q_{L}$
we see that $\frac{Q_{\mathrm{L}}}{Q_{\mathrm{H}}}=\frac{T_{\mathrm{L}}}{T_{\mathrm{H}}}$. Thus for a Carnot cycle,
the efficiency $e=1-\frac{Q_{\mathrm{L}}}{Q_{\mathrm{H}}}=1-\frac{T_{\mathrm{L}}}{T_{\mathrm{H}}}$

Refrigerators, Air Conditioners, and Heat Pumps
These appliances are essentially heat engines operating in reverse.

By doing work, heat is extracted from the cold reservoir and exhausted to the hot reservoir.

Refrigerator performance is measured by the coefficient of performance (COP):


$$
\operatorname{COP}=\frac{Q_{\mathrm{L}}}{W}=\frac{Q_{\mathrm{L}}}{Q_{\mathrm{H}}-Q_{\mathrm{L}}} .
$$

For an ideal Carnot refrigerator $Q_{H} / Q_{L}=T_{H} / T_{L}$, so

$$
\mathrm{COP}_{\text {ideal }}=\frac{T_{\mathrm{L}}}{T_{\mathrm{H}}-T_{\mathrm{L}}} .
$$

Refrigerators, Air Conditioners, and Heat Pumps A heat pump can heat a house in the winter:


The heat pump coefficient of performance is defined as

$$
\mathrm{COP}=\frac{Q_{\mathrm{H}}}{W} .
$$

As usual, it's what we want divided by what we pay for.

## Entropy

Definition of the change in entropy $S$ when an amount of heat $Q$ is added:

$$
\Delta S=\frac{Q}{T}
$$

if the process is reversible and the temperature is constant. Otherwise,

$$
d S=\frac{d Q}{T}
$$

## Entropy is a State Variable

For a Carnot cycle $Q_{\mathrm{H}} / Q_{\mathrm{L}}=T_{\mathrm{H}} / T_{\mathrm{L}}$ so $Q_{\mathrm{H}} / T_{\mathrm{H}}-Q_{\mathrm{L}} / T_{\mathrm{L}}=0$. Thus, if we approximate any reversible cycle (a) as an infinite sum of Carnot cycles as in (b), we see that the integral of $d Q / T$ around a closed path is zero. This means that entropy is a state variable like potential energy, the change in its value depends only on the initial and final states.


## Entropy \& the 2nd Law of Thermodynamics

The fact that after every interaction the entropy of the system plus the environment never decreases is another way of putting the 2nd Law:

The entropy of an isolated system never decreases. It either stays constant $\Delta S=0$ (reversible processes) or increases $\Delta \mathrm{S}>0$ (irreversible processes).
$\Delta \mathrm{S}=\mathrm{Q} / \mathrm{T}_{\mathrm{L}}-\mathrm{Q} / \mathrm{T}_{\mathrm{H}}>0$ for $\mathrm{T}_{\mathrm{L}} \stackrel{\mathrm{Q}}{\longleftrightarrow \mathrm{T}_{\mathrm{H}}}$ shows that
Heat can flow spontaneously from a hot object to a cold object; it will not flow spontaneously from a cold object to a hot object.
(Clausius 2nd Law)

How much higher entropy does a mole of ideal gas at $20^{\circ} \mathrm{C}$ occupying 100 liters have compared to a mole of gas at $20^{\circ} \mathrm{C}$ occupying 10 liters?
To calculate this, consider a reversible isothermal expansion. Since the internal energy of an ideal gas depends only on $T$, it doesn't change in the expansion. Thus $\mathrm{d} Q=\mathrm{d} W=P \mathrm{~d} V$, and $P=n R T / V$, so
$\Delta S=\int \mathrm{d} Q / T=\int(n R T / V) \mathrm{d} V / T=n R \ln \left(V_{\mathrm{f}} / V_{\mathrm{i}}\right)$
Here $\Delta S=R \ln 10=(2.0 \mathrm{cal} / \mathrm{K})(2.3)=4.6 \mathrm{cal} / \mathrm{K}$.

Statistical determination of entropy: Determine the change in entropy for the adiabatic free expansion of one mole of an ideal gas as its volume increases by a factor of 10 . Assume $\mathbb{W}$, the number of microstates for each macrostate, is the number of possible positions of the gas molecules, and use Boltzmann's formula $S=k \ln \mathscr{W}$.
When the volume increases by a factor of 10, the number of positions of each molecule increases by the same factor. Thus the number of microstates increases by $10{ }^{A}$, where $N_{A}=$ Avogadro's number. Then Boltzmann's formula for the entropy gives

$$
\Delta S=k \ln 10^{N_{A}}=k N_{A} \ln 10=R \ln 10
$$

in agreement with the thermodynamic calculation!

Life could not have arisen spontaneously from non-life because life is more ordered than nonlife, and this would imply a spontaneous decrease in entropy, which is forbidden by the second law of thermodynamics.

A. True

B. False because entropy can decrease in any system.
C. False because entropy can decrease in an open system such as a living organism.

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