Physical Principles in Biology
Biology 3550
Spring 2024

Lecture 24

Introduction to Thermodynamics:

Expansion of a Gas

Monday, 11 March 2024

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Announcements

- Midterm Exam:
  - Friday, 15 March
  - Will cover all material from before Spring Break
  - 50 min
- Review Session
  - 5:15 PM, Thursday, 14 March
  - HEB 2002
  - Come with questions!

Why is Thermodynamics Important?

- Thermodynamics is the fundamental science of energy, something almost everyone cares about! (because we pay for it)

- Defines the rules for interchange of different forms of energy.
  (*e.g.,* the conversion of an H^+ concentration gradient into mechanical motion in the bacterial rotary motor.)

- Places strict constraints on whether or not a physical, chemical or biological process is favorable under specified conditions.

  But, it won't say whether the process will take place, or by what mechanism or how fast!

- Particularly important in the context of climate change and society's need for energy.

Why is Thermodynamics Hard?

- The ideas are abstract and subtle.
- It depends on math! (And, the quantities are subtle.)
- The language can be confusing (and varies among disciplines).
- Historical confusion.
  - Developed over multiple generations of scientists in the 18^{th}–20^{th} centuries.
  - Periods of profound confusion.
- But it’s worth it!

Units of Energy

- Energy is the ability to do work.
- Unit of work or energy: $1\,\text{J} = 1\,\text{N}\cdot\text{m} = 1\,\text{Kg}\cdot\text{m}^2/\text{s}^2$
  Energy required to apply 1 N of force over a distance of 1 m.

  $1\,\text{J} = 1\,\text{watt}\cdot\text{s} \qquad 1\,\text{kwatt}\cdot\text{hr} = 3.6\times10^6\,\text{J}$
- Another unit of energy commonly used in thermodynamics: calorie
  - Originally defined as energy required to raise the temperature of 1 g of water by 1°C. (depends on starting temperature)
  - Now defined as exactly 4.184 J
- "Big C" Calorie, or "kg calorie": 1 Calorie = 1,000 calories.
  - Energy required to raise the temperature of 1 kg of water by 1°C.
  - Big C Calorie is the one used for nutritional information.
- Calorie units are still commonly used in thermodynamics because they directly relate energy to temperature.

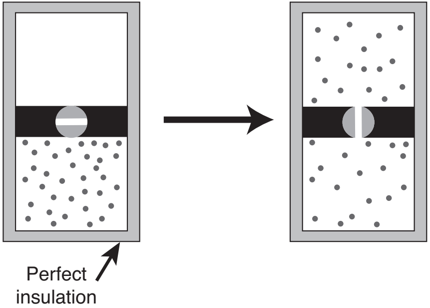
Temperature Versus Heat

- Temperature
  - A property of matter, which we measure with a thermometer.
  - Directly related to the kinetic energy of the molecules making up the matter.
  - For an ideal gas, $\mathrm{RMS}(E_\mathrm{k}) = 3kT/2$
    Three degrees of translational freedom, in x-, y-, and z-direction.
  - Non-ideal gasses, liquids and solids have additional motional modes and generally greater kinetic energy at a given temperature.
- Heat
  - Sometimes described as a “form of energy”, and it has the units of energy (joule or calorie).
  - Better definition: Flow of energy from a warmer object to a cooler one; equilibration of kinetic energy.
  - At one time, heat was thought to be a massless substance, called “caloric”, that moved within or between objects.

Our Starting Point for Thermodynamics: Expansion and Compression of Gasses

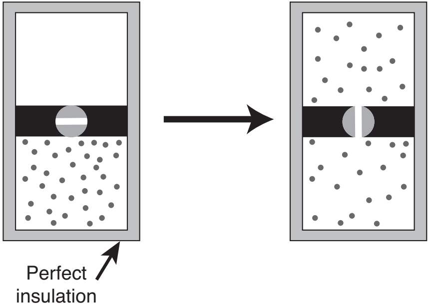
- Historical origins:
  - Development of thermodynamics was first motivated by the invention of the steam engine, and the desire to make better ones.
  - Many of the basic ideas were formulated in this context and are still easiest to visualize in it.
  - Original treatments did not consider molecular motion (because it wasn't understood) and were very abstract; "classical thermodynamics."
  - Molecular interpretation developed later, "statistical thermodynamics".
- We will use both classical and statistical viewpoints, which complement each other.
- An ideal gas is the simplest system in which to formulate ideas.
- Also ties back to our discussion of molecular motion in diffusion.

Adiabatic (without heat flow) Expansion of a Gas



- Insulation prevents heat flow into or out of device.
- What changes?

Clicker Question #1



Which of the following properties of the gas change?

A) Temperature

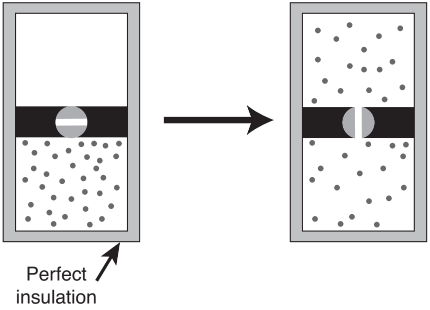
B) Pressure

C) Volume

D) Kinetic energy

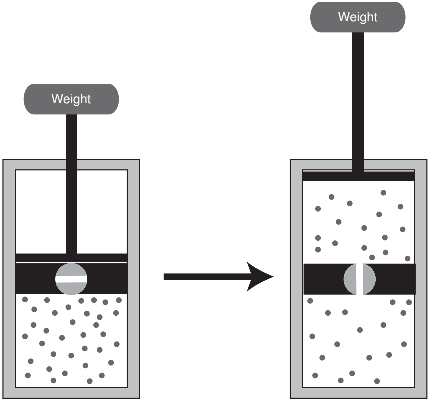
Any answers count for now!

Adiabatic (without heat flow) Expansion of a Gas



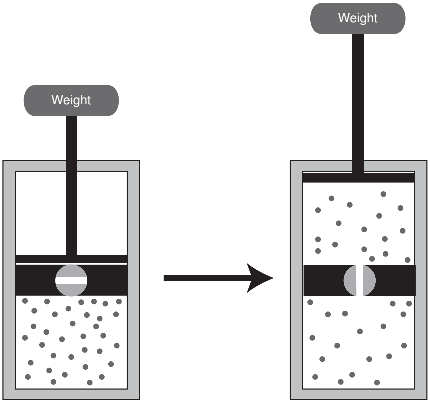
- Insulation prevents heat flow into or out of device.
  - Temperature stays constant.
- What changes?
  - Volume of gas increases.
  - Pressure of gas decreases ($PV = nRT$)
  - Does the energy stay constant? (yes)
  - Has any work been done? (no)
  - Has anything else changed?

Adiabatic Gas Expansion With Work



- Collisions of gas molecules with piston move the weight up.
- What changes?

Clicker Question #2



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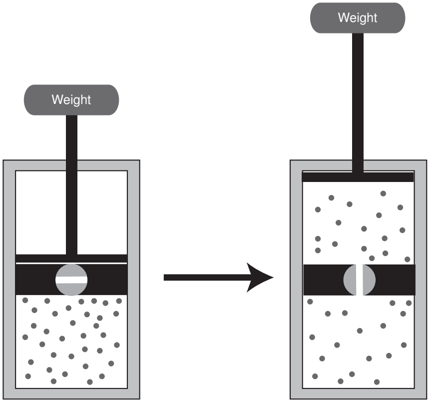
Adiabatic Gas Expansion With Work



- Collisions of gas molecules with piston move the weight up.
- What changes?
  - Volume of gas? (increases)
  - Temperature? (decreases as energy is transferred to piston)
  - Pressure? (decreases, more than without the piston)
  - Energy?
    Has any work been done? (yes)
  - Where did the energy to do the work come from?
    Gas molecules have lost kinetic energy.

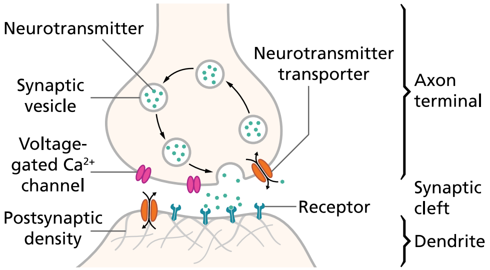
Rules for Keeping Score

- Change in energy of the gas molecules (the "system"):

$$\Delta E = E_{\text{final}} - E_{\text{start}}$$

- Work, w:
  - $w > 0$, when work is done <u>on</u> the system.
  - $w < 0$, when the system does work on the outside world, as in the expansion of the gas.
- For the adiabatic expansion of a gas with work:
  - $E_{\text{final}} < E_{\text{start}}$, and $\Delta E < 0$
  - $w < 0$, because the system did work.
  - $\Delta E = w$: Where else could the energy come from?
  - Does ΔE always equal w?
- Some books use the opposite sign convention for w.

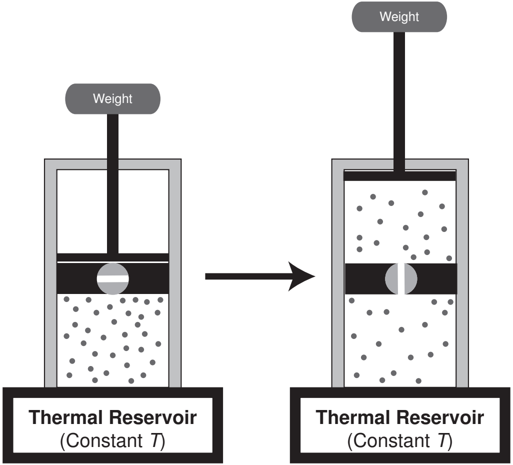
What Does This Have to Do with Biology?



- Dilution of molecules in solution is analogous to expansion of a gas.
- Work (energy) is required to package neurotransmitters into vesicles.
- How much energy is lost when neurotransmitters are released into a synapse?
- Other examples of dilution and concentration in biology?

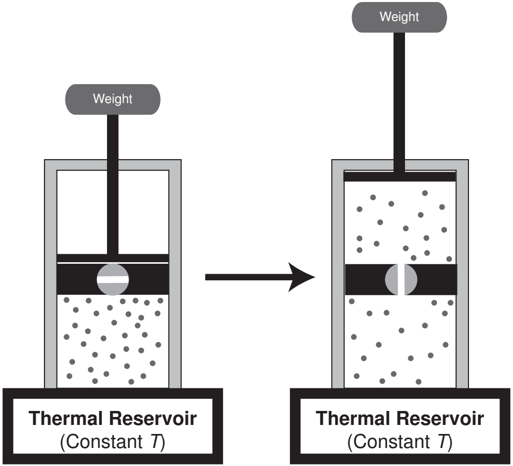
https://en.wikipedia.org/wiki/Chemical_synapse
Thomas Splettstoesser (www.scistyle.com)

Isothermal Expansion with Work



- Reservoir restores the gas temperature. (isothermal)
- What changes?

Clicker Question #3



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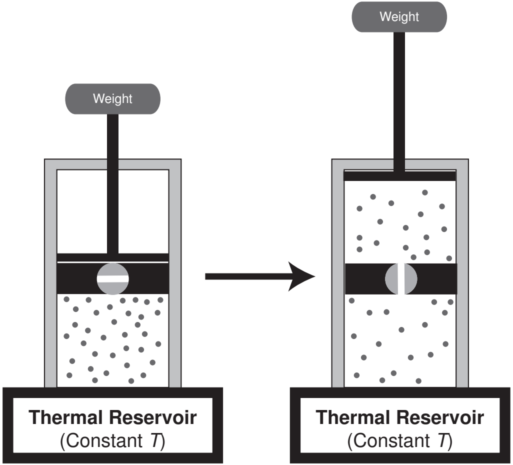
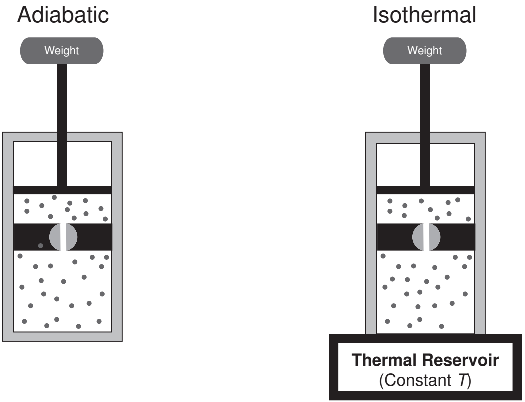
Isothermal Expansion with Work



- Reservoir restores the gas temperature.
- What changes?
  - Heat flows to keep gas temperature the same as the reservoir (which doesn't change).
  - As piston is pushed up, gas molecules lose energy, and temperature drops.
  - Heat flows from reservoir to restore temperature.
  - At the end, temperature is the same as at the beginning, *and* work has been done!

Is More Work Done in the Adiabatic or Isothermal Expansion?

Part way through the two expansion processes:

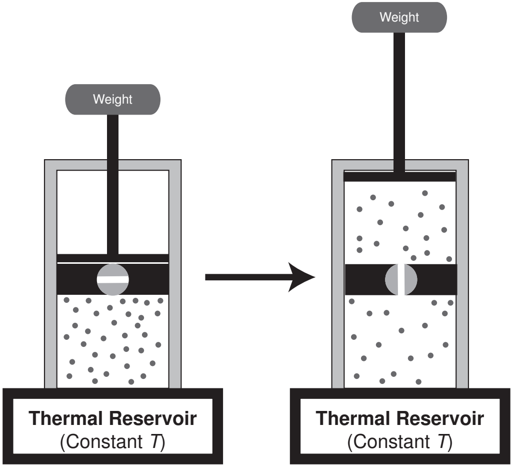


- $V_{ad} = V_{isot}$
- $T_{ad} < T_{isot}$
- $P_{ad} < P_{isot}$
- $F_{ad} < F_{isot}$

  P= Force/area.
- $w = -\int F dx$
- $w_{isot} < w_{ad}$

- A more negative value of w means that the system does more work on the surroundings.

Isothermal Expansion with Work



- The scorecard:
  - $\Delta E = 0$, temperature hasn't changed.
  - $w < 0$, because the system did work.
  - $\Delta E \neq w$
  - Where did the energy for work come from?
  - Heat flow into the system.

Scorecard for Isothermal Expansion with Work

- Energy, E. Temperature at start and end are equal, $\Delta E = 0$.
- Work, w. Work has been done by the system, $w < 0$.
- A new quantity: Heat, q.
  - $q > 0$, when heat flows <u>into</u> the system.
  - $q < 0$, when heat flows out of the system into the surroundings.
  - For both work, w, and heat, q, a positive value indicates a transfer <u>to</u> the system from the surroundings.
- For this case, $q > 0$.

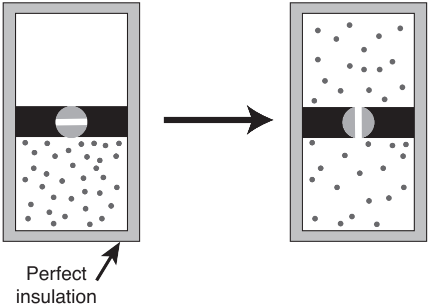
The First Law of Thermodynamics

- Common statements in words:
  - "The energy of the universe is conserved"
  - "Energy cannot be created or destroyed"
  - Later modified to account for interconversion of mass and energy. (Einstein's $E = mc^2$)
- The formal mathematical statement: For any process,

$$\Delta E = q + w$$

  - Any change in the energy of the system has to be accounted for by work or heat.
  - Work and heat represent the transfer of energy from the surroundings to the system.
  - Ignores other forms of energy, such as electromagnetic radiation.
- We can apply the first law to the three gas expansion experiments.

Adiabatic (without heat flow) Expansion of a Gas



First law summary

- $q = 0$

  Insulation prevents heat flow

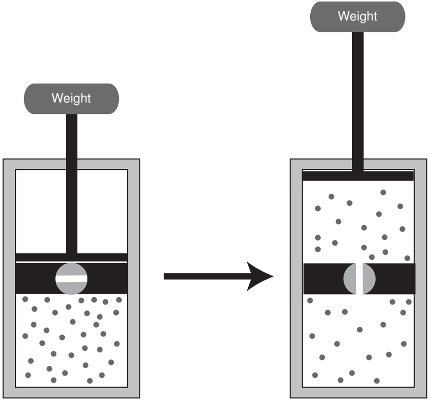
- $w = 0$

  No work is done

- $\Delta E = q + w = 0$

  Consistent with no temperature change.

Adiabatic Gas Expansion With Work



First law summary

- $q = 0$

  Insulation prevents heat flow.

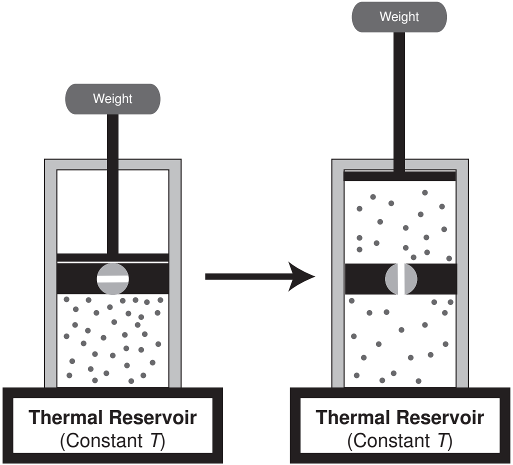
- $w < 0$

  Work is done by the system.

- $\Delta E = q + w = w < 0$

  Consistent with temperature decrease.

Isothermal Expansion with Work



First law summary

- $\Delta E = 0$

  Temperature doesn't change.

- $w < 0$

  Work is done <u>by</u> the system.

- $q > 0$

  Heat flows <u>into</u> the system.

- $\Delta E = q + w = 0$ and $q = -w$

  Heat flow and work are balanced, and temperature doesn't change.

Laws and Thermodynamics

- The laws of thermodynamics cannot be derived or proven!
- The laws are postulates, which no one has been able to disprove.

  And people have tried really hard!
- In 1775 the French Royal Academy of Sciences made the first law of thermodynamics (before it was called that) a legal law!

  Declared that the French patent office would no longer accept applications to patent perpetual motion machines.