Physical Principles in Biology
Biology 3550
Fall 2016

Lecture 24

Thermodynamics: Expansion and Compression of a Gas

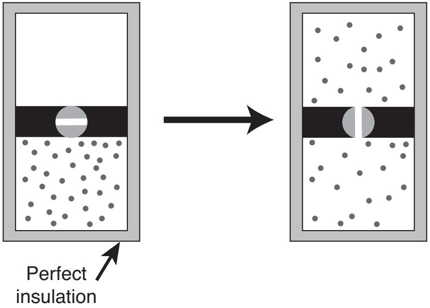
Wednesday, 26 October

©David P. Goldenberg
University of Utah
goldenberg@biology.utah.edu

Our Starting Point for Thermodynamics: Expansion and Compression of Gasses

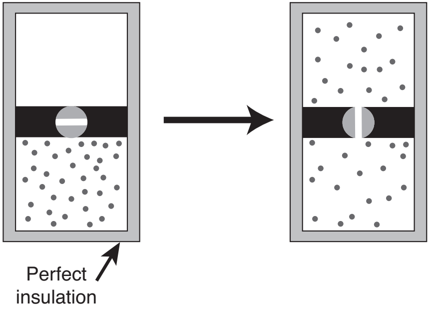
- Historical origins:
  - Development of thermodynamics was first motivated by the invention of the steam engine, and the desire to make better ones.
  - Many of the basic ideas were formulated in this context and are still easiest to visualize in it.
  - Original treatments did not consider molecular motion (because it wasn't understood) and were very abstract; "classical thermodynamics."
  - Molecular interpretation developed later, "statistical thermodynamics".
  - Classical and statistical thermodynamics are each self-sufficient and are consistent with one another.
- 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

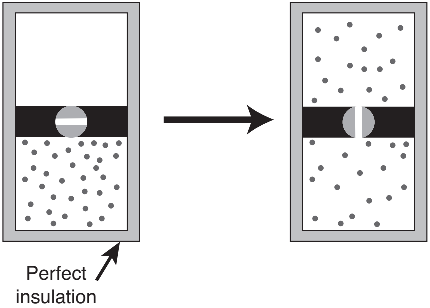


Which of the following properties of the gas change?

1. Temperature
2. Pressure
3. Volume
4. Kinetic energy

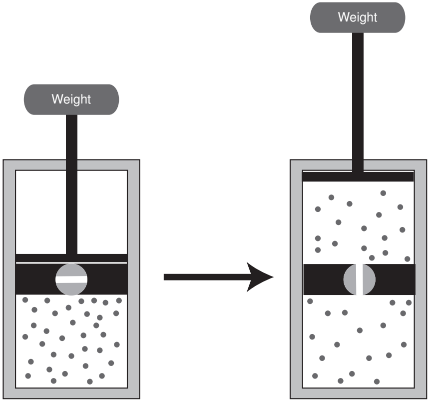
Any answers count for now!

Adiabatic (without heat flow) Expansion of a Gas



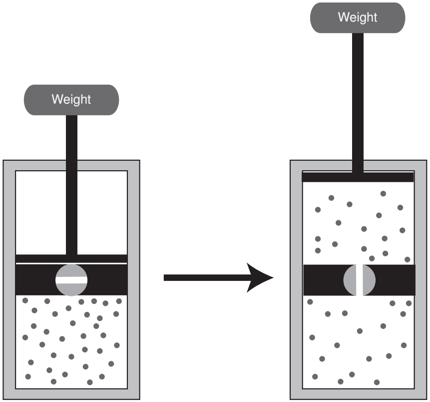
- Insulation prevents heat flow into or out of device.
- What changes?
  - Volume of gas increases.
  - Pressure of gas decreases ($PV = nRT$)
  - Temperature stays constant.
  - Energy stays constant?
  - Has any work been done? (no)
  - Anything else changed?

Adiabatic Gas Expansion With Work



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

Clicker Question #2



Which of the following properties of the gas change?

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4. Energy

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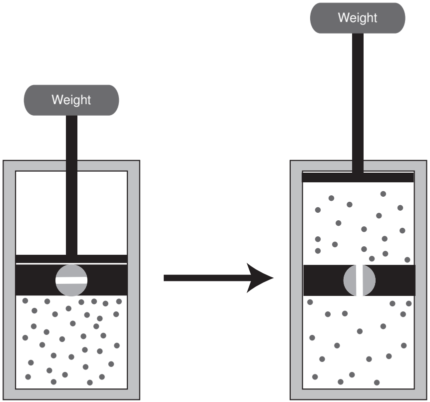
Adiabatic Gas Expansion With Work



- 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 weight)
  - Energy?
Has any work been done?
(yes)
  - Where did the energy to do the work come from?
Gas molecules have lost kinetic energy.

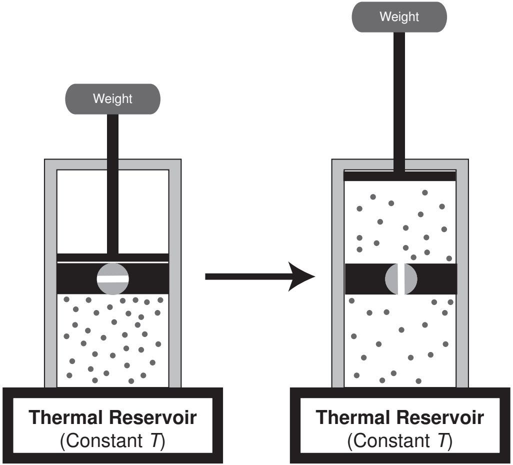
Rules for Keeping Score

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

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

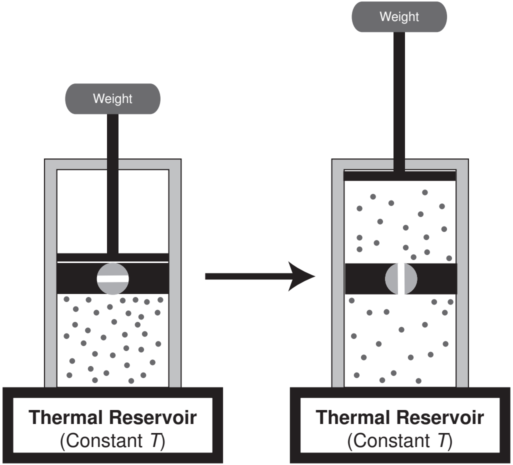
- Work, w:
  - $w > 0$, when work is done on the system.
  - $w < 0$, when the system does work on the outside world, as in the expansion of the gas.
- For the adiabatic expansion of a gas with work:
  - $E_{\text{final}} < E_{\text{start}}$, and $\Delta E < 0$
  - $w < 0$, because the system did work.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

Isothermal Expansion with Work



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

Clicker Question #3



Which of the following change?

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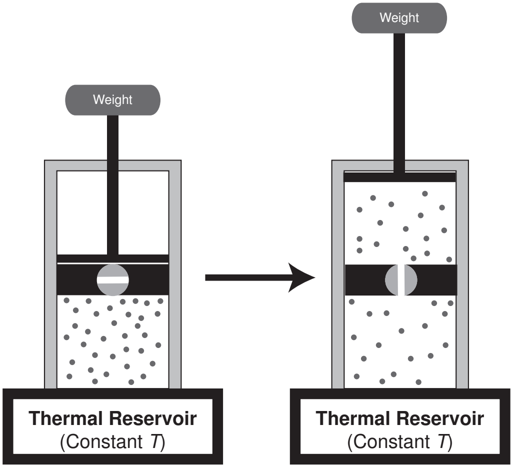
2. Pressure
3. Volume
4. Energy

Any answers count for now!

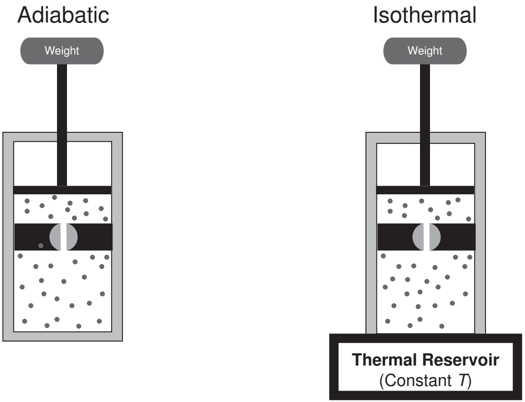
Isothermal Expansion with Work



- Reservoir keeps the gas temperature constant. (isothermal)
- 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:



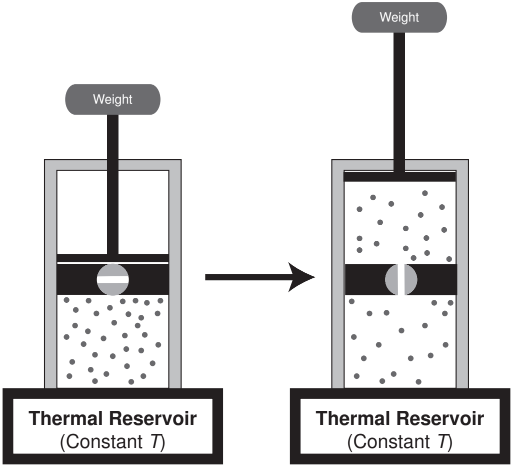
- $V_{ad} = V_{isot}$
- $T_{ad} < T_{isot}$
- $P_{ad} < P_{isot}$
- $F_{ad} < F_{isot}$

  $P =$ Force/area.

- $w_{isot} < w_{ad}$

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

Isothermal Expansion with Work

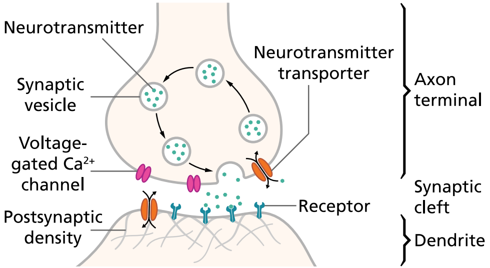


- The scorecard:
  - $\Delta E = 0$, temperature hasn't changed.
  - $w < 0$, because the system did work.
  - $\Delta E \neq w$
  - Where did the energy for work come from?
  - Heat flow into the system.

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 into 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 to the system from the surroundings.
- For this case, $q > 0$.

What Does This Have to Do with Biology?



- Dilution of molecules in solution is analogous to expansion of a gas.
- How much 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?

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.
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- For this case, $q > 0$.

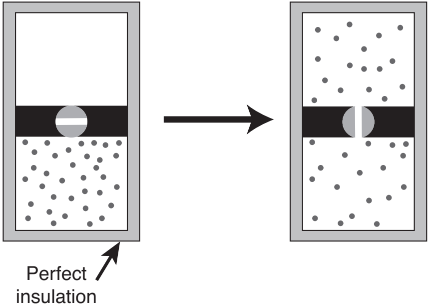
The First Law of Thermodynamics

- Common statements in words:
  - "The energy of the universe is conserved"
  - "Energy can not 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.
- 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

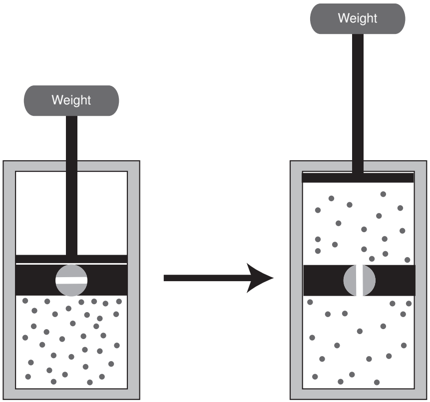
- $w = 0$

  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.

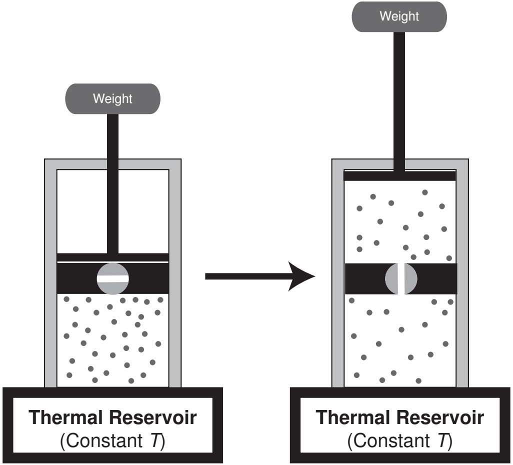
- $w < 0$

  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, that 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.

State Functions and Path-dependent Functions

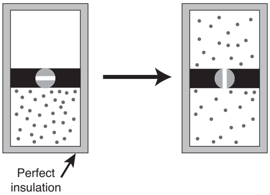
- State functions of a system depend only on the current state of the system and do not depend on history.
  Examples:
  - Temperature, T
  - Pressure, P
  - Volume, V
  - Energy, E
- For any change in a system, the change in a state function depends only on the beginning and ending states.

$$\Delta T = T_{\text{final}} - T_{\text{start}}$$
$$\Delta P = P_{\text{final}} - P_{\text{start}}$$
$$\Delta V = V_{\text{final}} - V_{\text{start}}$$
$$\Delta E = E_{\text{final}} - E_{\text{start}}$$

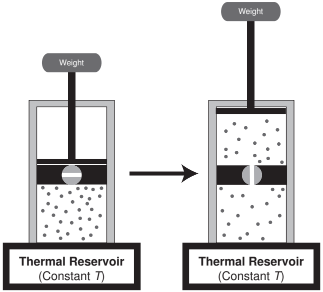
- Work, w, and heat, q, are <u>not</u> state functions.

Adiabatic vs. Isothermal Gas Expansion

Adiabatic



Isothermal



- The two processes start and end in the same states:

$$\Delta V_{ad} = \Delta V_{isot} > 0 \qquad \Delta P_{ad} = \Delta P_{isot} < 0$$

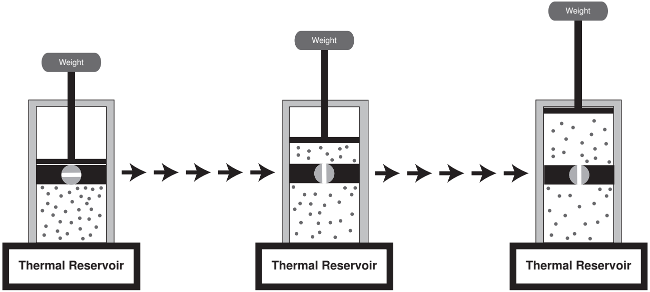
$$\Delta T_{ad} = \Delta T_{isot} = 0 \qquad \Delta E_{ad} = \Delta E_{isot} = 0$$

- But, the heat and work for the two processes are different:

$$w_{ad} = 0 \qquad w_{isot} < 0 \qquad q_{ad} = 0 \qquad q_{isot} > 0$$

- Heat and work are "path-dependent" functions.

The Maximum-work Path for Gas Expansion



- Piston is allowed to move upward in infinitesimally small steps.
- Temperature is never allowed to drop.
- Pressure drops as gas expands, so less work is done per step.
- If larger steps are ever taken:
  - The temperature drops.
  - The pressure drops <u>more</u> than it would in an infinitesimal step.
  - Less work is produced.