Physical Principles in Biology
Biology 3550
Fall 2017

Lecture 24

Thermodynamics: Energy, Heat and Work

and

The First Law

Wednesday, 25 October

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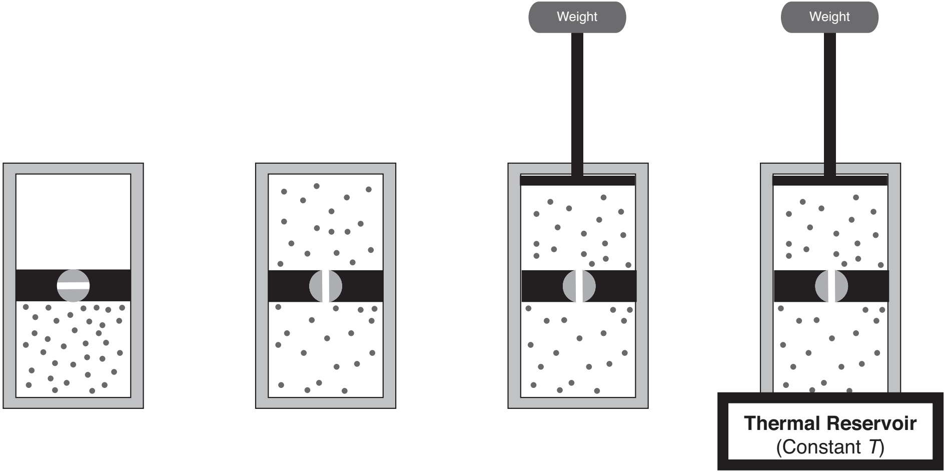
Different Ways to Allow a Gas to Expand



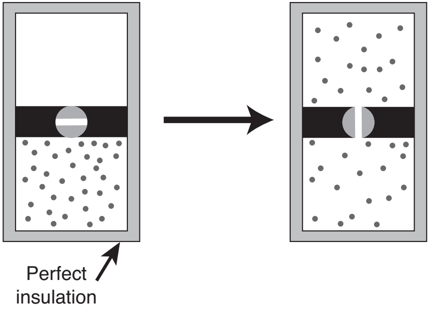
Starting state

Adiabatic expansion

Adiabatic expansion with work

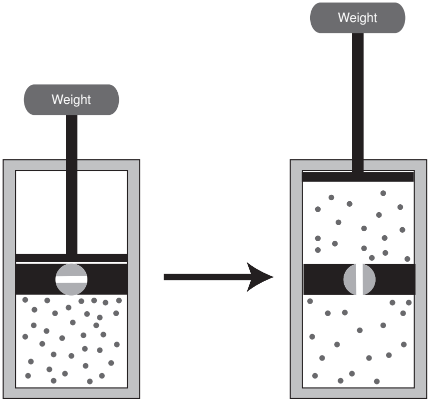
Isothermal expansion with work

Adiabatic (without heat flow) Expansion of a Gas



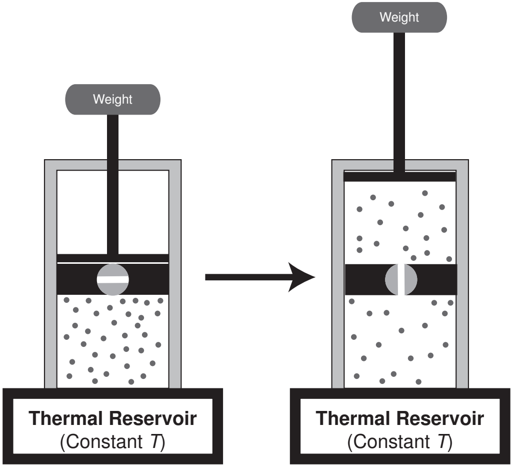
- Insulation prevents heat flow into or out of device.
- What changes?
  - Volume of gas increases.
  - Temperature stays constant.
  - Pressure of gas decreases ($P = nRT/V$)
  - Energy stays constant.
  - No work has been done.
  - Anything else changed?

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. ($P = nRT/V$)
  - Kinetic energy of gas molecules has decreased.
  - Work is done *by the system*, $w < 0$.

Isothermal Expansion with Work



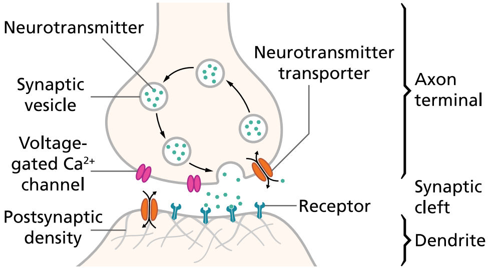
The scorecard:

- $\Delta E = 0$, 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, $q > 0$.

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?

The First Law of Thermodynamics

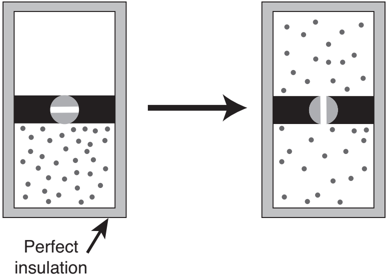
- Common statements in words:
  - "The energy of the universe is conserved"
  - "Energy can not be created or destroyed"
  - Later modified to account for interconversion of mass and energy. (Einstein's $E = mc^2$)
- The formal mathematical statement: For any process,

$$\Delta E = q + w$$

  - Any change in the total energy of the system has to be accounted for by work or heat.
  - Work and heat represent the exchange of energy between the surroundings and the system.
- We can apply the first law to the three gas expansion experiments.

Clicker Question #1

Adiabatic Expansion
Without Work



Which of the following is true?

1. $q < 0$
2. $q = 0$
3. $q > 0$
4. $w < 0$
5. $w = 0$
6. $w > 0$
7. $\Delta E < 0$
8. $\Delta E = 0$
9. $\Delta E > 0$

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

Up to 3 answers accepted.

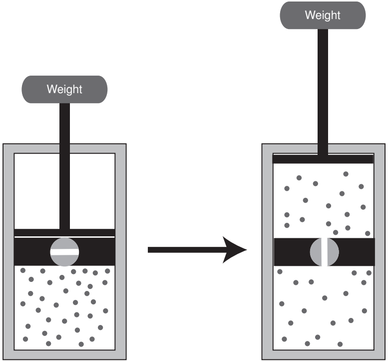
Correct answers are worth $\frac{1}{2}$ point.

Wrong answers cost $\frac{1}{2}$ point.

Total guaranteed to be ≥ 0.

Clicker Question #2

Adiabatic Expansion
With Work



Which of the following is true?

1. $q < 0$
2. $q = 0$
3. $q > 0$
4. $w < 0$
5. $w = 0$
6. $w > 0$
7. $\Delta E < 0$
8. $\Delta E = 0$
9. $\Delta E > 0$

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

Up to 3 answers accepted.

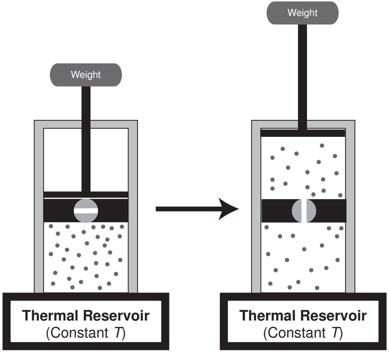
Correct answers are worth $\frac{1}{2}$ point.

Wrong answers cost $\frac{1}{2}$ point.

Total guaranteed to be ≥ 0.

Clicker Question #3

Isothermal Expansion
With Work



Which of the following is true?

1. $q < 0$
2. $q = 0$
3. $q > 0$
4. $w < 0$
5. $w = 0$
6. $w > 0$
7. $\Delta E < 0$
8. $\Delta E = 0$
9. $\Delta E > 0$

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

$$q = -w$$

Up to 3 answers accepted.

Correct answers are worth $\frac{1}{2}$ point.

Wrong answers cost $\frac{1}{2}$ point.

Total guaranteed to be ≥ 0.

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.
- Laws place limits on models and theories:

  If a model can be shown to violate a law of thermodynamics, it is wrong! (with %99.999 certainty)

State Functions and Path-dependent Functions

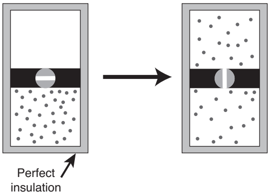
- State functions of a system depend only on the current state of the system and do not depend on history.
  Examples:
  - Temperature, T
  - Pressure, P
  - Volume, V
  - Energy, E
- For any change in a system, the change in a state function depends only on the beginning and ending states.

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

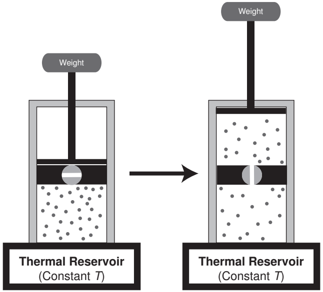
- Work, w, and heat, q, are not state functions.

Adiabatic vs. Isothermal Gas Expansion

Adiabatic



Isothermal



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

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

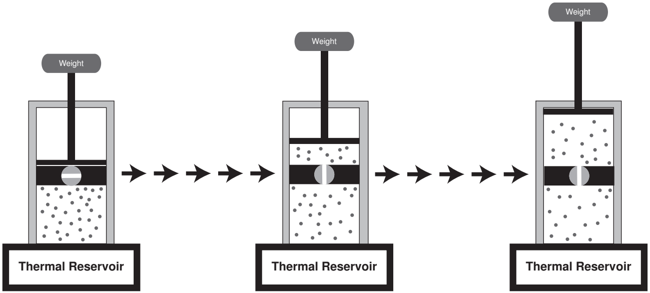
$$\Delta T_{ad} = \Delta T_{isot} = 0 \qquad \Delta E_{ad} = \Delta E_{isot} = 0$$

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

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

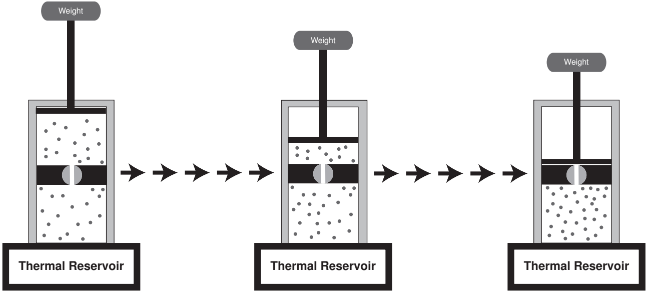
- Heat and work are "path-dependent" functions.

The Maximum-work Path for Gas Expansion



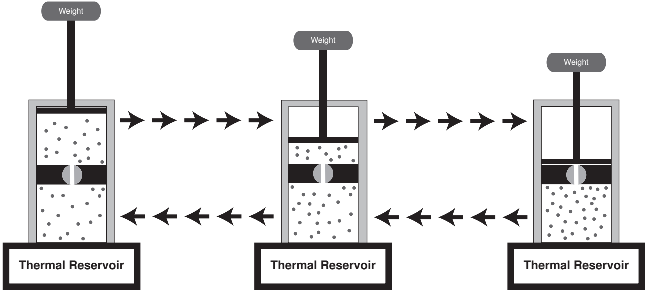
- Piston is allowed to move upward in infinitesimally small steps.
- Temperature is never allowed to drop.
- Pressure drops as gas expands, so less work is done per step.
- If larger steps are ever taken:
  - The temperature drops.
  - The pressure drops <u>more</u> than it would in an infinitesimal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

The *Minimum*-work Path for Gas *Compression*



- Piston is pushed down in infinitesimally small steps.
- Energy is transferred from piston to gas molecules.
- Temperature is never allowed to increase.
- *P* increases as gas is compressed, so more work is required per step.
- If larger steps are ever taken: Temperature increases, and more work is required.

A Reversible Cycle of Compression and Expansion



- Steps in both directions are infinitesimal.
- Compression and expansion are exactly the reverse of one another.

$$w_{\mathrm{comp}} = -w_{\mathrm{exp}} = -q_{\mathrm{comp}} = q_{\mathrm{exp}}$$

- For the complete cycle:

$$\Delta E = 0 \qquad w = 0 \qquad q = 0$$

- Either compression or expansion can be reversed at any point by an infinitesimal force in the opposite direction.