Physical Principles in Biology

Biology 3550

Spring 2024

Lecture 24

Thermodynamics:

The First Law, State Functions and Free Energy

Wednesday, 13 March 2024

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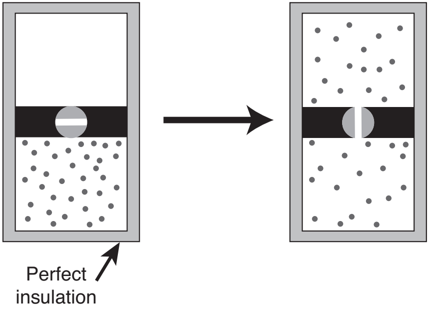
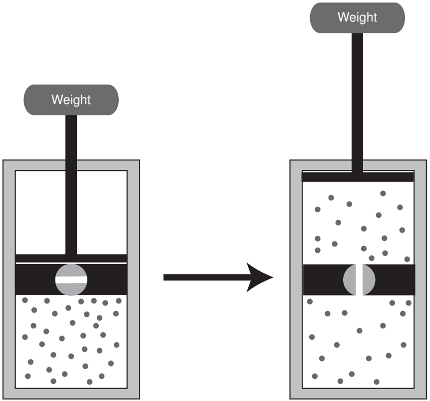
Announcements

- 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!

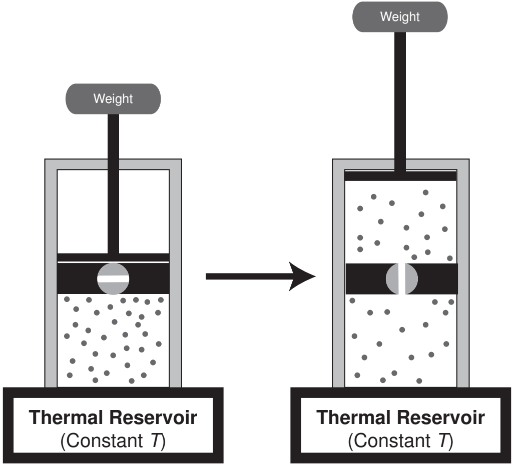
Adiabatic (without heat flow) Expansion of a Gas



Adiabatic Gas Expansion With Work



Isothermal Expansion with Work



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.
- 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.

The First Law of Thermodynamics

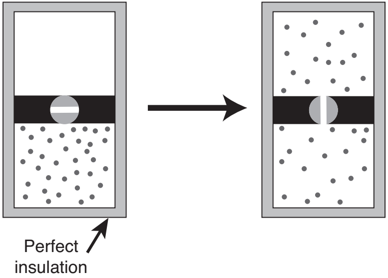
- Common statements in words:
  - “The energy of the universe is conserved”
  - “Energy cannot be created or destroyed” s
  - Later modified to account for interconversion of mass and energy. (Einstein’s $E = mc^2$)
- The formal mathematical statement: For any process,

$$\Delta E = q + w$$

  - 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.

Clicker Question #1

Adiabatic Expansion
Without Work



Which of the following is true?

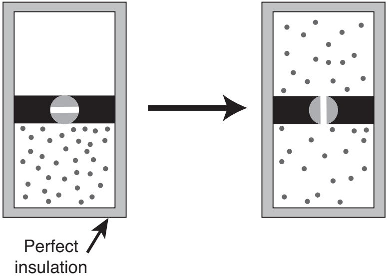
A) $q < 0$

B) $q = 0$

C) $q > 0$

Clicker Question #2

Adiabatic Expansion
Without Work



Which of the following is true?

- $q < 0$
- $q = 0$
- $q > 0$

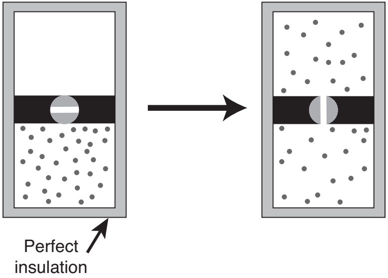
A) $w < 0$

B) $w = 0$

C) $w > 0$

Clicker Question #3

Adiabatic Expansion
Without Work



Which of the following is true?

- $q < 0$
- $q = 0$
- $q > 0$

- $w < 0$
- $w = 0$
- $w > 0$

A) $\Delta E < 0$

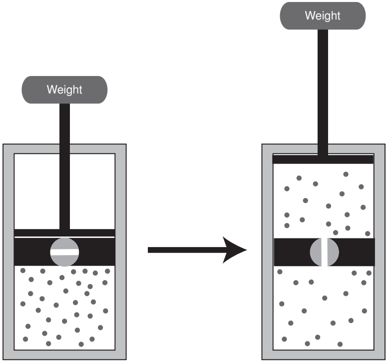
B) $\Delta E = 0$

C) $\Delta E > 0$

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

Clicker Question #4

Adiabatic Expansion
With Work



Which of the following is true?

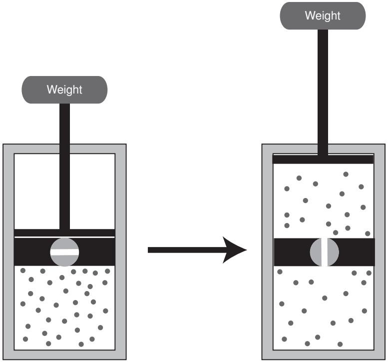
A) $q < 0$

B) $q = 0$

C) $q > 0$

Clicker Question #5

Adiabatic Expansion
With Work



Which of the following is true?

- $q < 0$
- $q = 0$
- $q > 0$

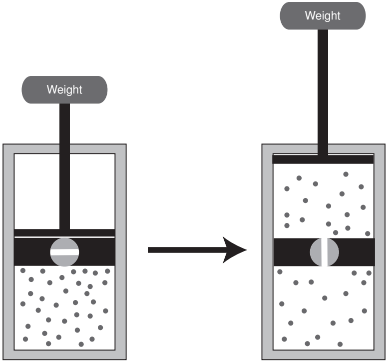
A) $w < 0$

B) $w = 0$

C) $w > 0$

Clicker Question #6

Adiabatic Expansion
With Work



Which of the following is true?

- $q < 0$
- $q = 0$
- $q > 0$

- $w < 0$
- $w = 0$
- $w > 0$

A) $\Delta E < 0$

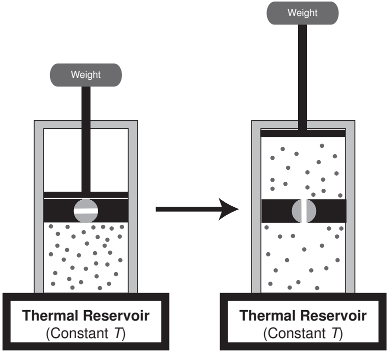
B) $\Delta E = 0$

C) $\Delta E > 0$

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

Clicker Question #7

Isothermal Expansion
With Work



Which of the following is true?

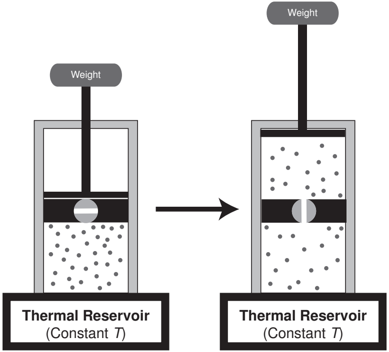
A) $q < 0$

B) $q = 0$

C) $q > 0$

Clicker Question #8

Isothermal Expansion
With Work



Which of the following is true?

- $q < 0$
- $q = 0$
- $q > 0$

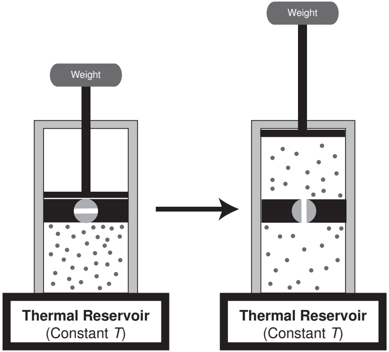
A) $w < 0$

B) $w = 0$

C) $w > 0$

Clicker Question #9

Isothermal Expansion
With Work



Which of the following is true?

- $q < 0$
- $q = 0$
- $q > 0$

- $w < 0$
- $w = 0$
- $w > 0$

A) $\Delta E < 0$

B) $\Delta E = 0$

C) $\Delta E > 0$

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

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.

$$\Delta T = T_{\text{final}} - T_{\text{start}}$$

$$\Delta P = P_{\text{final}} - P_{\text{start}}$$

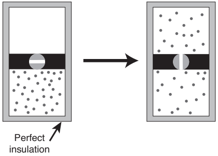
$$\Delta V = V_{\text{final}} - V_{\text{start}}$$

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

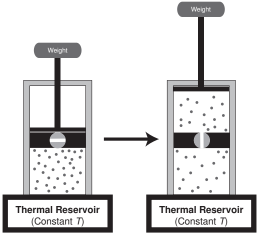
- Work, w, and heat, q, are not state functions.

Adiabatic vs. Isothermal Gas Expansion

Adiabatic



Isothermal



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

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

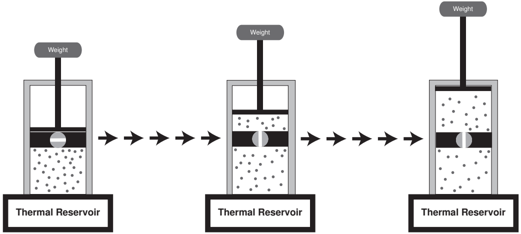
$$\Delta T_{\text{ad}} = \Delta T_{\text{isot}} = 0 \qquad \Delta E_{\text{ad}} = \Delta E_{\text{isot}} = 0$$

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

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

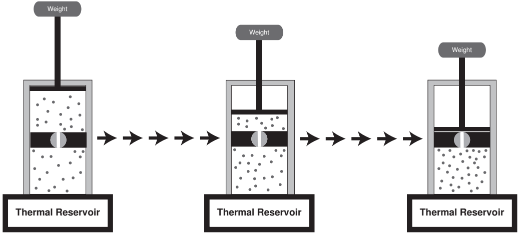
- Heat and work are “path-dependent” functions.

The Maximum-work Path for Gas Expansion



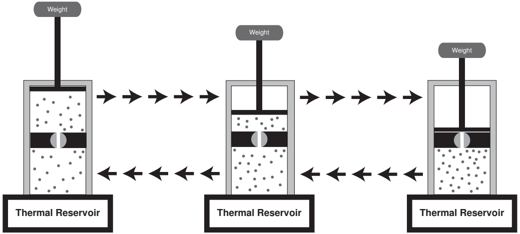
- Piston is allowed to move upward in infinitesimally small steps.
- Temperature is never allowed to drop.
- Pressure drops as gas expands, so less work is done per step.
- If larger steps are ever taken:
  - The temperature drops.
  - The pressure drops more than it would in an infinitesimal step.
  - 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.
- Excess energy flows to the reservoir as heat.
- P increases as gas is compressed, so more work is required per step.
- If larger steps are ever taken, 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.

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

- For the complete cycle:

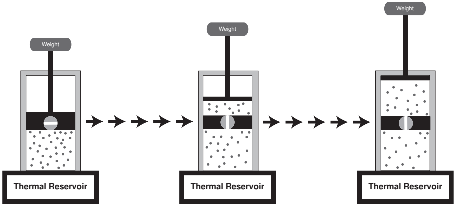
$$\Delta E = 0 \qquad w = 0 \qquad q = 0$$

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

Another Kind of State Function

- w and q are not state functions.
- BUT, we can define the value of w (or q) for a specific process linking two states to be a change in a state function.
- We define the work for the reversible (infinitely slow) conversion of one state to the another, w_{rev}, to be the change in the state function F.
  - ΔF is called the change in “free energy.” (Helmholtz free energy)
  - ΔF is the maximum amount of work that can be obtained from the change in state.
  - ΔF is “free energy” in the sense that it is energy that is available to do work.
  - “Free energy” is really the most expensive kind of energy!
    It’s the kind that we pay for to do work.
- The heat for a reversible process, q_{rev}, is also a state function that we will return to shortly.

Calculating the Work for the Reversible Isothermal Expansion of a Gas



- The work is calculated by integrating force with respect to distance.

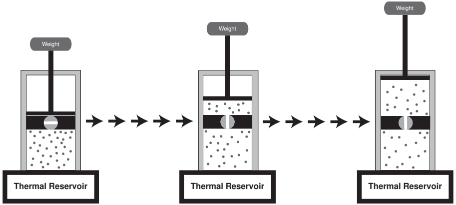
$$w_{\text{rev}} = \int_{x_1}^{x_2} f\,dx$$

f is force, and x represents the position of the piston.

- The force can be expressed in terms of pressure, P, and the area that the piston presents to the gas, A:

$$f = -P \cdot A$$

Calculating the Work for the Reversible Isothermal Expansion of a Gas



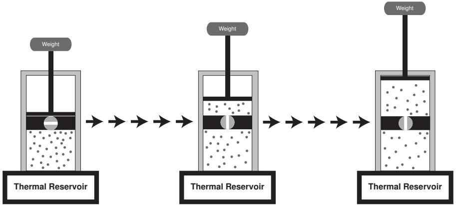
- From the previous slide:

$$w_{\text{rev}} = \int_{x_1}^{x_2} f\,dx = -\int_{x_1}^{x_2} P \cdot A dx$$

- For each small increment in x, there is a corresponding increment in volume, dV.

$$dV = Adx$$

Calculating the Work for the Reversible Isothermal Expansion of a Gas



- Substituting dV for Adx in the work integral:

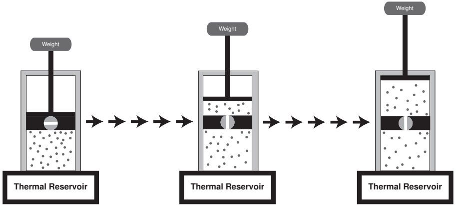
$$w_{\text{rev}} = -\int_{x_1}^{x_2} P \cdot Adx = -\int_{V_1}^{V_2} PdV$$

(The product PV has the units of energy or work!)

- From the ideal gas law, $P = nRT/V$. Substituting:

$$w_{\text{rev}} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

Calculating the Work for the Reversible Isothermal Expansion of a Gas



- From the previous slide:

$$w_{\text{rev}} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

- From calculus:

$$w_{\text{rev}} = -nRT \ln(V) \Big|_{V_1}^{V_2} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

- w_{rev} depends only on n, T, V_1 and V_2.
  w_{rev} represents a change in a state function, ΔF.

Clicker Question #10

Calculate the work, w_{rev}, for the reversible expansion of 0.5 mole of gas from 1 L to 5 L at 37°C.

$$R = 0.082\,\text{L} \cdot \text{atm} \cdot \text{K}^{-1}\text{mol}^{-1} = 8.3\,\text{J} \cdot \text{K}^{-1}\text{mol}^{-1}$$

A) -2100 J

B) -900 J

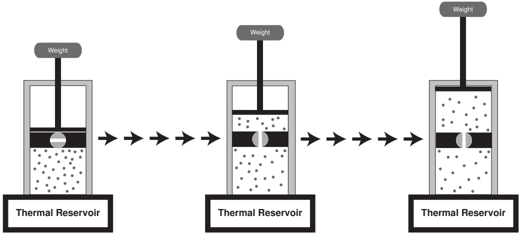
C) -250 J

D) 250 J

E) 900 J

$$w_{rev} = -nRT \ln\left(\frac{V_2}{V_1}\right) = -0.5\,\text{mol} \times 8.3\,\text{J} \cdot \text{K}^{-1}\text{mol}^{-1} \times 310\,\text{K} \times \ln\left(\frac{5\,\text{L}}{1\,\text{L}}\right)$$

Calculating the Work for the Reversible Isothermal Expansion of a Gas



- Since the number of moles remains constant, the change in volume can also be expressed in terms of a change in concentration:

$$C_1V_1 = \text{no. of moles} = C_2V_2$$
$$V_2/V_1 = C_1/C_2$$

- Substituting into the result from the previous slide:

$$w_{\text{rev}} = -nRT \ln\left(\frac{C_1}{C_2}\right)$$

q_{rev} for Isothermal Expansion

- For an isothermal process (regardless of path):

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

$$q = -w$$

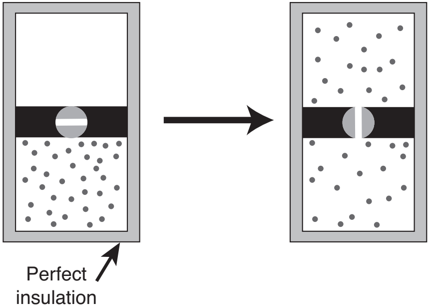
- For reversible isothermal expansion:

$$q_{rev} = -w_{rev} = nRT \ln\left(\frac{V_2}{V_1}\right)$$

- Sign check:
  For expansion, $V_2 > V_1$ and $q_{rev} > 0$, and the heat flow is <u>into</u> the system, as we expect.

- For any two states, there is, in principle, a reversible (infinitely slow) process separating them, and we can define q_{rev} and w_{rev}.

Reconsider the Adiabatic Expansion Without Work



- $q = 0$
- $w = 0$
- $\Delta E = q + w = 0$
- $\Delta F = w_{\text{rev}} = -nRT \ln\left(\frac{V_2}{V_1}\right) < 0$

- The energy available for work has decreased.
- We suspect that this has to do with the loss of order, or increase in entropy.
- But, what is entropy? How do we give it a number?