

Physical Principles in Biology

Biology 3550

Spring 2025

Lecture 26

More on the Second-Law and

Introduction to Chemical Thermodynamics

Wednesday, 19 March 2025

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# Announcements

- Quiz 4:
  - Friday, 28 March
  - 25 min, second half of class
  - Will cover material on thermodynamics
- Problem set 4
  - Due Friday, 28 March, 11:59 PM

# The “Classical” Definition of Entropy, $S$

- Entropy is a state function.
- For two states for which temperature remains constant during the reversible process of converting one to the other:

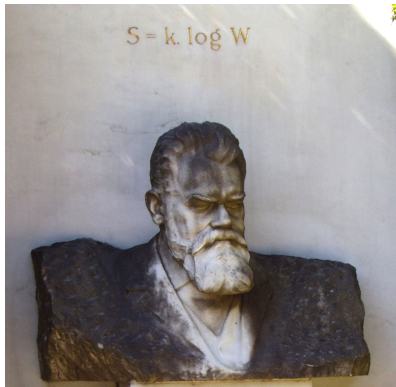
$$\Delta S = \frac{q_{\text{rev}}}{T}$$

- For two states separated by a reversible process for which the temperature does not stay constant:

$$\Delta S = \int_{T_1}^{T_2} \frac{q_{\text{rev}}}{T} dT$$

- Units for entropy: energy/temperature, J/K.

# The Statistical Definition of Entropy



Ludwig Boltzmann, 1844–1906  
Tombstone in Vienna, Austria

- $S = k \ln \Omega$   
 $k$  = Boltzmann's constant, with correct units for entropy (J/K).
- For a given state,  $\Omega$  is the number of equally probable ways to arrange the components making up that state.
- The different arrangements are called *microstates*.
- There is no proof! We believe it because it works.

# Entropy Change for Isothermal Expansion of a Gas

$$\Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \left( \frac{V_2}{V_1} \right) = nR \ln \left( \frac{C_1}{C_2} \right)$$

- $\Delta S$  is positive if volume increases (or concentration decreases).
- $\Delta S$  does not depend on temperature (in this case).
- The same result is obtained from the classical and statistical definitions!

# The Second Law of Thermodynamics

- For a spontaneous process, the total entropy of the universe (the system and its surroundings) will increase.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

- What does spontaneous mean?

Process occurs without an input of work to the system:  $w \leq 0$ .

If  $w < 0$ , the process produces work.

- Entropy change for the system:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

- Entropy change for the surroundings:

$$\Delta S_{\text{surr}} = -\frac{q}{T}$$

$q$  is the heat absorbed by the system during the specific process being considered.

# The Second Law of Thermodynamics

- For a spontaneous process at constant temperature:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \\ &= \frac{q_{\text{rev}}}{T} - \frac{q}{T} > 0\end{aligned}$$

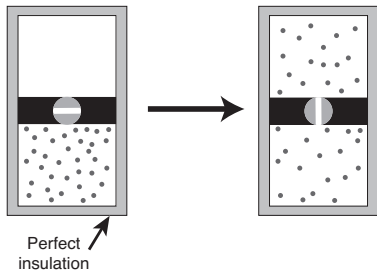
- $S_{\text{surr}}$  is not a state function!

$\Delta S_{\text{surr}}$  depends on the path of the change in the system.

- Flow of heat to surroundings represents an increase in entropy of the surroundings.
- Heat flows spontaneously to surroundings only if the system is warmer than the surroundings,
- Entropy of the system can decrease in a spontaneous process, if there is a flow of heat to the surroundings.

# Clicker Question #1

Adiabatic expansion of a gas  
without work:



What is  $\Delta S_{\text{univ}}$ ?

A) 0

B)  $nR \ln \frac{V_2}{V_1}$

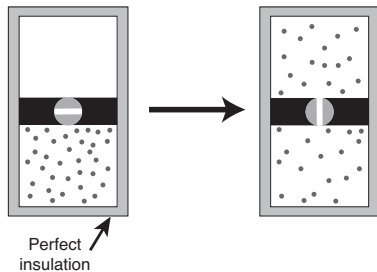
C)  $nR \ln \frac{V_1}{V_2}$

D)  $nRT \ln \frac{V_2}{V_1}$

E)  $nRT \ln \frac{V_1}{V_2}$



# Adiabatic Expansion of a Gas Without Work



- $q = 0$

- $w = 0$

- $\Delta S_{\text{sys}} = q_{\text{rev}}/T = nR \ln \left( \frac{V_2}{V_1} \right)$

- $\Delta S_{\text{surr}} = -q/T = 0$

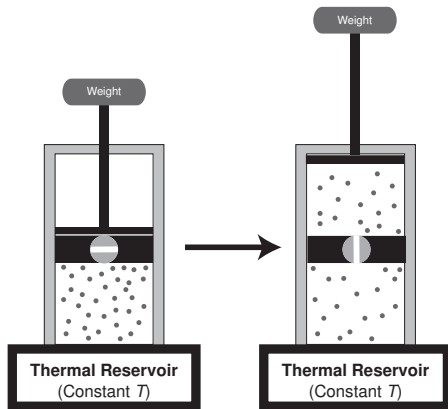
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = nR \ln \left( \frac{V_2}{V_1} \right)$

- If  $V_2 > V_1$ ,  $\Delta S_{\text{univ}} > 0$

The process is spontaneous.

## Clicker Question #2

Reversible isothermal  
expansion of a gas:



What is  $\Delta S_{\text{univ}}$ ?

A) 0

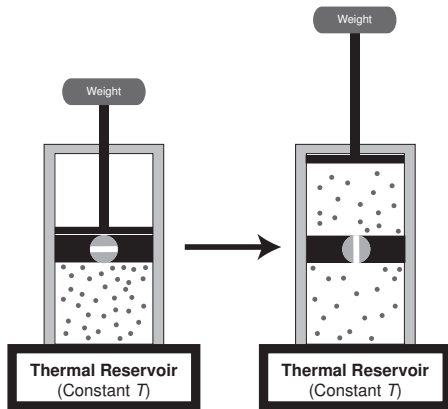
B)  $nR \ln \frac{V_2}{V_1}$

C)  $nR \ln \frac{V_1}{V_2}$

D)  $nRT \ln \frac{V_2}{V_1}$

E)  $nRT \ln \frac{V_1}{V_2}$

# Reversible Isothermal Expansion of a Gas



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

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

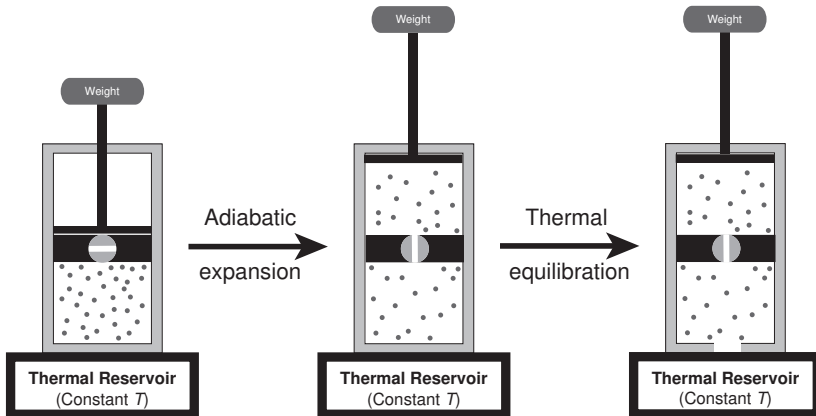
- $\Delta S_{\text{sys}} = q_{\text{rev}}/T = nR \ln \left( \frac{V_2}{V_1} \right)$

- $\Delta S_{\text{surr}} = -q/T = -nR \ln \left( \frac{V_2}{V_1} \right)$

- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

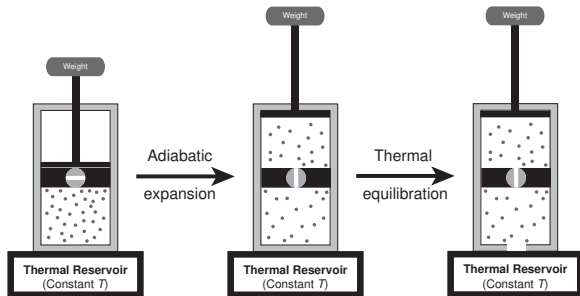
The process is on the edge of being spontaneous, because all of the available work has been obtained.

# Another Pathway for Gas Expansion



## Clicker Question #3

For the overall two-stage expansion:



Which of the following is true?

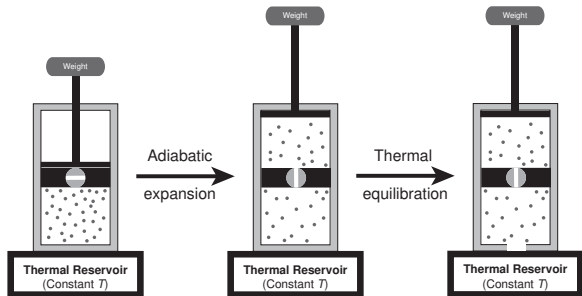
A)  $\Delta E < 0$

B)  $\Delta E = 0$

C)  $\Delta E > 0$

## Clicker Question #4

For the overall two-stage expansion:



Which of the following is true?

- A)  $w = nRT \ln \left( \frac{V_2}{V_1} \right)$
- B)  $0 < w < nRT \ln \left( \frac{V_2}{V_1} \right)$
- C)  $w = 0$
- D)  $0 > w > -nRT \ln \left( \frac{V_2}{V_1} \right)$
- E)  $w = -nRT \ln \left( \frac{V_2}{V_1} \right)$

## Work Done on the System in the Two-step Expansion

- Work done by the system =  $-w$
- The work done by the system must be less than the work done by the system in the reversible process,  $-w_{\text{rev}}$

$$-w < -w_{\text{rev}}$$

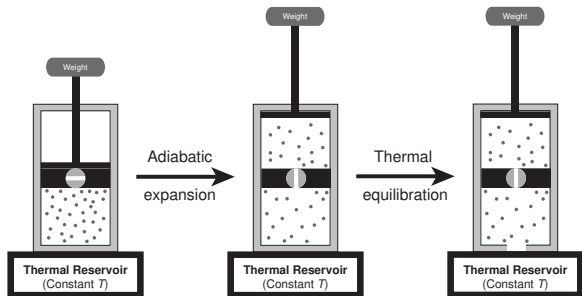
$$w > w_{\text{rev}} = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

- But *some* work is done, so  $w < 0$ , and:

$$0 > w > -nRT \ln \left( \frac{V_2}{V_1} \right)$$

## Clicker Question #5

For the overall two-stage expansion:



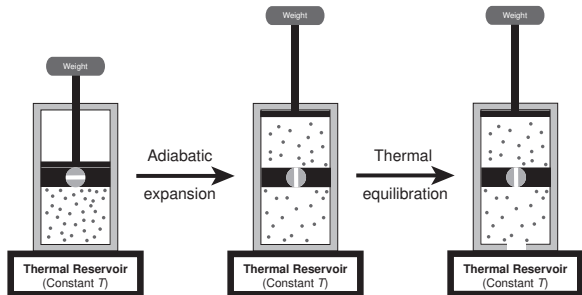
Which of the following is true?

- A)  $\Delta S_{\text{sys}} = nR \ln \left( \frac{V_2}{V_1} \right)$
- B)  $0 < \Delta S_{\text{sys}} < nR \ln \left( \frac{V_2}{V_1} \right)$
- C)  $\Delta S_{\text{sys}} = 0$
- D)  $0 > \Delta S_{\text{sys}} > -nR \ln \left( \frac{V_2}{V_1} \right)$
- E)  $\Delta S_{\text{sys}} = -nR \ln \left( \frac{V_2}{V_1} \right)$



## Clicker Question #6

For the overall two-stage expansion:



Which of the following is true?

- A)  $\Delta S_{\text{surr}} = nR \ln \left( \frac{V_2}{V_1} \right)$
- B)  $0 < \Delta S_{\text{surr}} < nR \ln \left( \frac{V_2}{V_1} \right)$
- C)  $\Delta S_{\text{surr}} = 0$
- D)  $0 > \Delta S_{\text{surr}} > -nR \ln \left( \frac{V_2}{V_1} \right)$
- E)  $\Delta S_{\text{surr}} = -nR \ln \left( \frac{V_2}{V_1} \right)$

## Entropy Change of the Surroundings for the Two-Step Expansion

- Entropy change for the surroundings:

$$\Delta S_{\text{surr}} = -\frac{q}{T}$$

$$0 > w > -nRT \ln \left( \frac{V_2}{V_1} \right)$$

- Heat flowing into the system:

$$0 > -q > -nRT \ln \left( \frac{V_2}{V_1} \right)$$

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

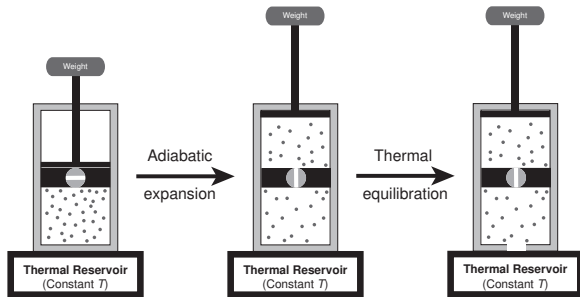
$$-q = w$$

$$0 > -\frac{q}{T} > -nR \ln \left( \frac{V_2}{V_1} \right)$$

$$0 > \Delta S_{\text{surr}} > -nR \ln \left( \frac{V_2}{V_1} \right)$$

## Clicker Question #7

For the overall two-stage expansion:



Which of the following is true?

A)  $\Delta S_{\text{univ}} = nR \ln \left( \frac{V_2}{V_1} \right)$

B)  $\Delta S_{\text{univ}} > 0$

C)  $\Delta S_{\text{univ}} = 0$

D)  $\Delta S_{\text{univ}} < 0$

E)  $\Delta S_{\text{univ}} = -nR \ln \left( \frac{V_2}{V_1} \right)$

## Entropy Change of the Universe for the Two-Step Expansion

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

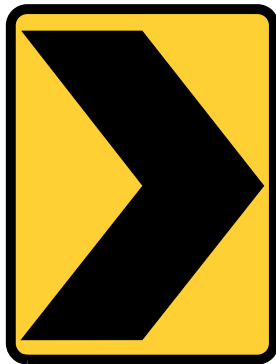
$$\Delta S_{\text{sys}} = nR \ln \left( \frac{V_2}{V_1} \right)$$

$$\Delta S_{\text{surr}} > -nR \ln \left( \frac{V_2}{V_1} \right)$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

- The process is spontaneous and produces work on the surroundings!
- But, it does less work than the reversible process.
- Also absorbs less heat.

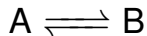
# Warning!



## Direction Change

Thermodynamics of Chemical Reactions

# Thermodynamics and Chemical Reactions



Energy reconsidered:

- For ideal gasses, the only energy is translational kinetic energy:

$$E = E_k = 3kT/2$$

- Real molecules have additional modes of motion and greater kinetic energy:

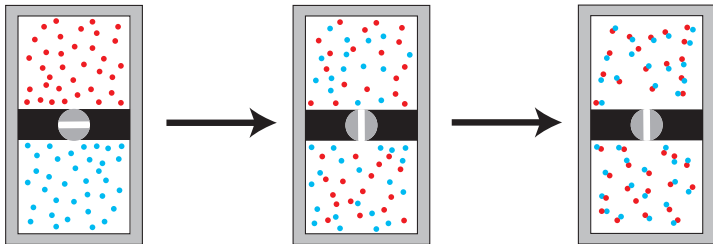
$$E_k > 3kT/2$$

$$E_k \propto kT$$

- Real molecules also possess *potential energy*, energy that can be absorbed or released through chemical reactions.

# A Hypothetical Example

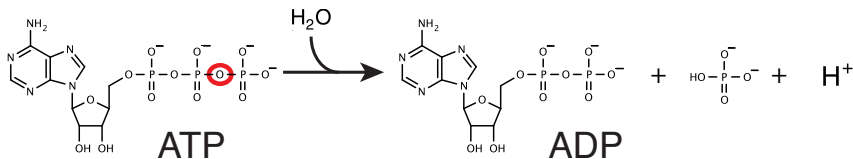
- What happens if a chemical reaction takes place in a perfectly insulated chamber?



- $q = 0$  and  $w = 0$ , so  $\Delta E$  must be zero.
- Can the temperature change?
- Potential energy of the molecules can be converted to kinetic energy (thermal energy), or vice versa.

# Potential Energy of Molecules

- When atoms or molecules react chemically, their energies often change.
  - Forming a chemical bond *usually* reduces potential energy of molecules.
  - Breaking a chemical bond *usually* increases potential energy of molecules.
- What about ATP?



We are told that:

- ATP has a “high-energy bond”.
- Forming the bond requires energy and breaking it releases energy.

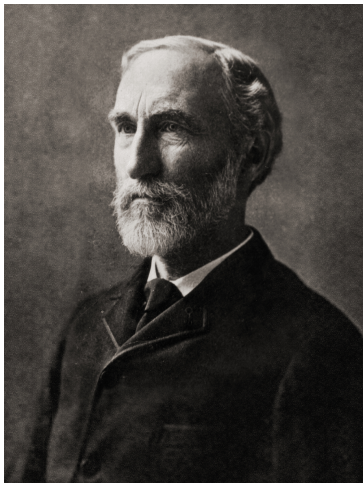
These statements aren't quite right!



# Potential Energy of Molecules

- When atoms or molecules react chemically, their energies often change.
- If the potential energy decreases, where can that energy go?
  - Kinetic energy (temperature) increases.
  - Heat flows out of the system. ( $q < 0$ )
  - Work is done by the system. ( $w < 0$ )
  - Some combination of the above.
- Exactly what happens depends on pathways available for heat flow or work.
- Using the second law directly, with  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$ , gets awkward.

# J. Willard Gibbs



1839–1903

- Arguably the first great American theoretical scientist.
- Consolidated thermodynamics into a consistent theory.
- Applied thermodynamics to chemistry.
- Also made important contributions in math and optics.