

Physical Principles in Biology

Biology 3550

Spring 2024

Lecture 26

More Second-Law Examples and
Introduction to Chemical Thermodynamics

Wednesday, 20 March 2024

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Announcements

- Problem Set 4:
 - Due Monday, 1 April at 11:59 PM
 - Submit pdf file on Gradescope
- Quiz 4:
 - Friday, 29 March
 - 25 min, second half of class
 - Will cover thermodynamics
 - 50 min
- Review Session:
 - 5:15 PM, Thursday, 28 March
 - HEB 2002
 - Come with questions!
- No class on Monday, 8 April

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:

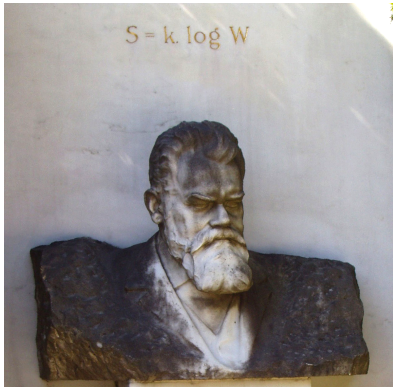
$$\Delta S = \frac{q_{\text{rev}}}{T}$$

- 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, Ω 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

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

- ΔS is positive if volume increases (or concentration decreases).
- ΔS 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:

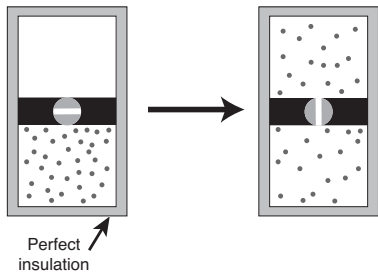
$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \\ &= \frac{q_{\text{rev}}}{T} - \frac{q}{T} > 0\end{aligned}$$

- S_{surr} is not a state function!

ΔS_{surr} depends on the path of the change in the system.

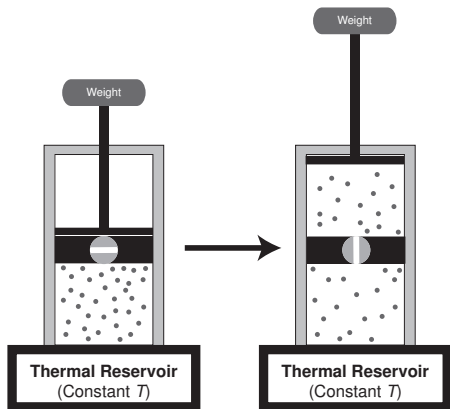
- Flow of heat to surroundings represents an increase in entropy of the surroundings.
- Heat flows spontaneously to surroundings only if the system is warmer than the surroundings,
- Entropy of the system can decrease in a spontaneous process, if there is a flow of heat to the surroundings.

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.

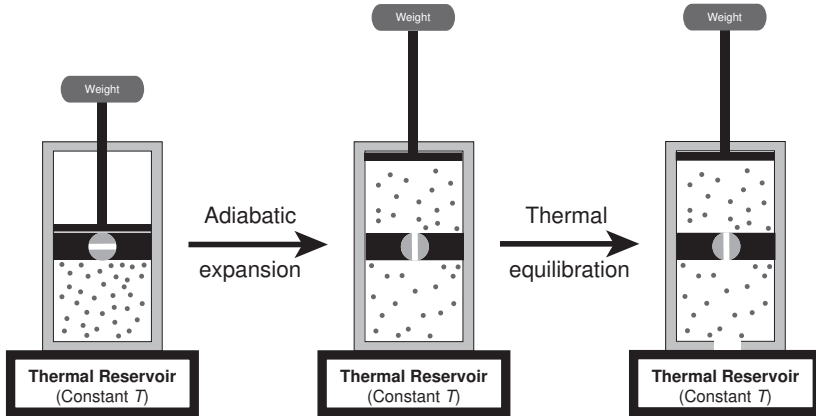
Reversible Isothermal Expansion of a Gas



- $w = w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1} \right)$
- $q = q_{\text{rev}} = nRT \ln \left(\frac{V_2}{V_1} \right)$
- $\Delta S_{\text{sys}} = q_{\text{rev}}/T = nR \ln \left(\frac{V_2}{V_1} \right)$
- $\Delta S_{\text{surr}} = -q/T = -nR \ln \left(\frac{V_2}{V_1} \right)$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

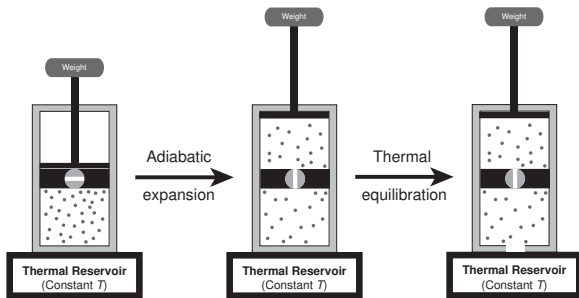
The process is on the edge of being spontaneous, because all of the available work has been obtained.

Another Pathway for Gas Expansion



Clicker Question #1

For the overall two-stage expansion:



Which of the following is true?

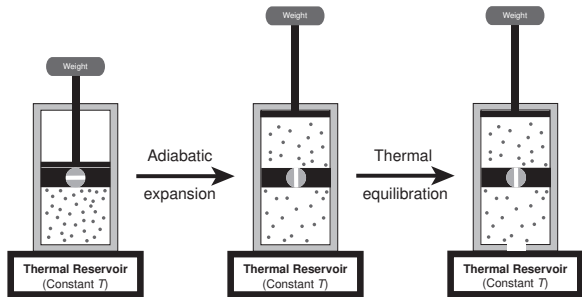
A) $\Delta E < 0$

B) $\Delta E = 0$

C) $\Delta E > 0$

Clicker Question #2

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, $-w_{\text{rev}}$

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

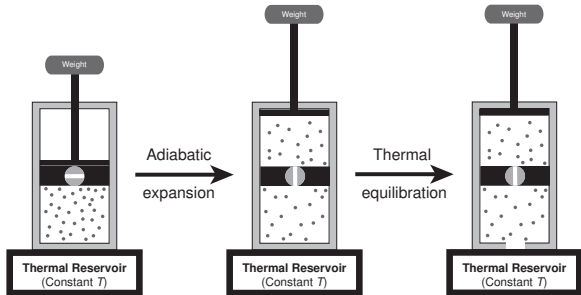
$$w > w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

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

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

Clicker Question #3

For the overall two-stage expansion:

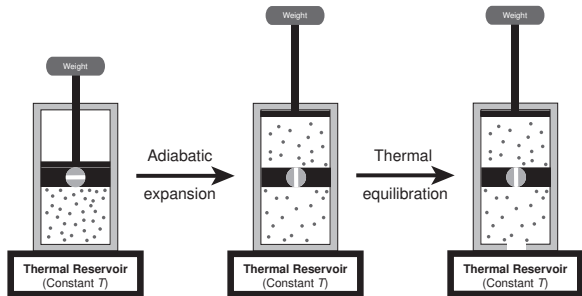


Which of the following is true?

- 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 #4

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:

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

- Heat flowing into the system:

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

$$-q = w$$

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

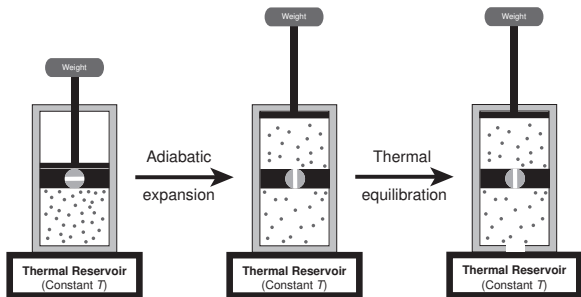
$$0 > -q > -nRT \ln \left(\frac{V_2}{V_1} \right)$$

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

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

Clicker Question #5

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

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

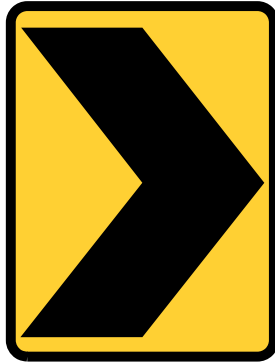
$$\Delta S_{\text{sys}} = nR \ln \left(\frac{V_2}{V_1} \right)$$

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

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

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

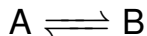
Warning!



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:

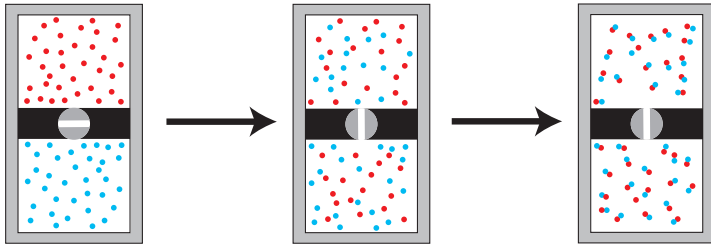
$$E_k > 3kT/2$$

$$E_k \propto kT$$

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

A Hypothetical Example

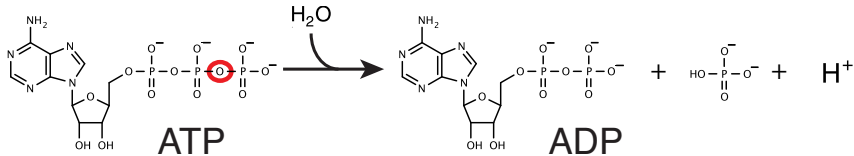
- What happens if a chemical reaction takes place in a perfectly insulated chamber?



- $q = 0$ and $w = 0$, so ΔE 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!