

Physical Principles in Biology
Biology 3550
Fall 2017

Lecture 26

Thermodynamics: Entropy and the Second Law

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

Entropy: Two Definitions

For a constant temperature process.

- The classical definition:

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

Defined in terms of the reversible process between two states.

- The statistical definition:

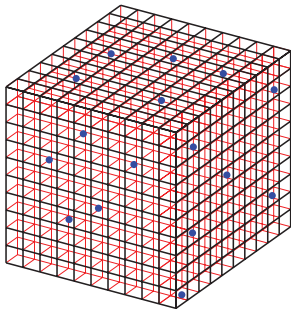
$$\Delta S = k \ln \frac{\Omega_2}{\Omega_1}$$

Ω_1 and Ω_2 are number of of equal-probability microstates before and after the process.

- S is a state function, and ΔS does not depend on path between states.

Calculating Entropy Change for Isothermal Gas Expansion

- Divide volume of gas into small cubes:



- No. of molecules: N
- Volume of little cubes: V_c
- Total volume: V
- No. of little cubes: $N_c = V/V_c$

- Entropy of starting state:

$$S_1 = k \ln \frac{N_{c,1}^N}{N!}$$

- Entropy of end state:

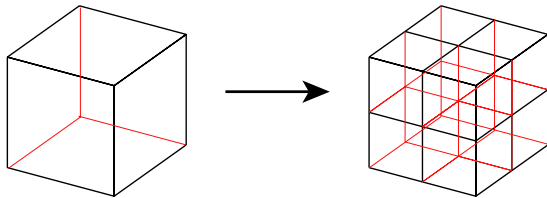
$$S_2 = k \ln \frac{N_{c,2}^N}{N!}$$

- Entropy change for volume change:

$$\begin{aligned}\Delta S &= k \ln \frac{N_{c,2}^N}{N!} - k \ln \frac{N_{c,1}^N}{N!} \\ &= k \ln \frac{N_{c,2}^N}{N_{c,1}^N} = kN \ln \frac{N_{c,2}}{N_{c,1}}\end{aligned}$$

What About the Size of the Little Cubes?

- Suppose that we divide each of the original cubes into 8 smaller cubes.



- If $N_{c,1}$ and $N_{c,2}$ are the numbers of the original cubes making up V_1 and V_2 , for the smaller cubes, we have:

$$V_1 = (8 \times N_{c,1}) \times V_{c,s}$$

$$V_2 = (8 \times N_{c,2}) \times V_{c,s}$$

where $V_{c,s}$ is the volume of the new, smaller cubes.

What About the Size of the Little Cubes?

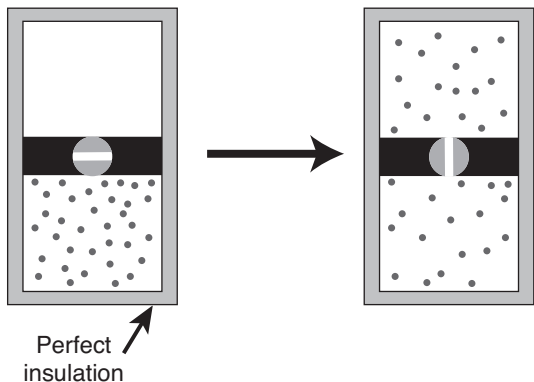
- Change in entropy for changing the volume:

$$\begin{aligned}\Delta S &= S_2 - S_1 = k \ln \Omega_2 - k \ln \Omega_1 \\ &= k \ln \left(\frac{(8 \times N_{c,2})^N}{N!} \right) - k \ln \left(\frac{(8 \times N_{c,1})^N}{N!} \right)\end{aligned}$$

$$\begin{aligned}\Delta S &= k \ln \left(\frac{(8 \times N_{c,2})^N}{N!} \cdot \frac{N!}{(8 \times N_{c,1})^N} \right) = k \ln \left(\frac{N_{c,2}}{N_{c,1}} \right)^N \\ &= Nk \ln \left(\frac{N_{c,2}}{N_{c,1}} \right)\end{aligned}$$

- The size factor (8) cancels out!

Entropy Change for Isothermal Expansion of an Ideal Gas



- From either classical or statistical definition:

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$$\Delta S = nR \ln \frac{C_1}{C_2}$$

- Though derived for ideal gasses, relationship is a useful approximation for real molecules in gasses or relatively dilute solutions.

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.

- ΔS_{sys} is the quantity we have been working with so far.
- What is ΔS_{surr} ?

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

q is the heat absorbed by the system during the specific process being considered. $-q$ is the heat released to the surroundings.

The Second Law of Thermodynamics

- For a spontaneous process:

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

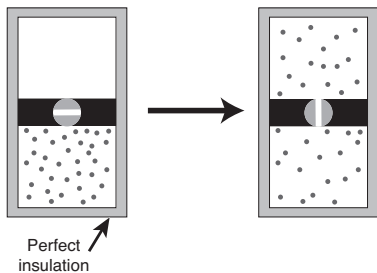
- S_{surr} is not a state function!

It 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 to surroundings only if the system is warmer than the surroundings: Another statement of the second law.
- 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 ΔS_{univ} ?

1 0

2 $nR \ln \frac{V_2}{V_1}$

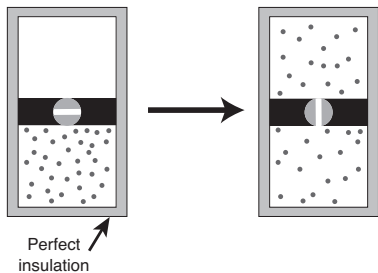
3 $nR \ln \frac{V_1}{V_2}$

4 $nRT \ln \frac{V_2}{V_1}$

5 q_{rev}/T

6 w_{rev}/T

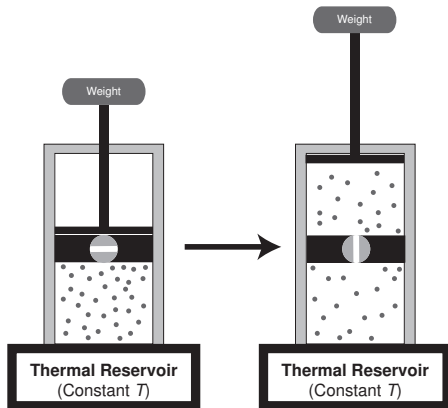
Adiabatic Expansion of a Gas Without Work



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

1 0

2 $nR \ln \frac{V_2}{V_1}$

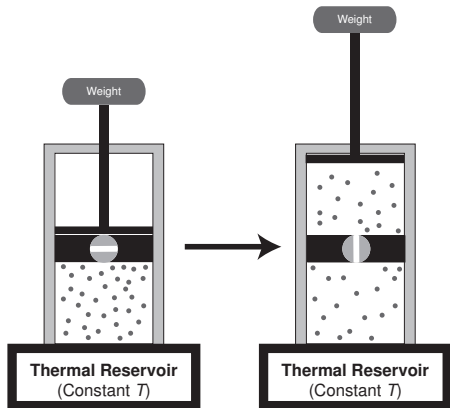
3 $nR \ln \frac{V_1}{V_2}$

4 $nRT \ln \frac{V_2}{V_1}$

5 q_{rev}/T

6 w_{rev}/T

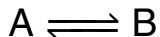
Reversible Isothermal Expansion of a Gas



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

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

Thermodynamics and Chemical Reactions



Energy reconsidered:

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

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

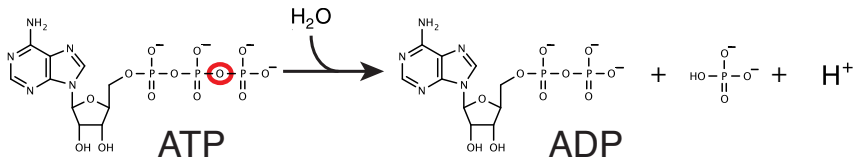
- Real molecules have additional modes of motion and greater kinetic energy:

$$E_k > 3kT/2$$

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

Potential Energy of Molecules

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



We are told that:

- ATP has a “high-energy bond”.
- Breaking that bond releases energy.

These statements aren't quite right!

Potential Energy of Molecules

- When atoms or molecules react chemically, their energies often change.
 - Forming a chemical bond reduces potential energy of molecules.
 - Breaking a chemical bond increases potential energy of molecules.
- If the potential energy decreases, where can that energy go?
 - Thermal 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 ΔS_{sys} and ΔS_{surr} , gets awkward.