Physical Principles in Biology
Biology 3550
Spring 2023
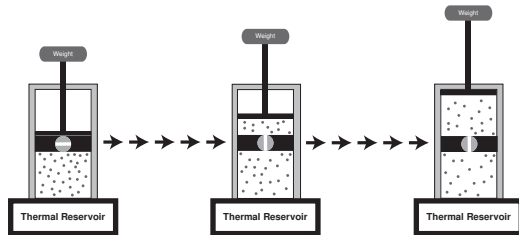
Lecture 25

Entropy and the Second Law

Monday, 18 March 2023

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# The Maximum-work Path for Isothermal 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.

Work for the Isothermal Reversible Gas Expansion

$$w_{\text{rev}} = -nRT \ln(V) \Big|_{V_1}^{V_2} = -nRT \ln\left(\frac{V_2}{V_1}\right) = -nRT \ln\left(\frac{C_1}{C_2}\right)$$

- w_{rev} depends only on n, T, V_1 and V_2.
  w_{rev} represents a change in a state function, ΔF.
- If $V_2 > V_1$, the gas expands and the system does work on the surroundings.
- If $V_2 < V1$, the gas is compressed, and work is done on the system.

Reconsider the Adiabatic Expansion Without Work

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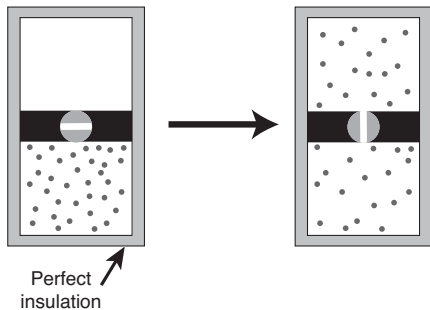
- $q = 0$
- $w = 0$
- $\Delta E = q + w = 0$
- $\Delta F = w_{rev} = -nRT \ln\left(\frac{V_2}{V_1}\right) < 0$

- 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?

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:

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

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

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

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

Entropy Change for Isothermal Expansion of a Gas

- From before, q_{rev}:

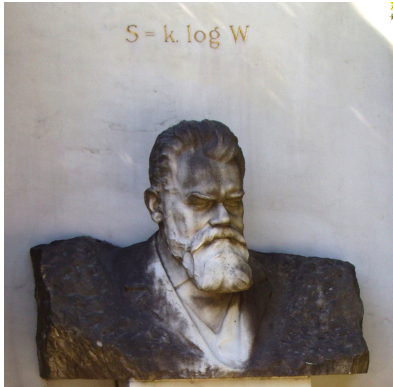$$q_{rev} = -w_{rev} = nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{C_1}{C_2}\right)$$

- Entropy:

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

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

- ΔS does not depend on temperature (in this case).

- What does this have to do with order or disorder?

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).

- What is Ω?

- 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.

- The state of the system at any instant is defined by the positions and velocities of each of the molecules.

- For a gas, there are a vast number of different microstates with different positions and velocities for each molecule.

- But, if the temperature isn't going to change, we can focus just on the positions.

- Divide volume of gas into small cubes:
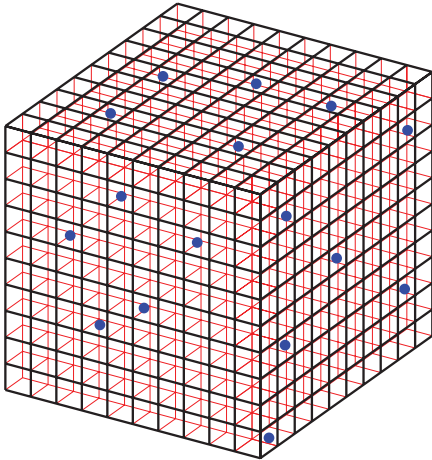
- No. of molecules: N

- Total volume: V

- Volume of little cubes: V_c

- No. of little cubes: $N_c = V/V_c \gg N$

- It is very unlikely that any of the little cubes will have more than one molecule in it, and most will have none.

Calculating Ω For Gas Molecules in a Container

- N is the number of molecules, and N_c is the number of little cubes that contain a molecule. $N_c \gg N$.

- How many ways can we place N molecules in N_c positions?

- There are N_c ways to place the first molecule.

- There are $N_c - 1$ ways to place the second molecule. But, $N_c - 1 \approx N_c$

- The number of ways to place all N molecules is

  $\approx N_c \cdot N_c \cdot N_c \cdots N_c \cdot N_c \cdot N_c = N_c^N$

- But, all of the molecules are identical, so we have to divide this number by the number of ways of choosing the molecules, $N!$

  $$\Omega = \frac{N_c^N}{N!}$$

- From Boltzmann:

$$S = k \ln \Omega = k \ln \left(\frac{N_c^N}{N!} \right)$$

- What if we divided the volume up into smaller cubes?
  Would the the entropy change?

- It's OK, if we limit ourselves to *changes* in entropy.

- Define starting and ending volumes in terms of the number of little cubes they contain, $N_{c,1}$ and $N_{c,2}$.

- The volumes of the individual little cubes is the same, V_c.

- Change in entropy for changing the volume:

$$\Delta S = S_2 - S_1 = k \ln \Omega_2 - k \ln \Omega_1$$

$$= k \ln \left(\frac{N_{c,2}^N}{N!} \right) - k \ln \left(\frac{N_{c,1}^N}{N!} \right)$$

Quick Review of Some Rules for Logarithms

$$\ln(a \cdot b) = \ln(a) + \ln(b)$$

$$\ln\left(\frac{1}{a}\right) = -\ln(a)$$

$$\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b)$$

$$\ln(a^b) = b\ln(a)$$

■ Change in entropy for changing the volume:

$$\Delta S = S_2 - S_1 = k \ln \Omega_2 - k \ln \Omega_1$$

$$= k \ln \left(\frac{N_{c,2}^N}{N!} \right) - k \ln \left(\frac{N_{c,1}^N}{N!} \right) = k \ln \left(\frac{N_{c,2}^N}{N!} \right) + k \ln \left(\frac{N!}{N_{c,1}^N} \right)$$

$$\Delta S = k \ln \left(\frac{N_{c,2}^N}{N!} \cdot \frac{N!}{N_{c,1}^N} \right) = k \ln \left(\frac{N_{c,2}^N}{N_{c,1}^N} \right) = k \ln \left(\frac{N_{c,2}}{N_{c,1}} \right)^N$$

$$= N k \ln \left(\frac{N_{c,2}}{N_{c,1}} \right)$$

Calculating ΔS for a Change in Gas Volume

- From the previous slide:

$$\Delta S = Nk \ln \left(\frac{N_{c,2}}{N_{c,1}} \right)$$

- $N_{c,2}$ and $N_{c,1}$ (the number of little cubes in the two volumes) are related to the volumes according to:

$$\frac{N_{c,2}}{N_{c,1}} = \frac{V_2}{V_1}$$

$$\Delta S = Nk \ln \left(\frac{V_2}{V_1} \right)$$

Calculating ΔS for a Change in Gas Volume

- From the previous slide:

$$\Delta S = Nk \ln\left(\frac{V_2}{V_1}\right)$$

- N is the number of molecules. If n is the number of moles, $N = nN_A$

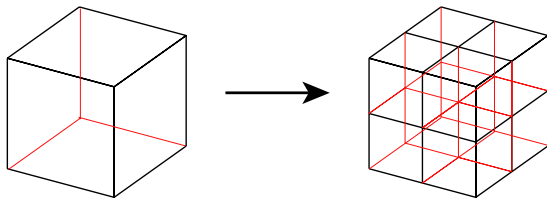$$\Delta S = nN_A k \ln\left(\frac{V_2}{V_1}\right)$$

- k is the gas constant, R, divided by N_A. So, $kN_A = R$, and:

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

- Exactly the same as the result from the classical definition!

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:

$$\Delta S = S_2 - S_1 = k \ln \Omega_2 - k \ln \Omega_1$$

$$= k \ln \left(\frac{(8 \times N_{c,2})^N}{N!} \right) - k \ln \left(\frac{(8 \times N_{c,1})^N}{N!} \right)$$

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

$$= N k \ln \left(\frac{N_{c,2}}{N_{c,1}} \right)$$

- The size factor (8) cancels out!

The Second Law of Thermodynamics

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

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

- 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}?

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

  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 at constant temperature:

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

$$= \frac{q_{rev}}{T} - \frac{q}{T} > 0$$

- S_{surr} is <u>not</u> 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 <u>only</u> 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.

Adiabatic expansion of a gas without work:

Perfect insulation

What is ΔS_{univ}?
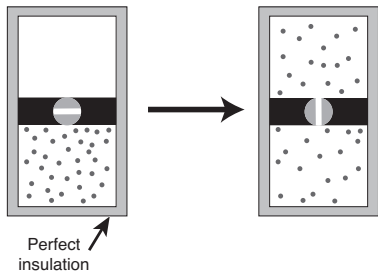
A) 0
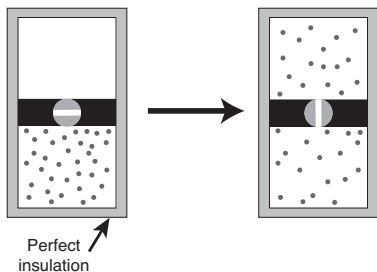
B) $nR \ln \dfrac{V_2}{V_1}$

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

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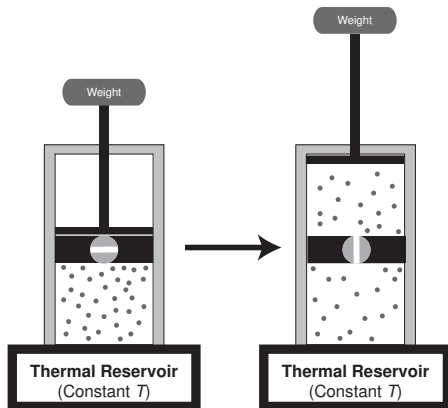
E) $nRT \ln \frac{V_1}{V_2}$

Adiabatic Expansion of a Gas Without Work

Perfect insulation

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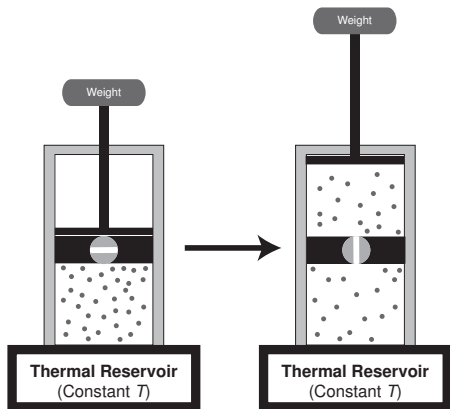- If $V_2 > V_1$, $\Delta S_{\text{univ}} > 0$

  The process is spontaneous.

Reversible isothermal
expansion of a gas:

What is ΔS_{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