Module 8: Thermodynamics II, Lecture 1

Spontaneous Change
The Concept of Entropy

Learning Objective	Openstax 2e Chapter
Spontaneous Change	**16.1**
Microstates and Entropy (S)	**16.2**

Suggested Practice Problems

Chapter 16 Exercises – Questions: 7, 9, 11

Answers can be found in the Chapter 16 Answer Key

What we have learnt already in the Fall
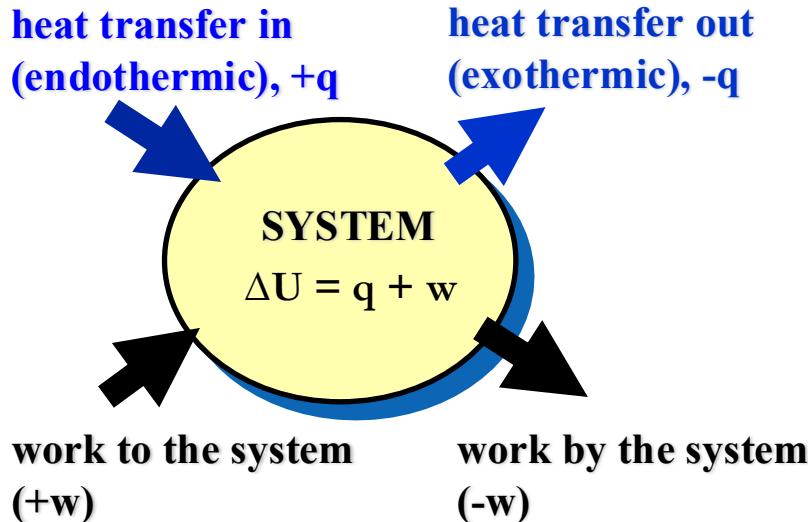
First Law of Thermodynamics: Energy cannot be created or destroyed; it can only be converted from one form to another.

State function: pressure (P), temperature (T), volume (V), internal energy (U), enthalpy (H)
Path function: heat (q), work (w)

Enthalpy of formation, bond enthalpy, enthalpy of reaction, exothermic and endothermic reactions

Standard conditions vs STP

heat transfer in (endothermic), +q

heat transfer out (exothermic), -q

SYSTEM

$\Delta U = q + w$

work to the system (+w)

work by the system (-w)

Important equations:
$\Delta U = q + w$
$\Delta U = \Delta H - P\Delta V$
$\Delta_r H° = \Sigma\, n\Delta_f H°_{(products)} - \Sigma\, n\Delta_f H°_{(reactants)}$

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Spontaneous Change

Spontaneous processes: Processes that occur without any outside intervention

Examples:

Ice cube melting

Rusting

Key points
1. If a process is spontaneous, its reverse process is non-spontaneous.
2. Spontaneous processes *occur without* outside intervention while non-spontaneous processes can only occur with external intervention.
3. Spontaneous processes *can be very fast or very slow.*

Spontaneous Change

Spontaneous processes: Processes that occur without any outside intervention

Examples:

Ice cube melting

Rusting

In terms of **Enthalpy change (ΔH)**, reactions are of two types: Exothermic ($\Delta_r H < 0$) and Endothermic ($\Delta_r H > 0$)

Enthalpy change, ΔH, is *not* a reliable criterion for determining whether or not a particular process or change will occur spontaneously.

Spontaneity is a thermodynamic term, telling us reaction / process direction, but nothing about the speed of the reaction /process.

The Concept of Entropy (S)

EVERYTHING IN THE UNIVERSE IS, OVER TIME, MOVING TO GREATER DISORDER.

THAT'S CALLED ENTROPY.

A LIT FIRE MOVES FROM SOLID FUEL TO ASH AND GAS.

THAT'S ENTROPY.

ENTROPY

ICE CUBES MELTING IN A GLASS OF WHISKEY POURED IN THE MIDDLE OF THE DAY.

THAT'S ENTROPY.

MY LIFE. THAT'S... WAIT.. WHAT WERE WE TALKING ABOUT?
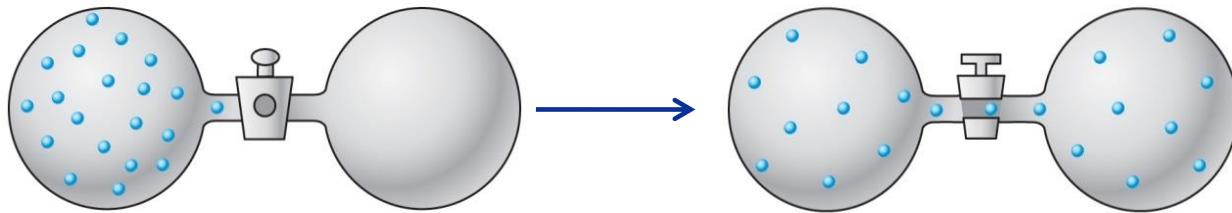
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https://www.youtube.com/watch?v=DxL2HoqLbyA

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Entropy (S)
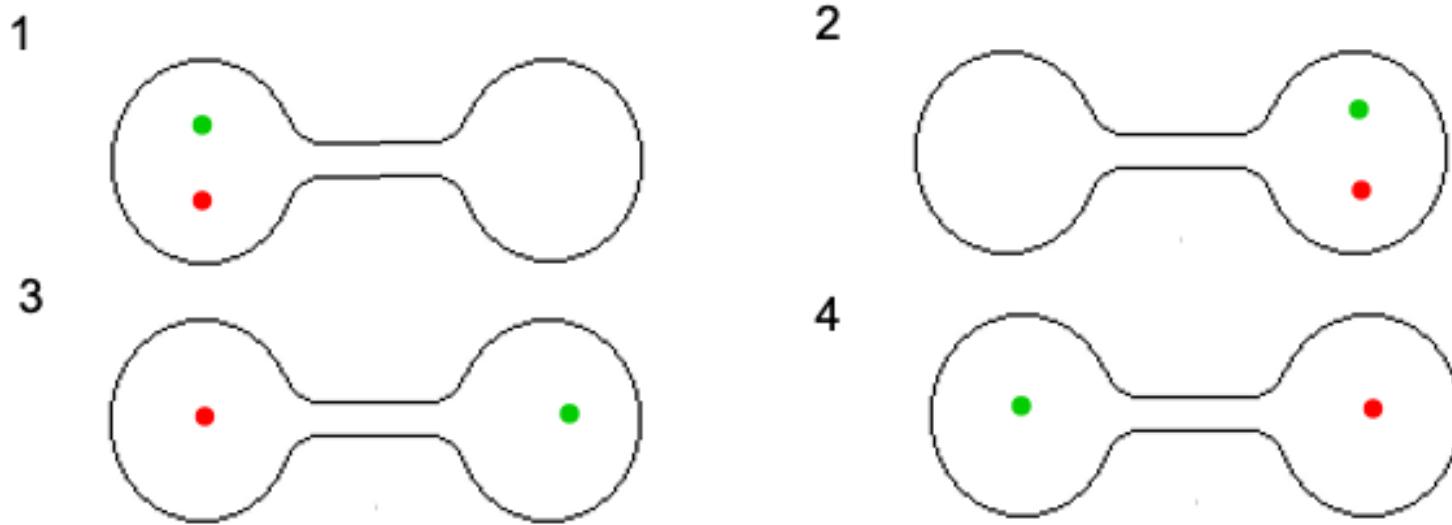
- Consider two flasks, one evacuated and one filled with a gas. They are separated by a closed valve that can be opened.

- The gas flows into the evacuated flask on its own.
  - Why?
  - It has to do with statistics and probability.
  - Each molecule of gas acts on its own and has an equal chance of being in either flask. Thus, on average, both flasks will contain equal numbers of molecules.

Entropy (S)
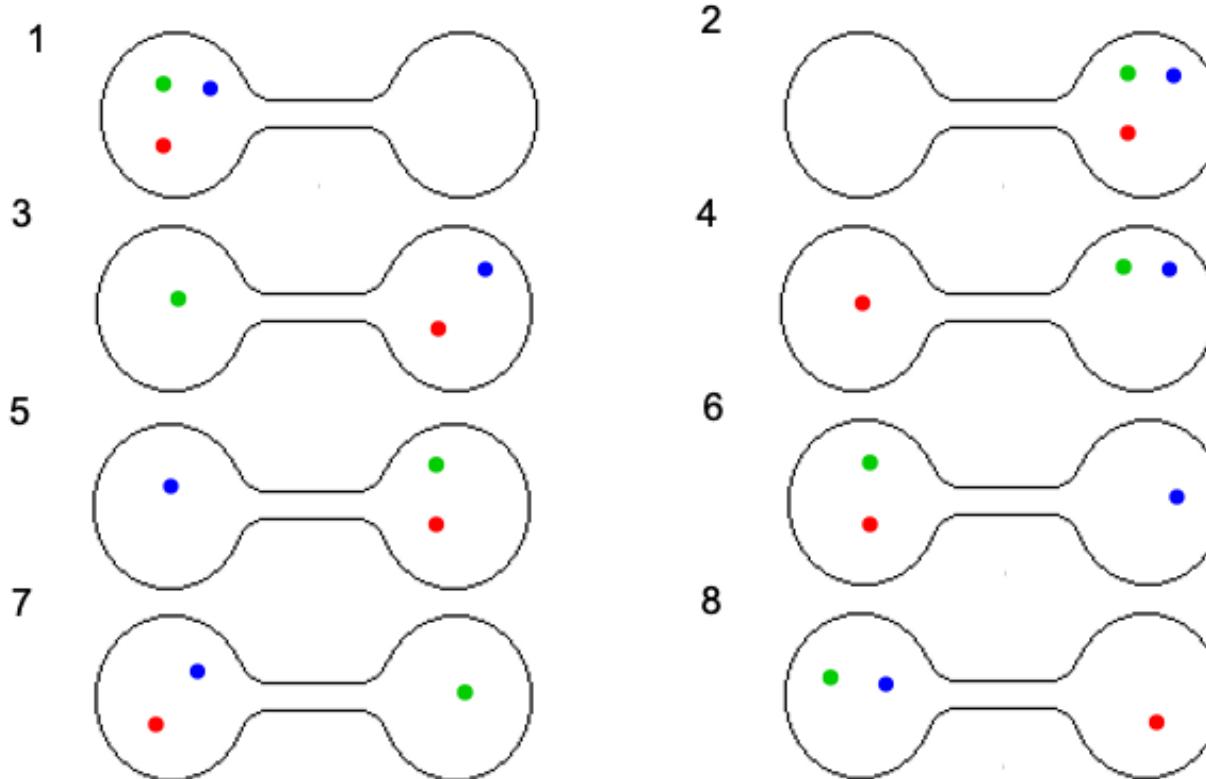
- Let's consider all the possibilities for a system of only **two molecules**: (these are called *microstates*).

Note that there are 2 of 4 microstates in which both molecules are in the same container. There is a 2 out of 4 **(50%)** chance that the molecules are distributed in both the containers.

Entropy (S)

- Let's consider all the possibilities for a system of **three molecules**

This time, there are 6 out of 8 microstates **(75%)** where molecules are distributed in both containers. <u>If we have many many molecules, it becomes a near certainty that they will be evenly distributed</u>.

Microstates:

Macroscopic systems are made up of many particles.

A macroscopic system is easily characterized by *n, T, V, P,* etc.

**Microscopic systems are not easily characterized.**
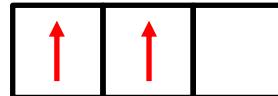
Position, velocity, and energy of individual molecules change from one instant to the next.

According to quantum mechanics a **microstate** is a specific microscopic configuration describing how the particles of a system are distributed among the available energy levels.
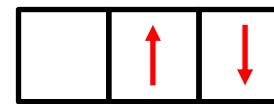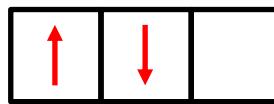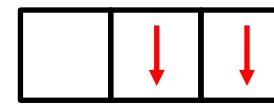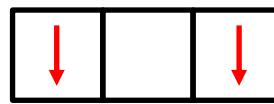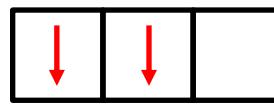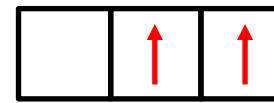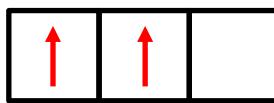
# *Example – Counting Microstates*

Let us consider placing two electrons into the three 2p orbitals in an atom.
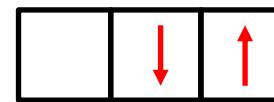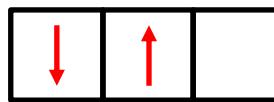
The Hund's rule: Every degenerate orbital should be singly occupied before any orbital is doubly occupied. However, Hund's rule does not specify how the two electron spins should be related (in fact, the two spins are uncorrelated). For convenience, we often draw this configuration as:

How many microstates are there for the two electrons in the three 2p orbitals that follow Hund's rule?
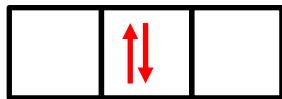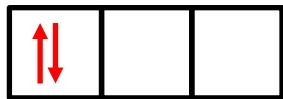
There are 12 microstates that follow Hund's rule!

Example – Counting Microstates

How many microstates are there for the two electrons in the three 2p orbitals that **do not** follow Hund's rule?

There are only 3 microstates that do not follow Hund's rule!

Thus, from a simple statistical point of view, the electron ground-state configuration following the Hund's rule has a much greater chance (80%) to occur than those violate the Hund's rule (20%).

How can we quantify this microstate/probability argument ?
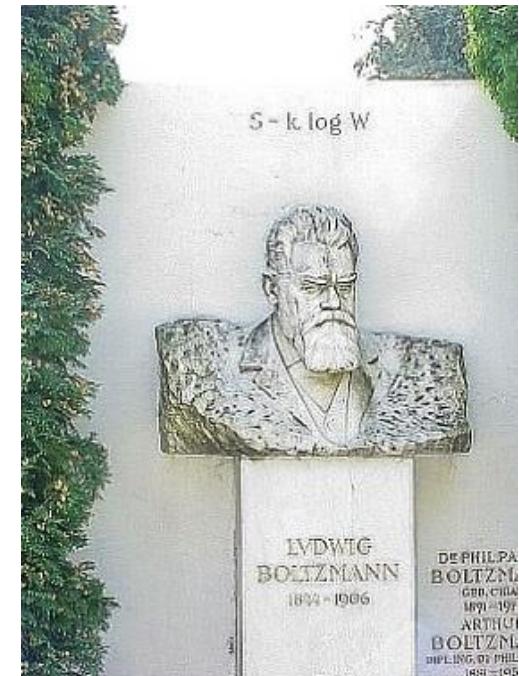
Boltzmann's Concept of Entropy

Boltzmann postulated that the number of microstates (W) and the entropy (S) of the system are related as:

$$S = k_B \ln W$$

where, W = number of microstates and
k_B (Boltzmann's constant) = *1.3806 x 10⁻²³ J K⁻¹*

In fact, k_B = R/N_A (Gas constant/Avogadro constant).
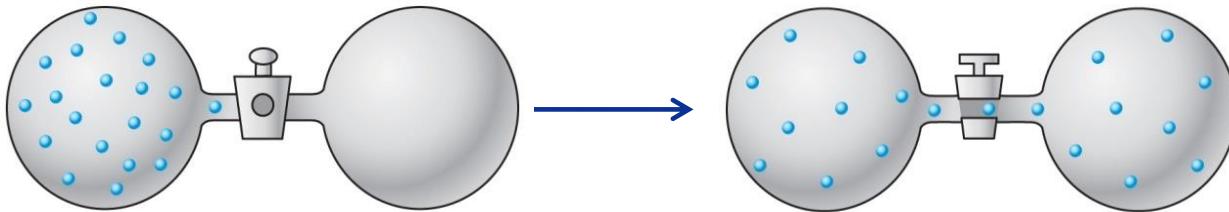
Boltzmann's equation relates the entropy (*S*) of an ideal gas to the number of microstates.

The greater the number of arrangements (i.e., microstates) of the microscopic particles (atoms, ions, molecules) among the energy levels in a particular state of a system, the greater the entropy of the system.

Boltzmann's View of Entropy

Ideal gas isothermal expansion: what is driving this process?

For an ideal gas, the number of microstates is a function of energy (E), volume (V) and number of molecules (N):

$$W(E, V, N) = \text{const.} \; V^N E^{3N/2}$$

Available volume to the gas molecules increased ⟹ Number of microstates increased
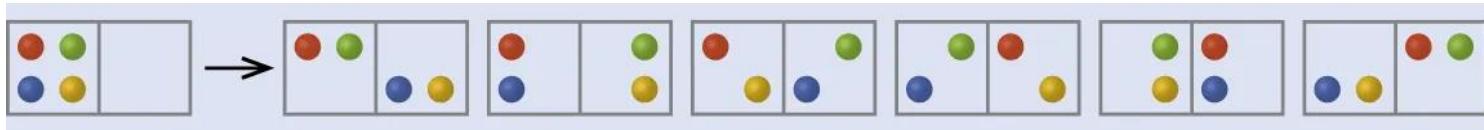
$$\Delta S = S_f - S_i$$
$$= k_B \ln W_f - k_B \ln W_i$$
$$= k_B \ln \frac{W_f}{W_i} = k_B \ln \frac{V_f^{\,N}}{V_i^{\,N}} = N k_B \ln \frac{V_f}{V_i}$$

Since $V_f > V_i$ $\Delta S > 0$

Driving force: increased disorder $\Rightarrow$ ***entropy*** increases

Entropy – Example Problem

Calculate the change in entropy (ΔS) for the process depicted below:

1 microstate   6 microstates

$$\Delta S = S_f - S_i$$

$$\Delta S = k_B \ln(W_f) - k_B \ln(W_i)$$

$$\Delta S = k_B \ln\left(\frac{W_f}{W_i}\right)$$

$$\Delta S = 1.38 \times 10^{-23} \frac{J}{K} \times \ln\left(\frac{6}{1}\right)$$

$$\Delta S = 2.47 \times 10^{-23} \frac{J}{K}$$