Unit4Day4-Crawford

Monday, November 18, 2013
3:15 PM

Vanden Bout/LaBrake/Crawford

CH301

Why does that happen backwards?
The 2nd Law of Thermodynamics
Entropy

UNIT 4 Day 4

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Important Information

LM31 & LM32 Due Th 9AM

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What are we going to learn today?

* Second Law of Thermodynamics *

Concept of Entropy

QUIZ: iClicker Question 1

Which of the following is not a "formation" reaction?

1. Reactants- elements, std. state
2. Products- 1 product, 1 mole

A) $Mg_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow MgO_{(s)}$
B) $\frac{1}{2} N_{2(g)} + 3/2\ H_{2(g)} \rightarrow NH_{3(g)}$
C) $NaF_{(s)} + Li_{(s)} \rightarrow LiF_{(s)} + Na_{(s)}$
D) $Li_{(s)} + \frac{1}{2} F_{2(g)} \rightarrow LiF_{(s)}$

QUIZ: iClicker Question 2

Which of the following methods would be expected to give the same value of ΔH_{rxn}?

1. Computation from bond energy data → estimation
2. Computation from heats of formation data
3. Computation from ΔH_{rxn} of reactions that can be manipulated by adding to get the desired net reaction using Hess's law.

Which of the following methods would be expected to give the same value of ΔH_{rxn}?

1. Computation from bond energy data
2. Computation from heats of formation data
3. Computation from ΔH_{rxn} of reactions that can be manipulated by adding to get the desired net reaction using Hess's law.

A) 1 and 2
B) 1, 2 and 3
C) 2 and 3
D) 1 and 3

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Spontaneity

Almost every process in the world happens in only one direction (in isolation = "on its own")

Imagine the following situations. Are they spontaneous?

Dropping an object - spon.
Burning logs spon
A gas expanding into the room spon
Heat flow from high T to low T spon
Ice melting in a glass of water spon

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Spontaneity

"feasible"

We will refer to any process that happens in isolation as *spontaneous.* The forward reaction will happen but the reverse reaction will never happen. (i.e. The movie played backward doesn't make sense)

A → B spon.

A ↚ B not spon.

How might these processes be reversed?

Dropping an object
Burning logs
A gas expanding into the room
Heat flow from high T to low T
Ice melting in a glass of water

The Second Law of Thermodynamics

The Second Law of Thermodynamics states that any process that happens spontaneously will lead to an increase in the *entropy* of the universe

entropy ↓ S

$$\Delta S_{universe} > 0$$

$$\Delta S_{total} > 0$$

Entropy

The entropy of the universe is the total entropy of the system and surroundings.

2nd law of thermo $\Delta S_{universe} > 0$ Spontaneous

The entropy of the universe is the total entropy of the system and surroundings.

2nd law of thermo $\Delta S_{universe} > 0$ Spontaneous

$$\Delta S_{universe} = \Delta S_{total}$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

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

Entropy

What is Entropy? What words or ideas pop into your head with respect to Entropy?

~~random~~ ~~chaos~~ ~~disorder~~ ~~destruction~~

~~discourse~~

Entropy

Entropy is related to the dispersal of energy at a given temperature.

The more energy dispersed, the greater the entropy change. The wider the energy dispersal, the greater the entropy change. The lower the temperature, the greater the entropy change for a given amount of energy.

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

lower the temperature, the greater the entropy change for a given amount of energy.

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

Entropy Examples

When we drop an object, identify the

System ball

Surrounding room, floor, 

Initial State high PE

Final State low PE

POLL: iClicker Question 3

When we drop an object, ΔS_{total} is

↑ ΔS_{univ}

A. > 0 (circled)
B. = 0
C. < 0
D. No way to know

$\Delta S_{univ} > 0$

ΔS_{total}

Spontaneity

For a process that is spontaneous

$$\Delta S_{total} > 0$$

2nd law

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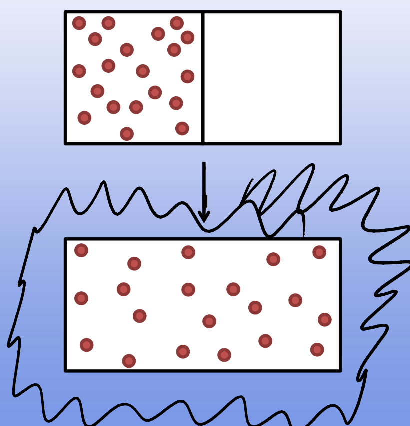
POLL: iClicker Question 4

When a gas expands in a vacuum, $\Delta S_{total} > 0$ and ΔS_{system} is

A. > 0
B. = 0
C. < 0
D. No way to know



$\Delta S_{univ} > 0$

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

$+ = + \quad 0$

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Entropy Examples

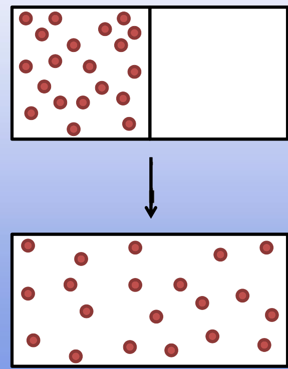
When a gas expands in a vacuum, identify the

System gas inside

Surrounding outside container

Initial State small V

Final State larger V



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Entropy Examples

A container of gas was opened and the gas was allowed to fill the room. In this example, the system is the gas and the surroundings is the room. **Increasing volume leads to an increase in entropy.**

The process was spontaneous

$$\Delta S_{total} = (\Delta S_{system} + \Delta S_{surroundings}) > 0$$

The surroundings are unchanged

$$\Delta S_{surroundings} = 0$$

The expansion led to an increase in the entropy of the system

$$\Delta S_{system} > 0$$

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Entropy

Why does the increase in volume lead to an increase in entropy?

↑V, ↑ΔS

We must use a microscopic view of dispersal of energy. Unfortunately, it is difficult to “visualize” energy, but it is easy to visualize molecules.

States of highest entropy are simply the most likely to happen

↓ probability

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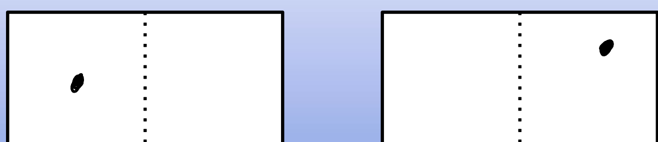
Microstates

Let’s imagine the gas in our previous example, where the gas is in a container with a left-hand side and a right-hand side

What if we only had one gas particle?



There are two possibilities, both of which are equally likely

* microstates – distinct possible outcomes

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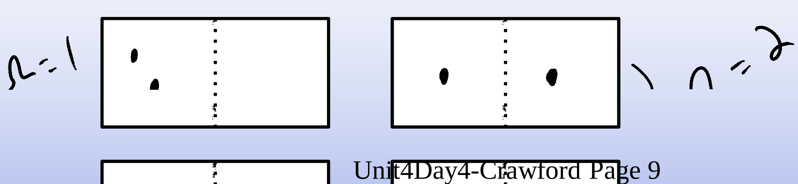
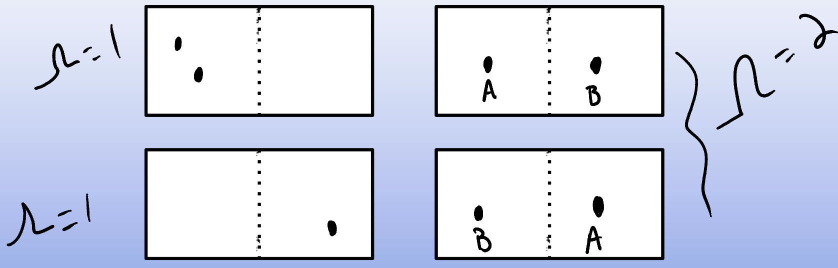
Microstates

What if we only had two gas particles?



What if we only had two gas particles?

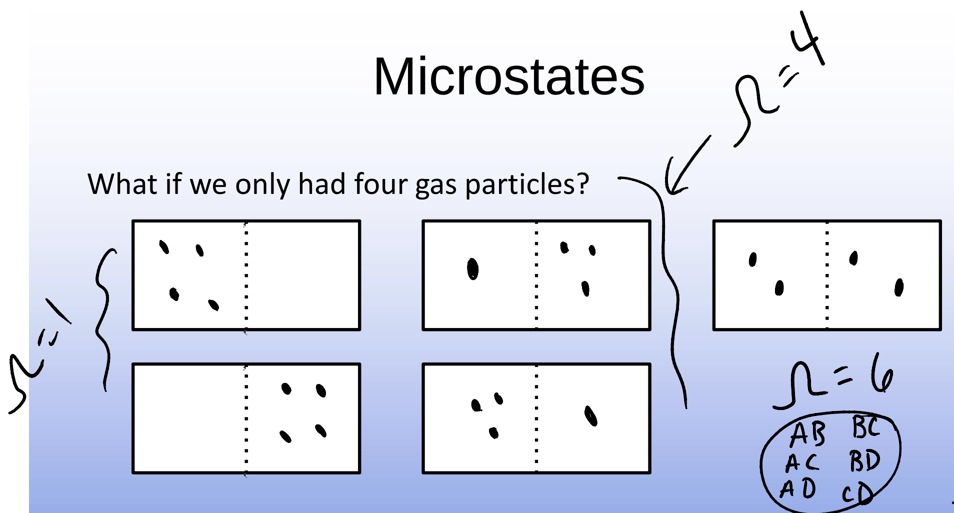


There are four possibilities, but they are no longer equally likely

A *microstate* is the specific way in which we can arrange the energy of a system.

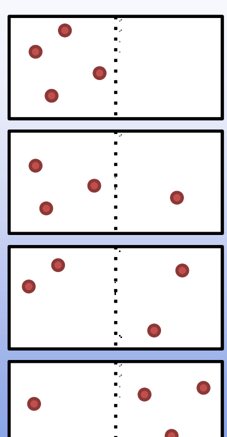
Microstates

What if we only had four gas particles?

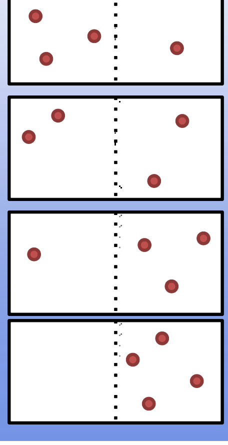


There are five possibilities. It is highly unlikely that we will find all the molecules entirely on the left or right side. The most likely situation will have two particles on each side.

Microstates



Ω = 1	**Unlikely**	Likely	Very Likely
Ω = 4	Unlikely	**Likely**	Very Likely
Ω =6	Unlikely	Likely	**Very Likely**
Ω =4	Unlikely	Likely	Very Likely

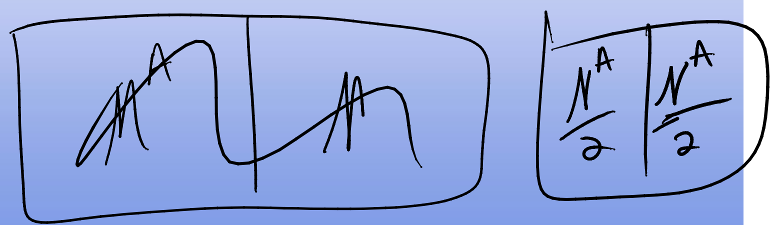


Ω = 4	Unlikely	Likely	Very Likely
Ω =6	Unlikely	Likely	Very Likely
Ω =4	Unlikely	Likely	Very Likely
Ω =1	Unlikely	Likely	Very Likely

Microstates

What if we only had Avogadro's number of particles?

It is extremely unlikely that we will find all the molecules entirely on the left or right side. The most likely situation will have half of the particles on each side.



Entropy and Microstates (Ω)

Entropy is measure of the number of equivalent microstates.

$$S \propto \ln \Omega$$

$$S = k \ln \Omega$$

k_B

More volume	more microstates	more entropy
More molecules	more microstates	more entropy
Higher temperature	more microstates	more entropy
Higher Energy	more microstates	more entropy

memorize

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Entropy and Microstates

It is harder to visualize microstates for energy, but it is the same idea, where more microstates means higher entropy

Macroscopically, we can quantify this with heat flow

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

The heat will always be the reversible heat for the processes we investigate in this course

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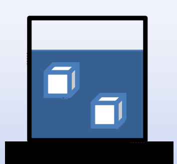
Entropy Examples

Physical change

When ice melts, identify the

System $H_2O_{(s)} \rightarrow H_2O_{(l)}$ $T = 0°C$



Entropy Examples

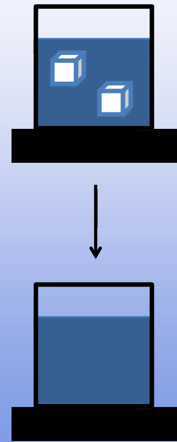
When ice melts, identify the

System $H_2O_{(s)} \rightarrow H_2O_{(l)}$ $T = 0°C$

Surrounding room, container $T = 25°C$

Initial State ice, cold low S

Final State water, warm high S



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Entropy Examples

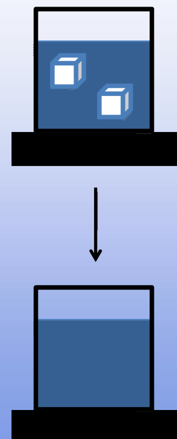
When ice melts, identify the

System – water (solid + liquid), T = 273 K

Surrounding – the room, T = 298 K

Initial State – solid

Final State – liquid



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POLL: iClicker Question 5

$\Delta S = \frac{q}{T}$

$\Delta S_{univ} > 0$ (+)

When ice melts,

endo $q_{sys} = +$

A. $|\Delta S_{sys}| > |\Delta S_{surr}|$
B. $|\Delta S_{sys}| < |\Delta S_{surr}|$
C. $|\Delta S_{sys}| = |\Delta S_{surr}|$
D. Not enough information

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

(+) +

B. | ΔS_{sys} | < | ΔS_{surr} |
C. | ΔS_{sys} | = | ΔS_{surr} |
D. Not enough information

(+). +. m.T

$|\Delta S_{sys}| > |\Delta S_{surr}|$

Entropy of the Surroundings

We typically define heat from the perspective of the system. Therefore, when we look at changes for the surroundings, we see the relationship is

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

$$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{-q_{sys}}{T}$$

Entropy Examples

When methanol is burned, identify the

System methanol reaction

Surrounding the room T= 25°C

Initial State Reactants $CH_3OH + O_2$

Final State Products $CO_2 + H_2O$

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

Entropy Examples

When methanol is burned, identify the

System – reactants and products

Surrounding – the room, T = 298 K

Initial State – Methanol and Oxygen

Final State – Carbon Dioxide and Water

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POLL: iClicker Question 6

When methanol is burned, $\Delta S_{surroundings}$ is

A. > 0
B. = 0
C. < 0
D. No way to know

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

$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O + heat$

$q_{sys} = -$

$q_{surr} = +$

$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{+}{T} = +$

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POLL: iClicker Question 7

When methanol is burned, ΔS_{system} is

A. > 0
B. = 0
C. < 0

POLL: iClicker Question 7

When methanol is burned, ΔS_{system} is

A. > 0
B. = 0
C. < 0
D. No way to know

↓ ΔS_{rxn}

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Demonstration

$Ba(OH)_2 \bullet 4H_2O_{(s)} + NaNO_{3(s)}$ → Liquid

(NH_4 written over Na)

$Ba(NO_3)_2\ (aq) + NH_3\ (g) + H_2O\ (l)$

stinky → $NH_3\ (g)$

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POLL: iClicker Question 8

In the demonstration, ΔS_{system} is

A. > 0
B. = 0
C. < 0
D. No way to know

$\Delta S_{univ} > 0$ +

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

(+) ↑ (−)

$q_{sys} = +$

$q_{surr} = - \rightarrow \Delta S_{surr} = -$

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Demonstration

Stretched vs. Relaxed Rubber Bands

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POLL: iClicker Question 9

For the process of releasing a stretched rubber band to a relaxed rubber band, ΔS_{sys} is

A. > 0
B. = 0
C. < 0
D. No way to know

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Learning Outcomes

Understand the concept of entropy, S, and change in entropy ΔS.

Understand the concept of change in entropy of a system,
surroundings and universe.

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