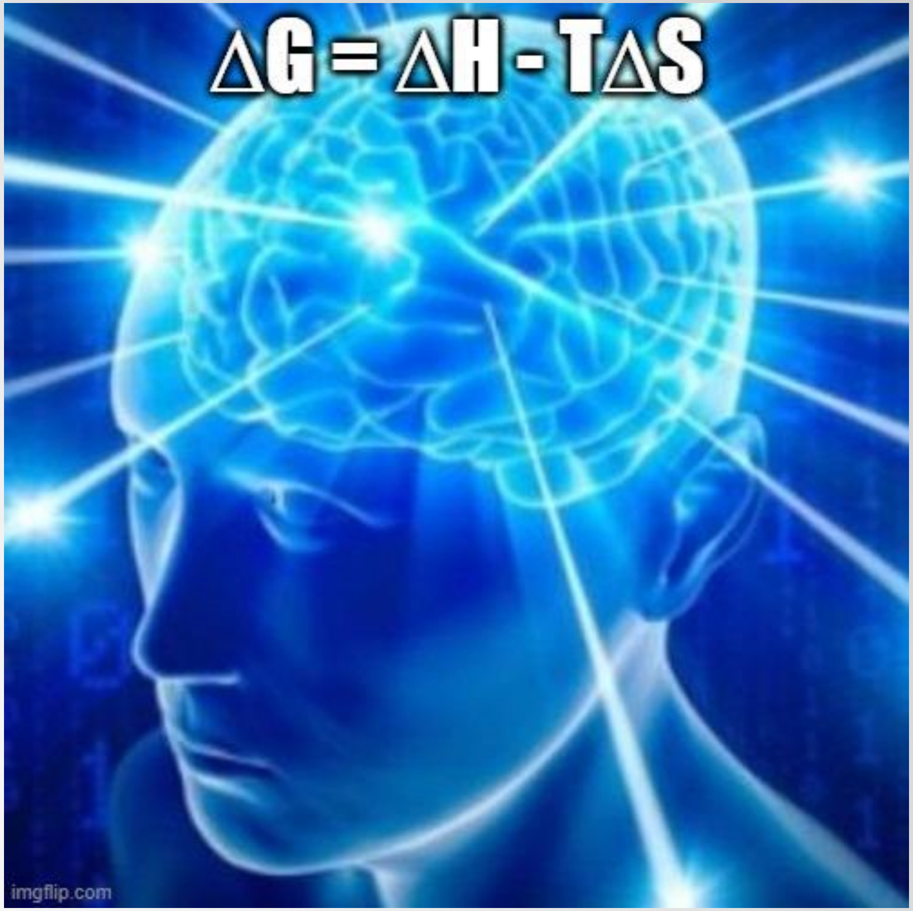
# Seminar 1: Thermodynamics




Biophysics

Course 2022-2023


Alberto Meseguer
Irene Acero

# The Gibbs free energy equation

$$\Delta G = \Delta H - T \cdot \Delta S$$

# Entropy

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This definition can be applied to any type of energy, such as:

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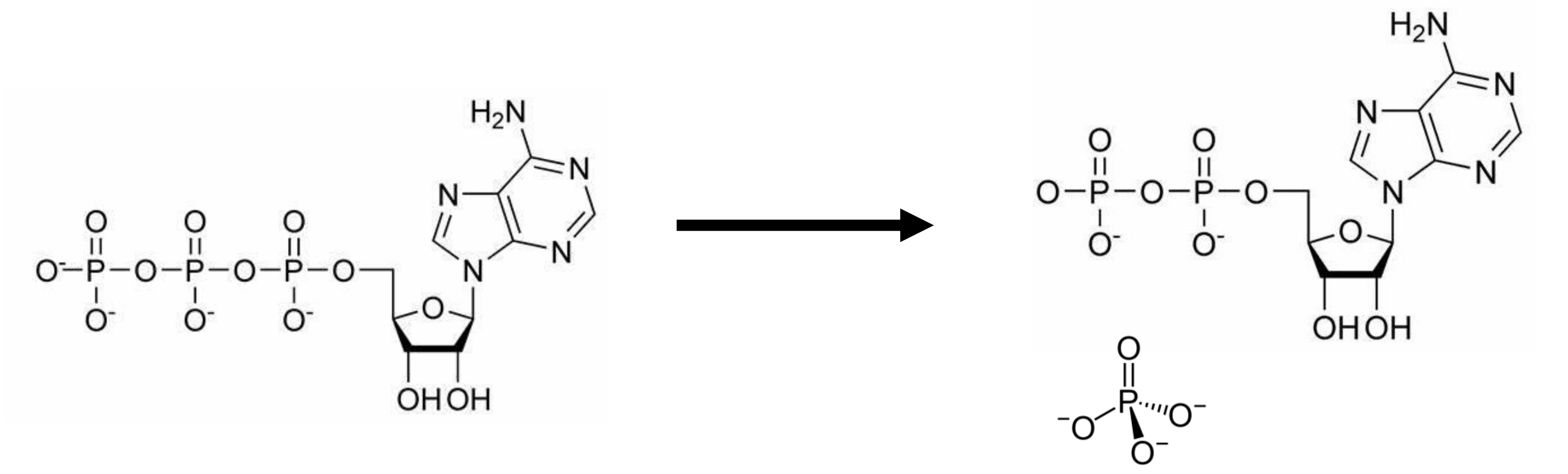

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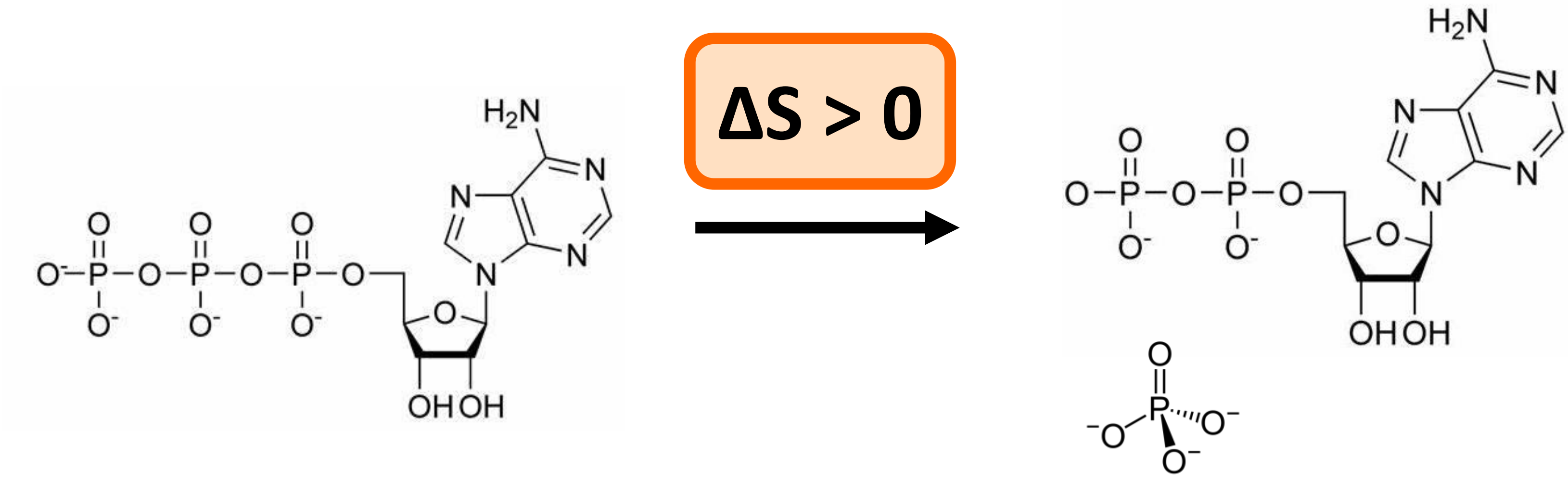

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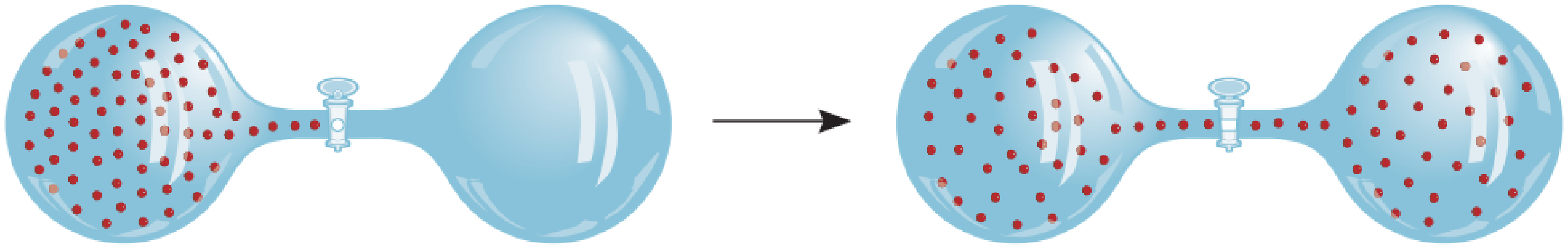

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This definition can be applied to any type of energy, such as:

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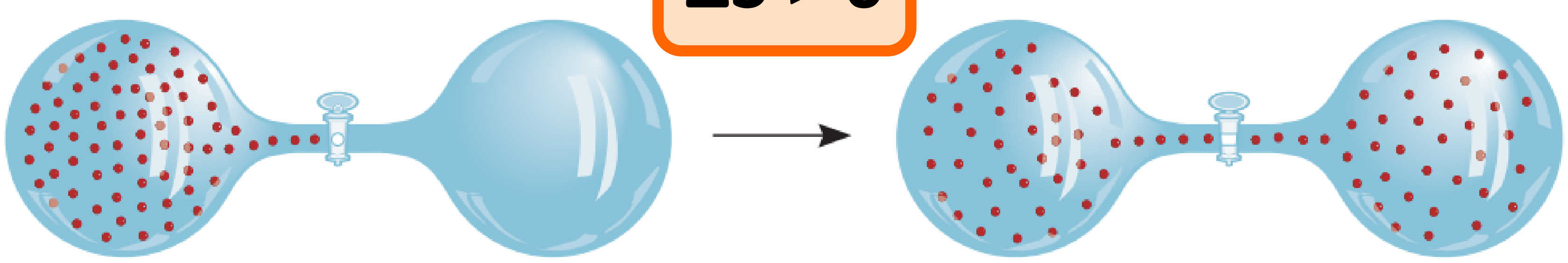
$$\Delta S > 0$$



# Entropy

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- Thermal energy

$\Delta S > 0$ $\longrightarrow$

# Entropy

**And to proof this I brought you an <u>Stirling engine!!</u>**

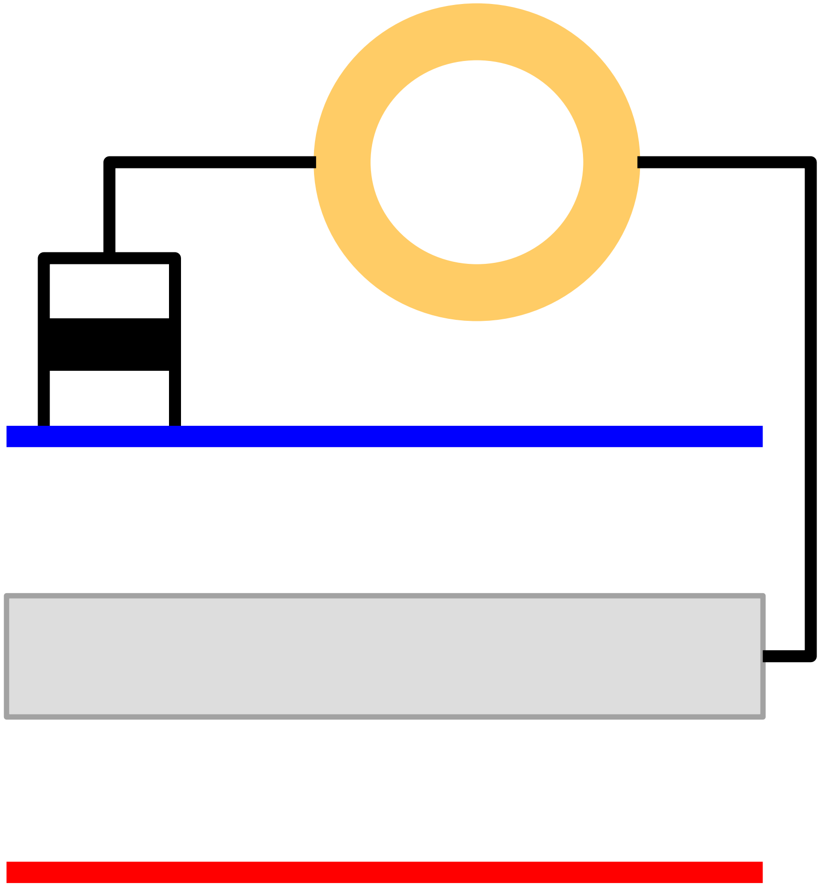
# The Stirling engine

$$\Delta G = \Delta H - T \cdot \Delta S$$

**An Stirling engine is an external combustion engine**

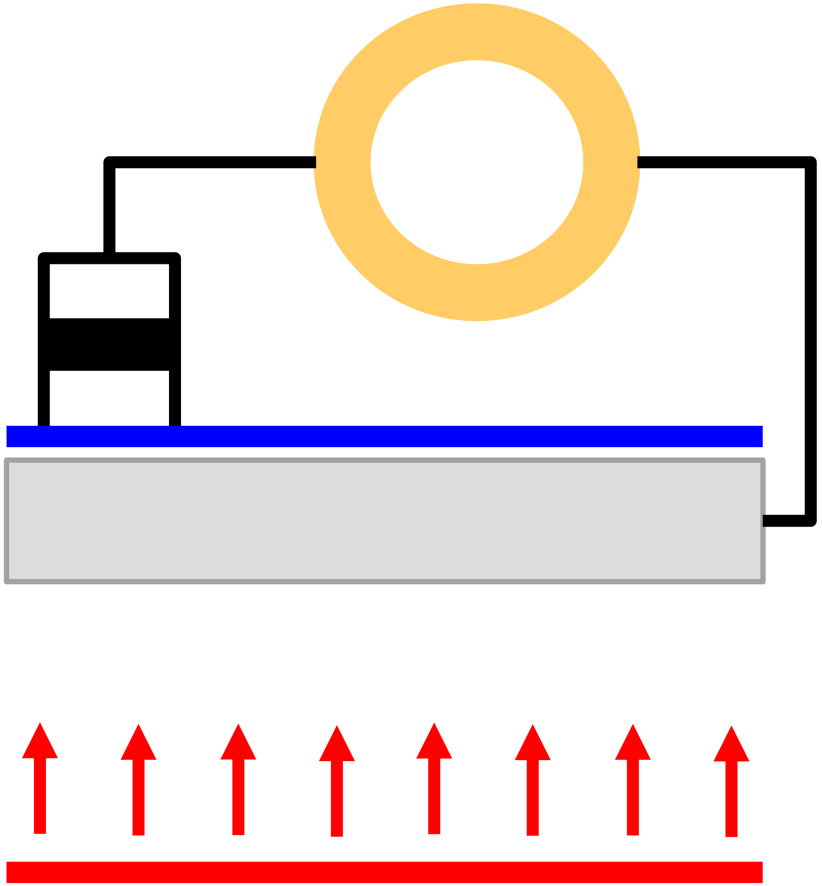
# The Stirling engine

This is an scheme of the Stirling engine with all its important parts



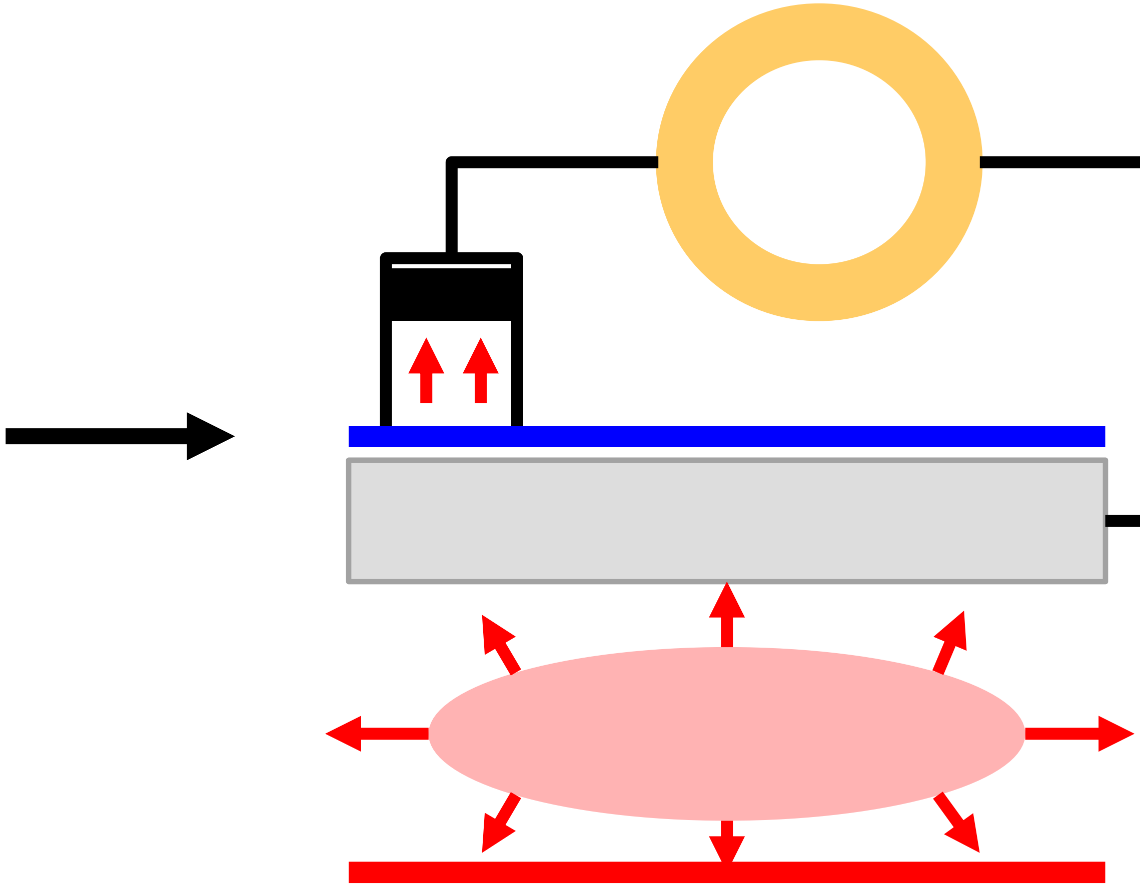
# The Stirling engine

When we start the engine we make the foam go up. The air in the chamber gets in contact with the hot plate and gets warmed up.



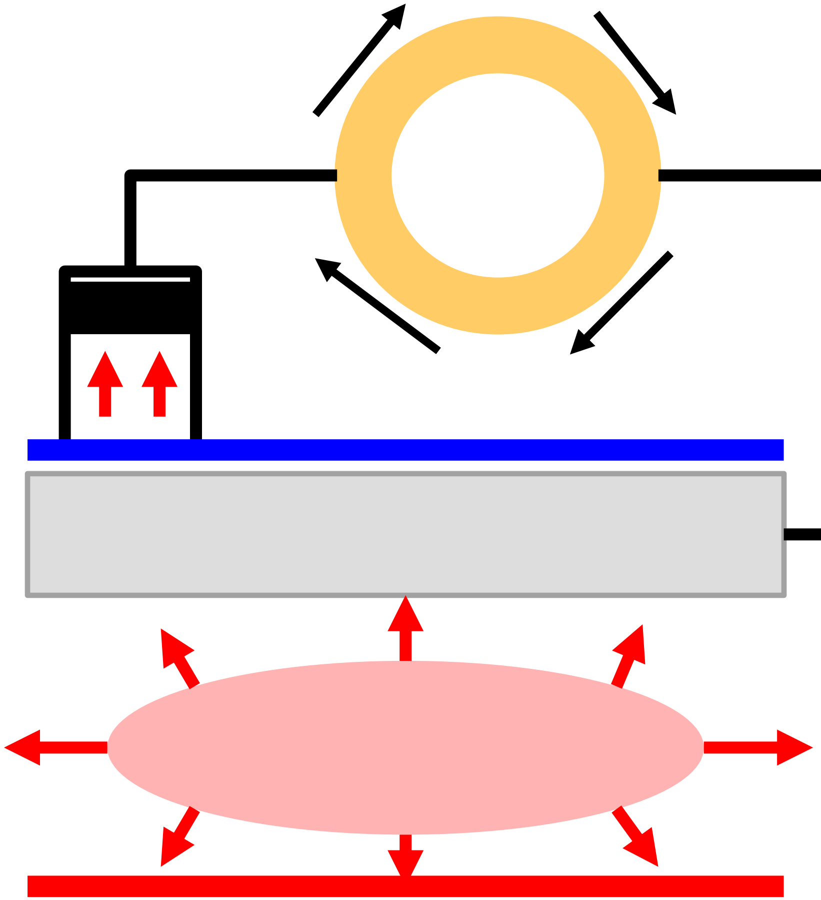
# The Stirling engine

**As the air in the chamber gets hot, it expands itself. This moves the piston up.**



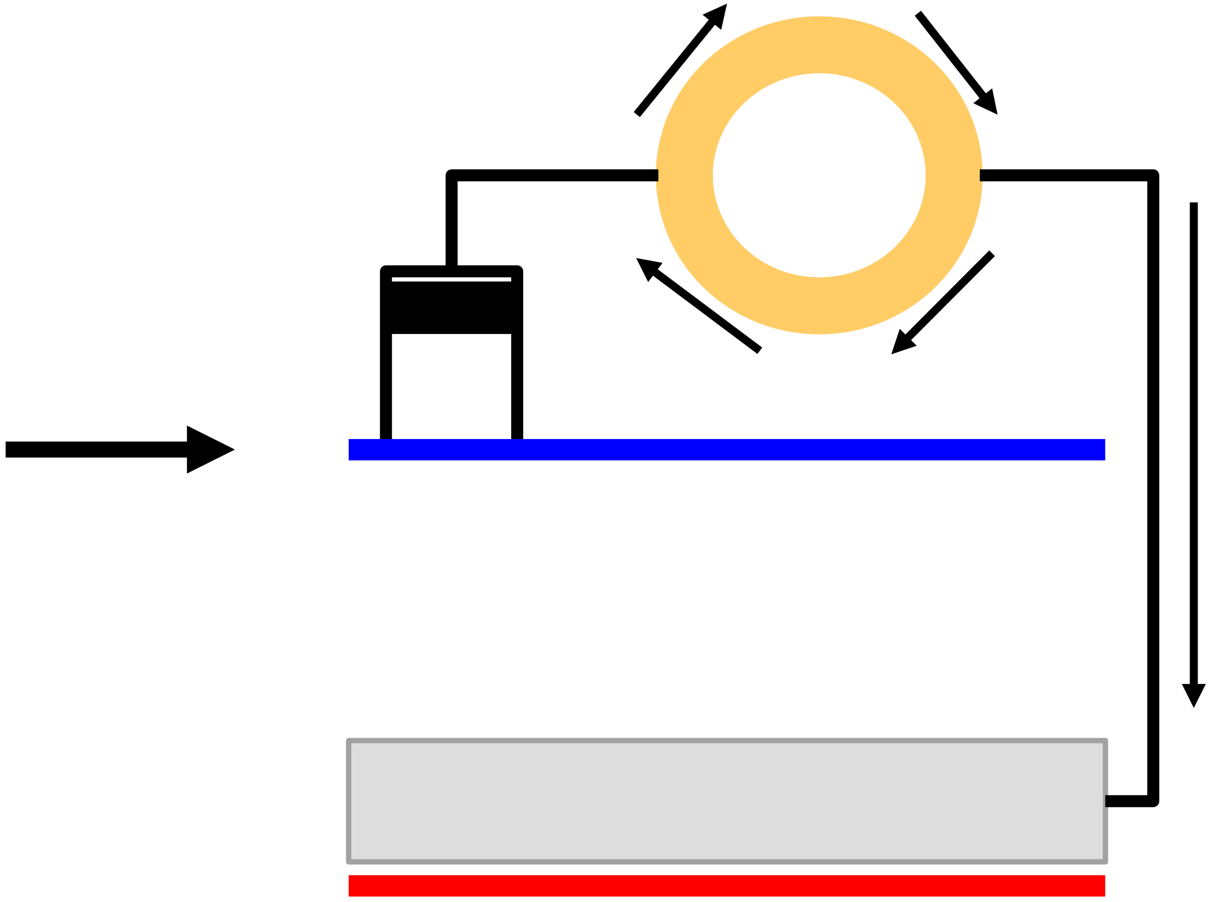
# The Stirling engine

The piston is connected to the wheel, which starts turning.



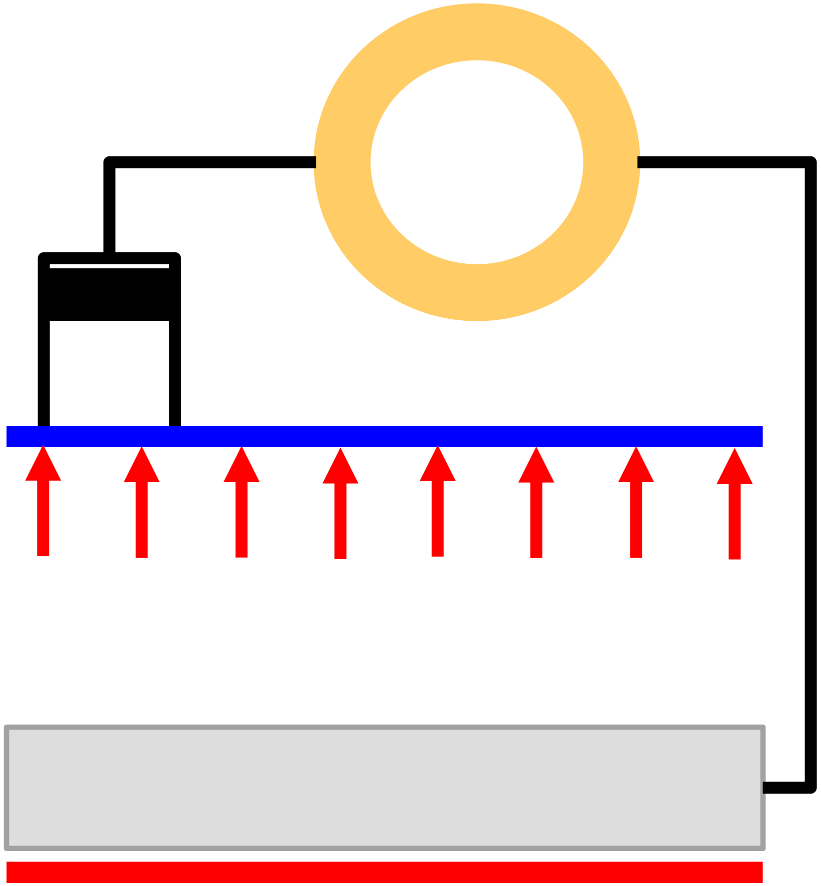
# The Stirling engine

The wheel is connected to the block of foam, when it moves it pushes the foam down.



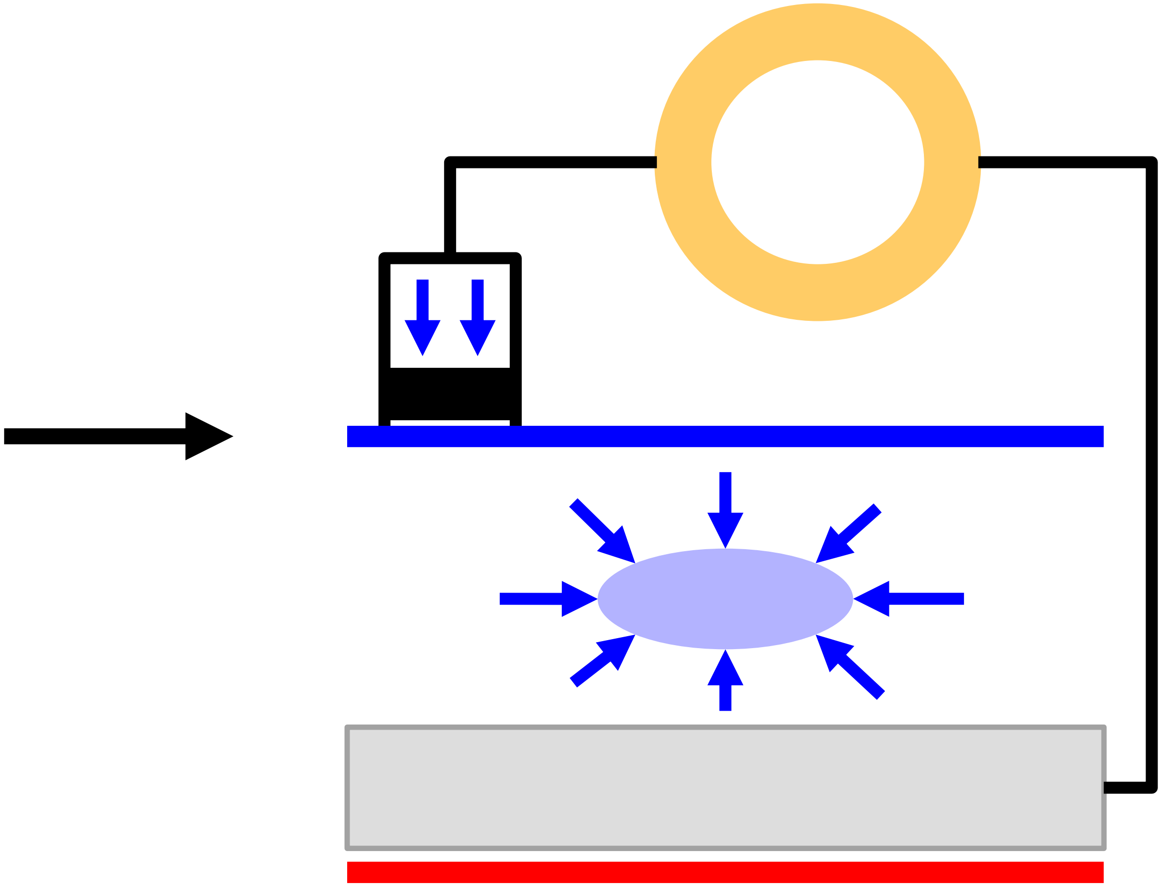
# The Stirling engine

**The hot air in the chamber transfers heat to the cold plate.**



# The Stirling engine

**As the air in the chamber gets cold, it compresses itself. This moves the piston down.**



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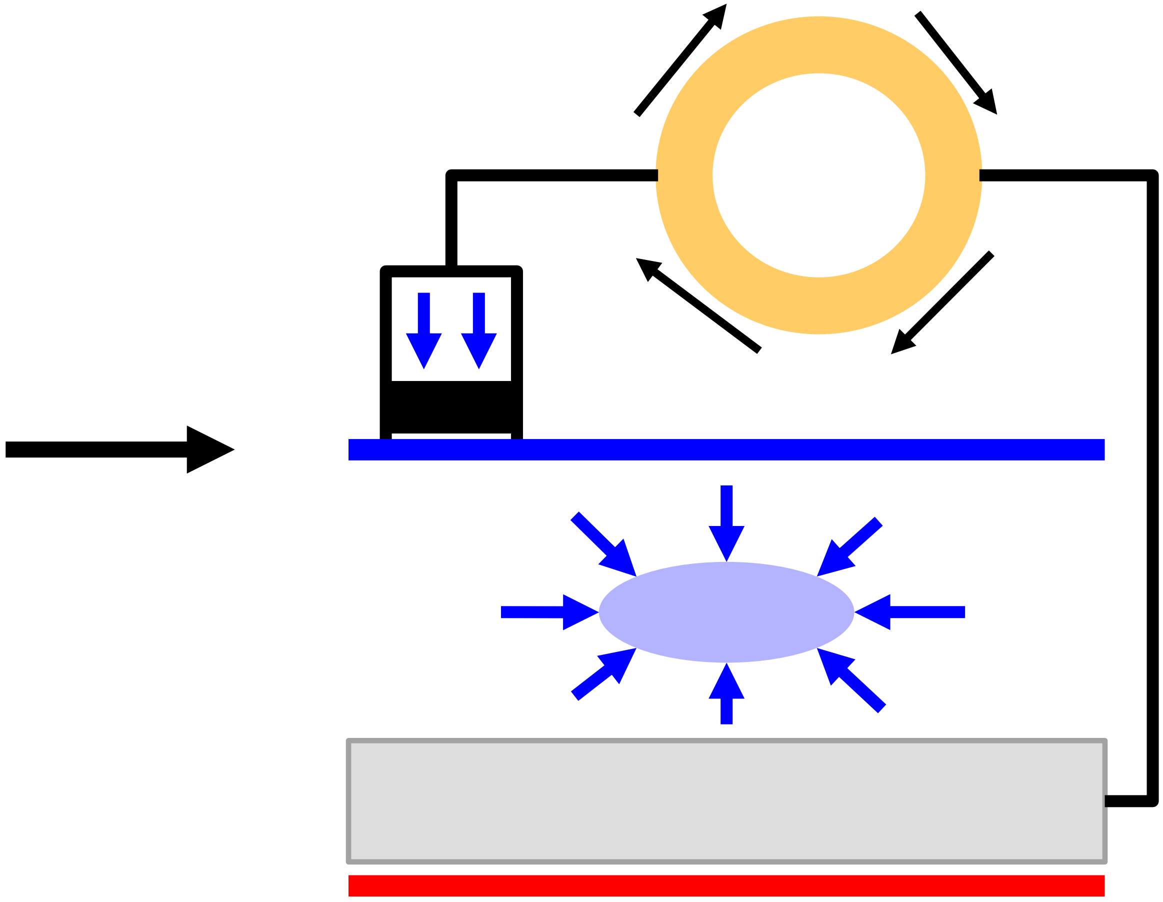
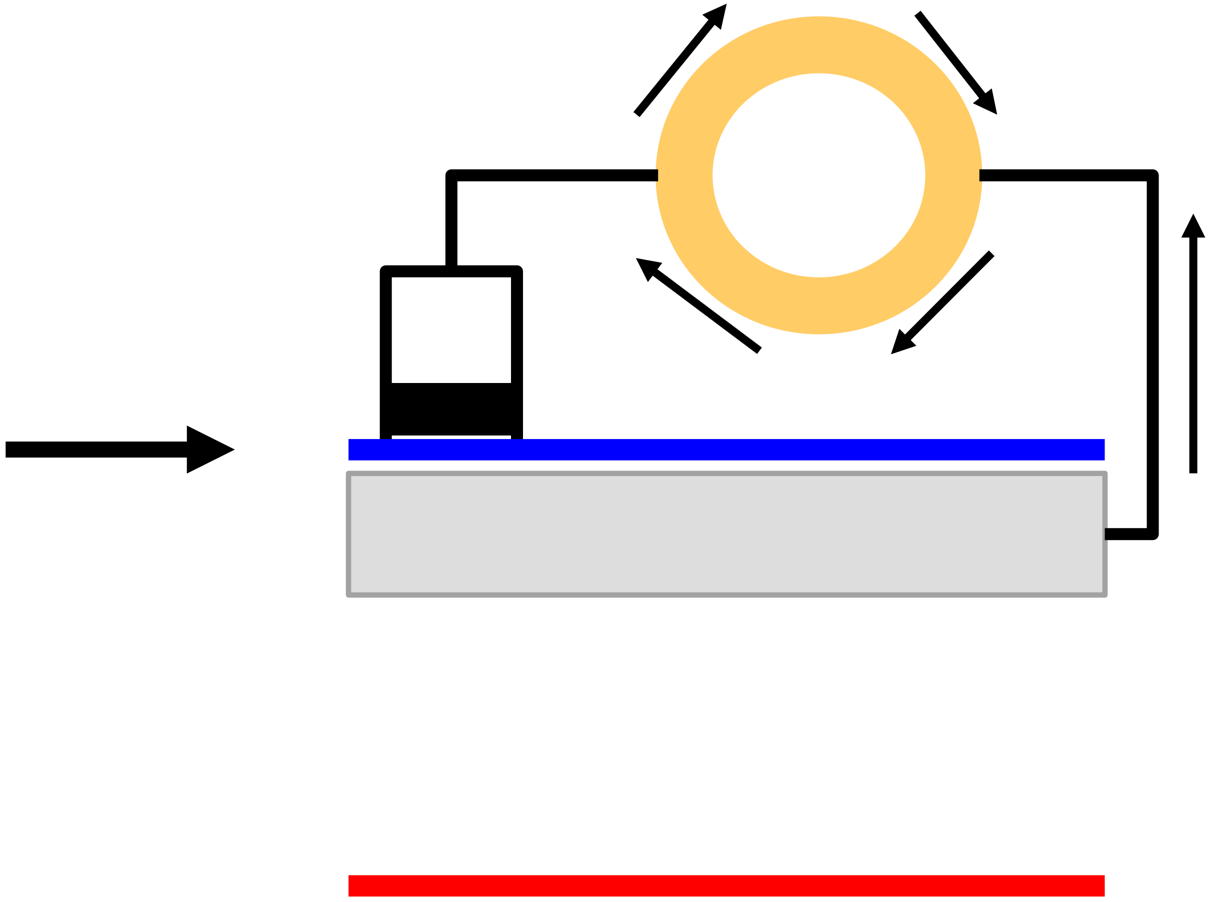


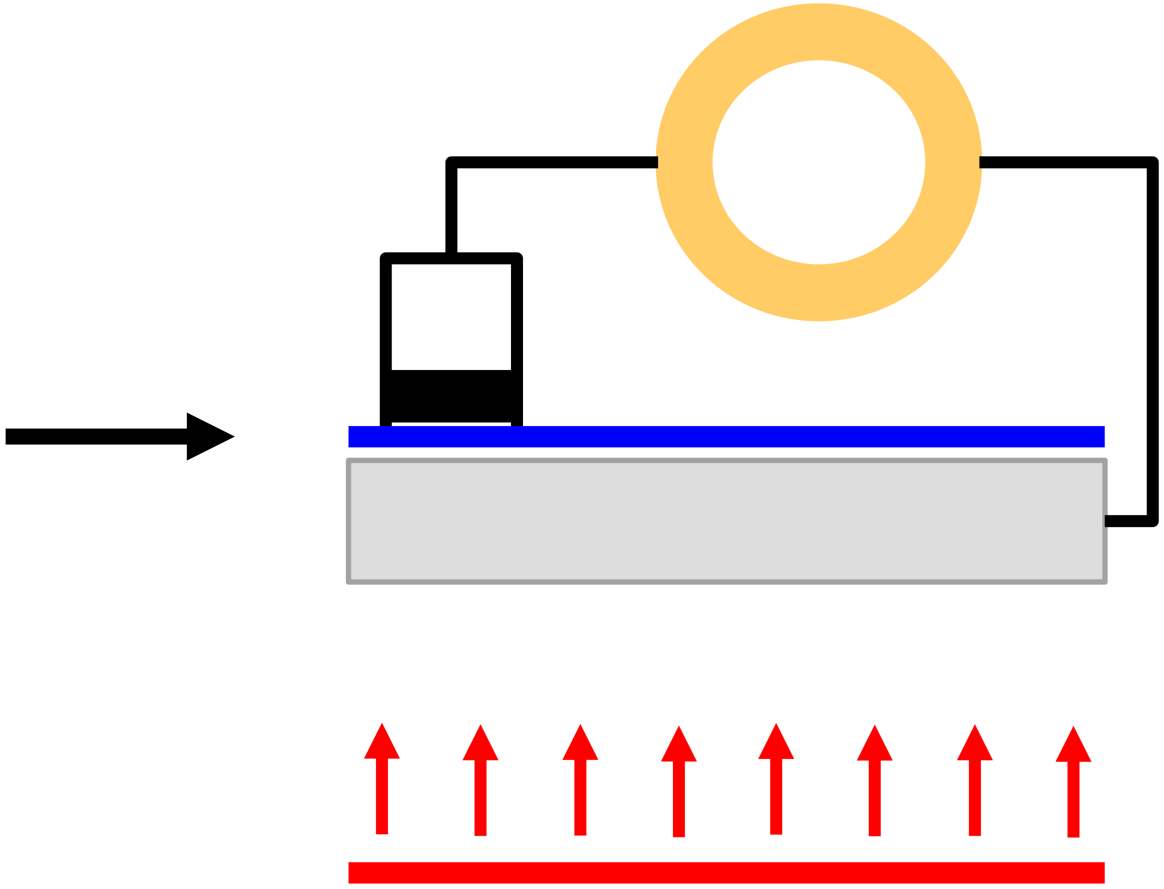
# The Stirling engine

**The wheel is connected to the block of foam, when it moves it pushes the foam up.**



# The Stirling engine

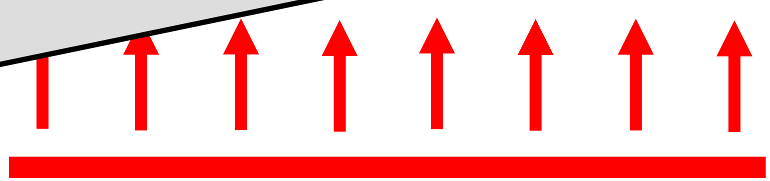
**This is where we were at the beggining. The air in the chamber gets in contact with the hot plate and gets warmed up.**



# The Stirling engine

This is where we were
gets i

**And this process repeats again and again**



# The Stirling engine

## Some questions for you to answer

1. What is the role of entropy in the functioning of an Stirling engine?

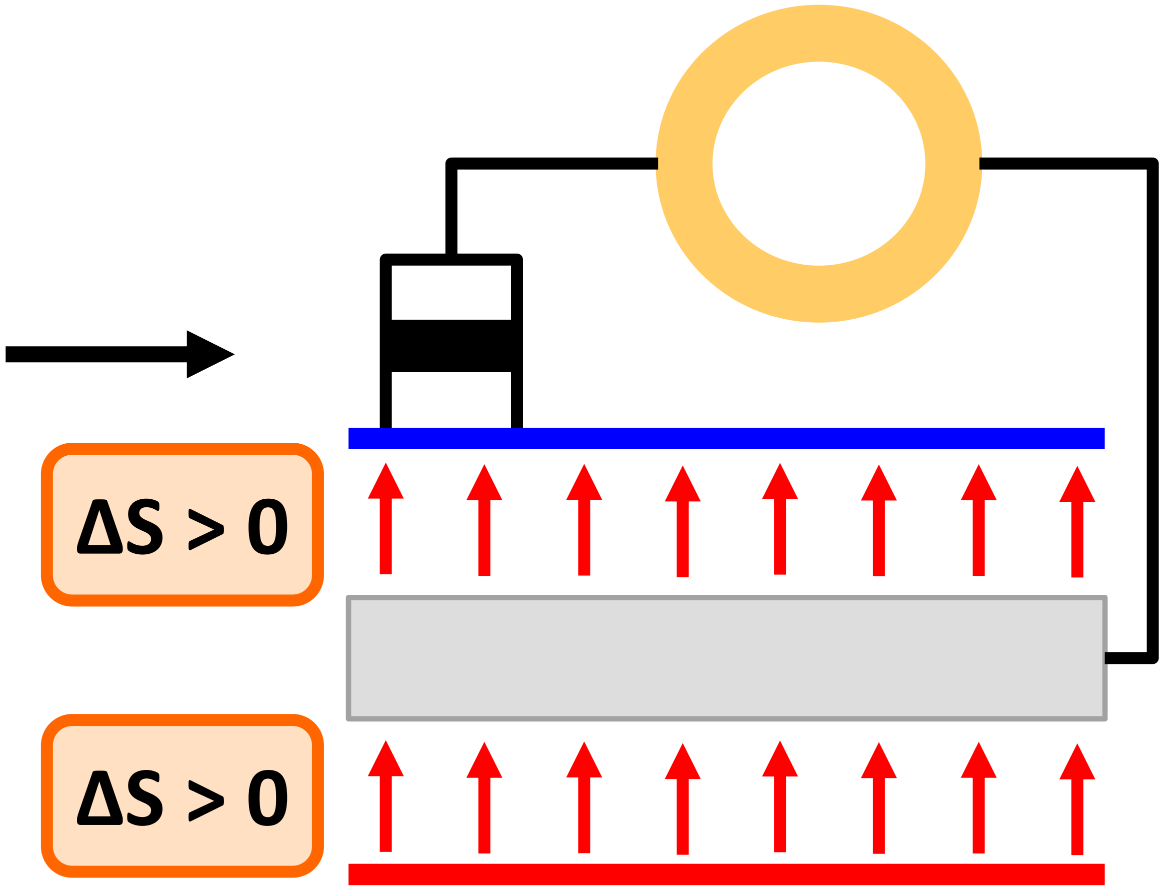
2. Do you think this engine can run forever from the heat of a cup of hot water? Why?

3. If we put the engine in a very hot room, do you think it will be able to run using the heat of a cup of hot water? Why?

4. Do you think this engine can run using a source of cold instead of a source of heat? Why?

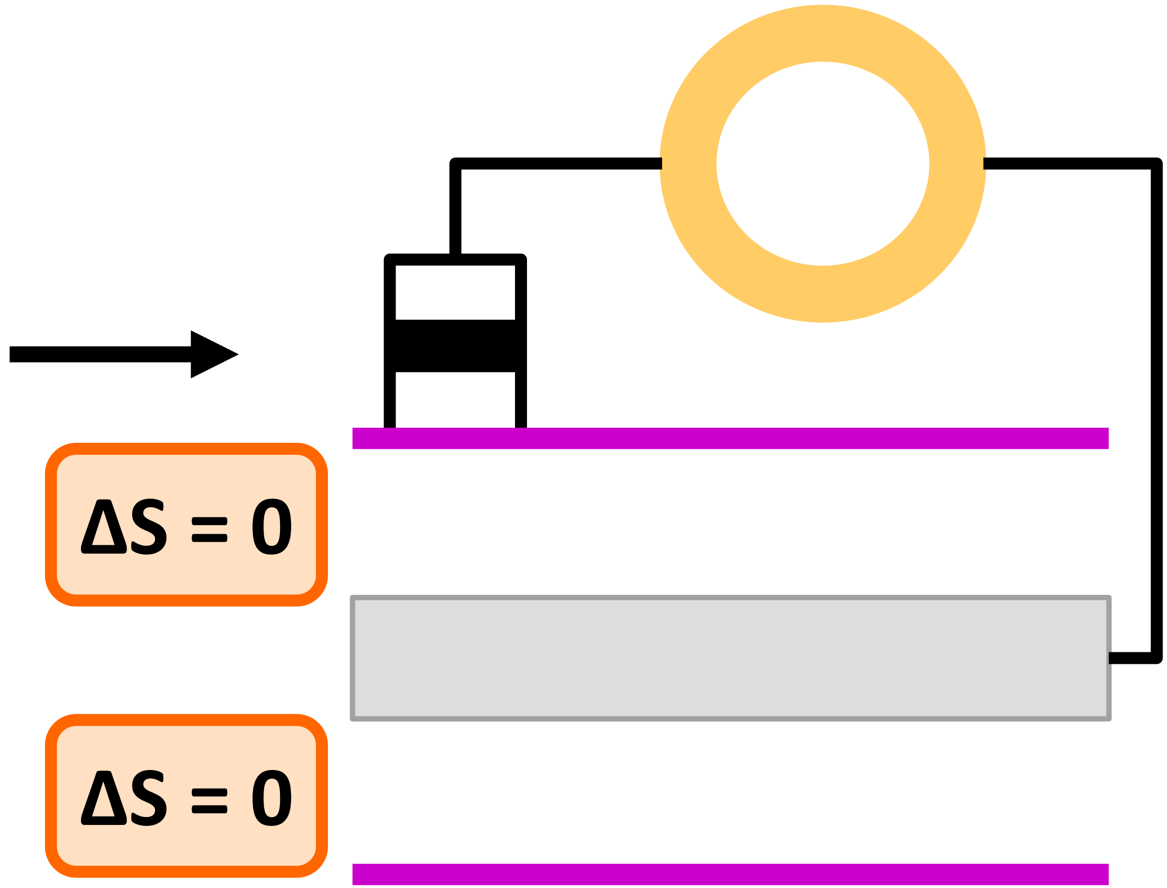
# The Stirling engine

**1. What is the role of entropy in the functioning of an Stirling engine?**



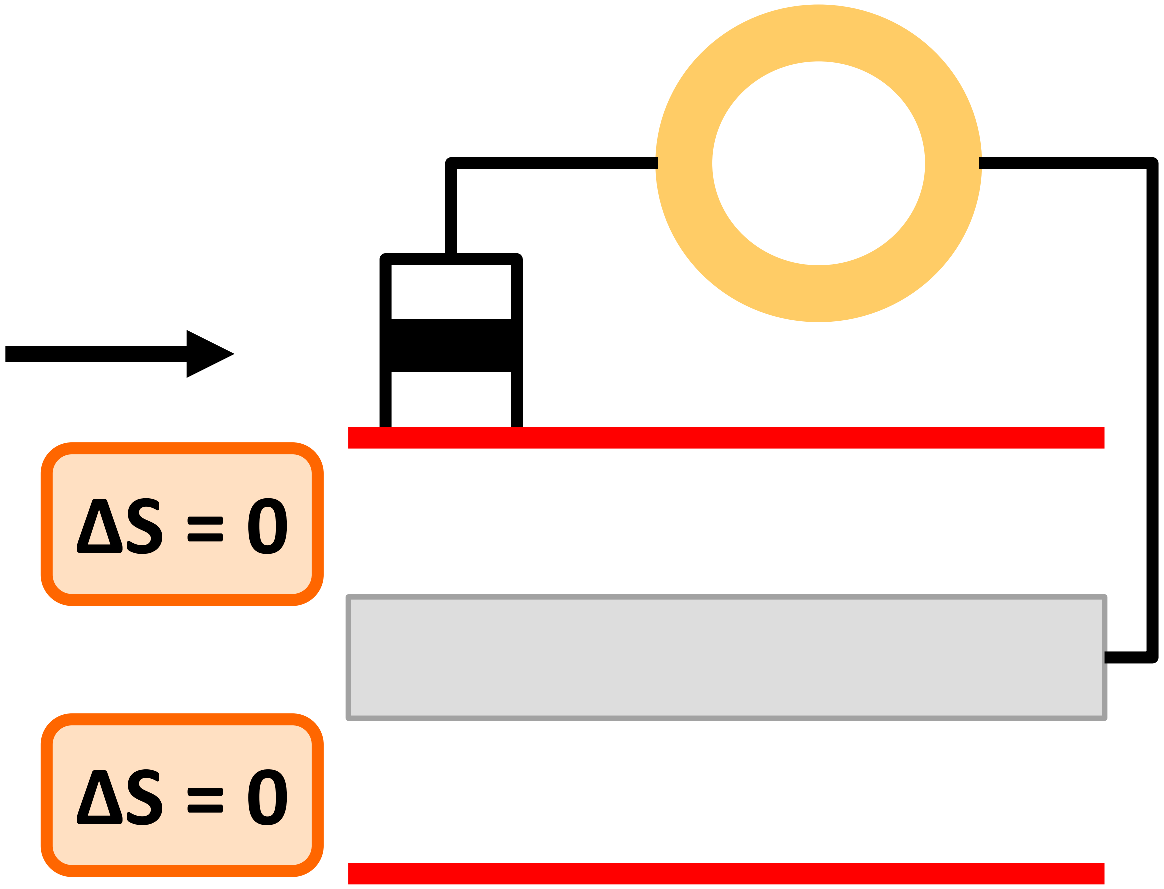
# The Stirling engine

**2. Do you think this engine can run forever from the heat of a cup of hot water? Why?**



# The Stirling engine

**3. If we put the engine in a very hot room, do you think it will be able to run using the heat of a cup of hot water? Why?**



# The Stirling engine

3. If we put the engine i...

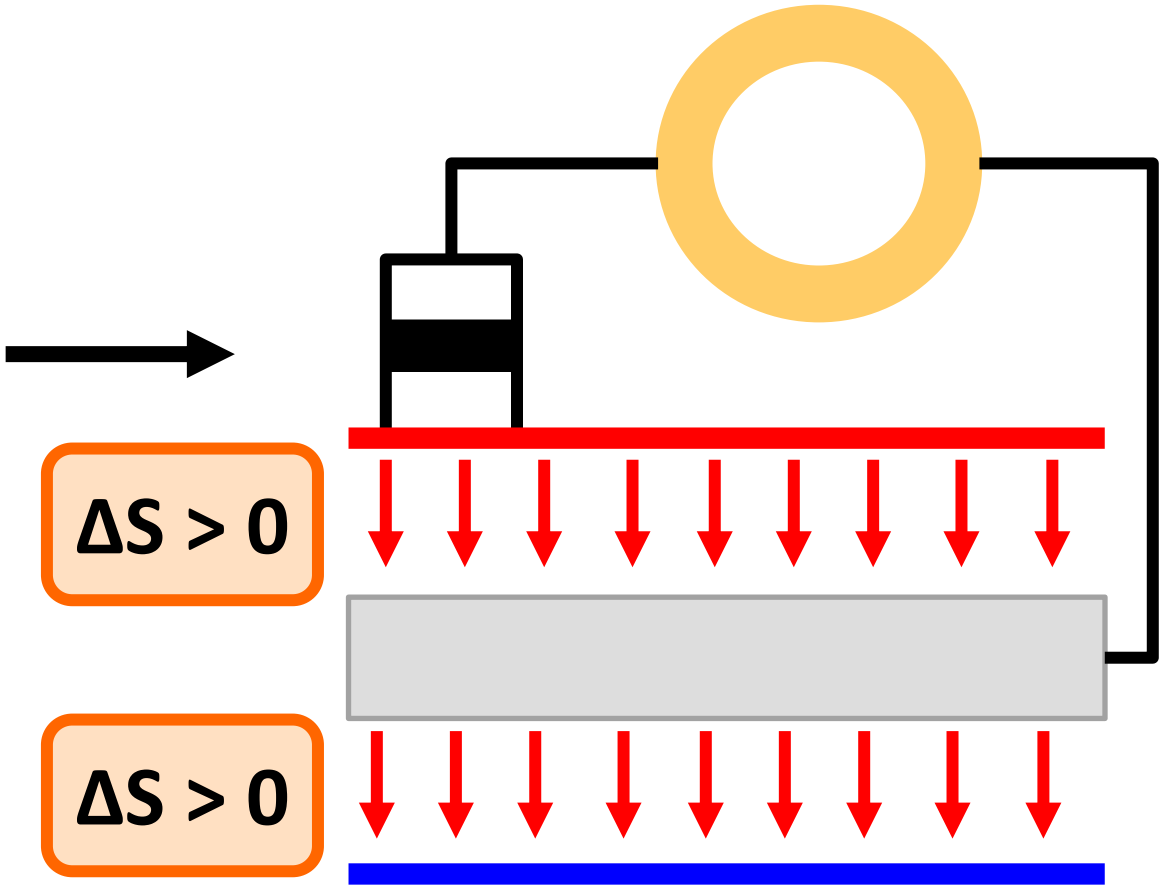
abl...

This engine requires a difference in temperature between the two plates to run

$\Delta S = 0$

# The Stirling engine

**4. Do you think this engine can run using a source of cold instead of a source of heat? Why?**

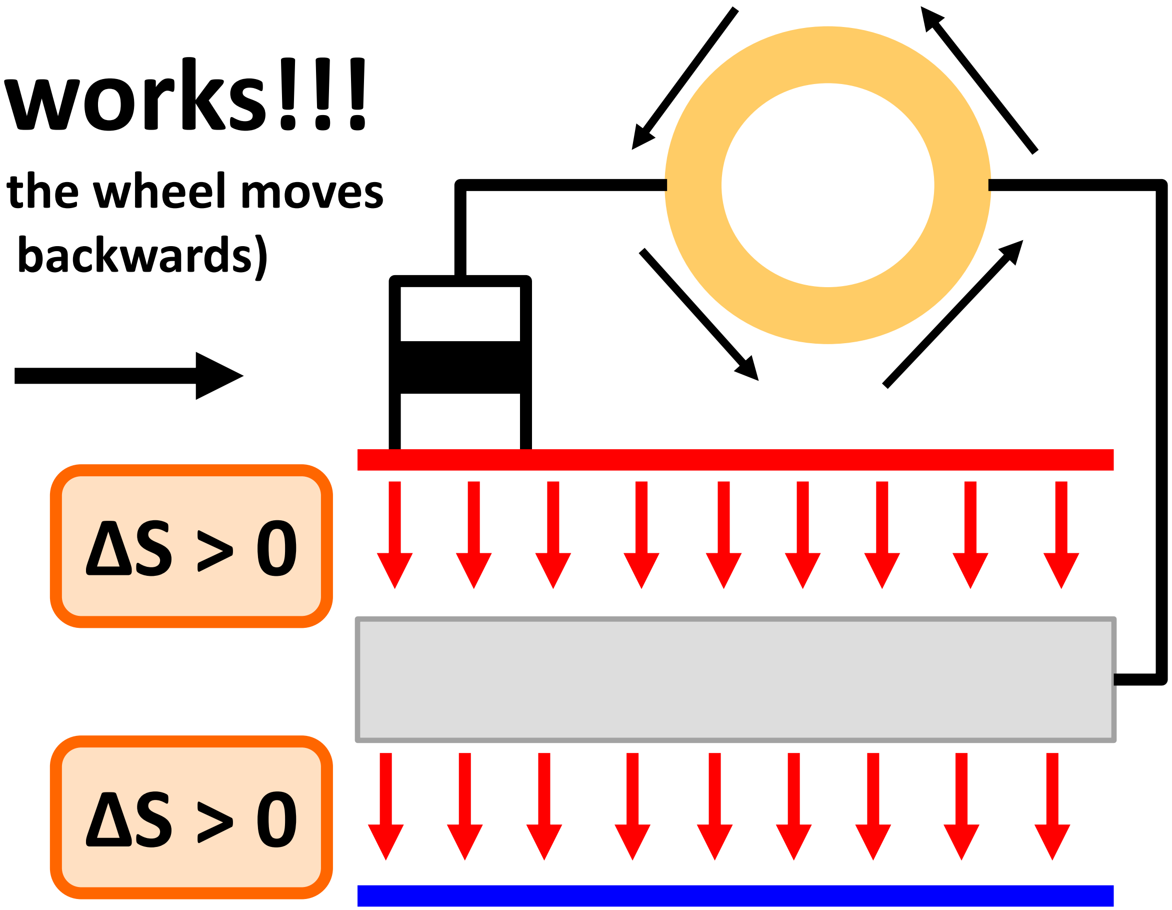


# The Stirling engine

**4. Do you think this engine can run using a source of cold instead of a source of heat? Why?**

**It works!!!**

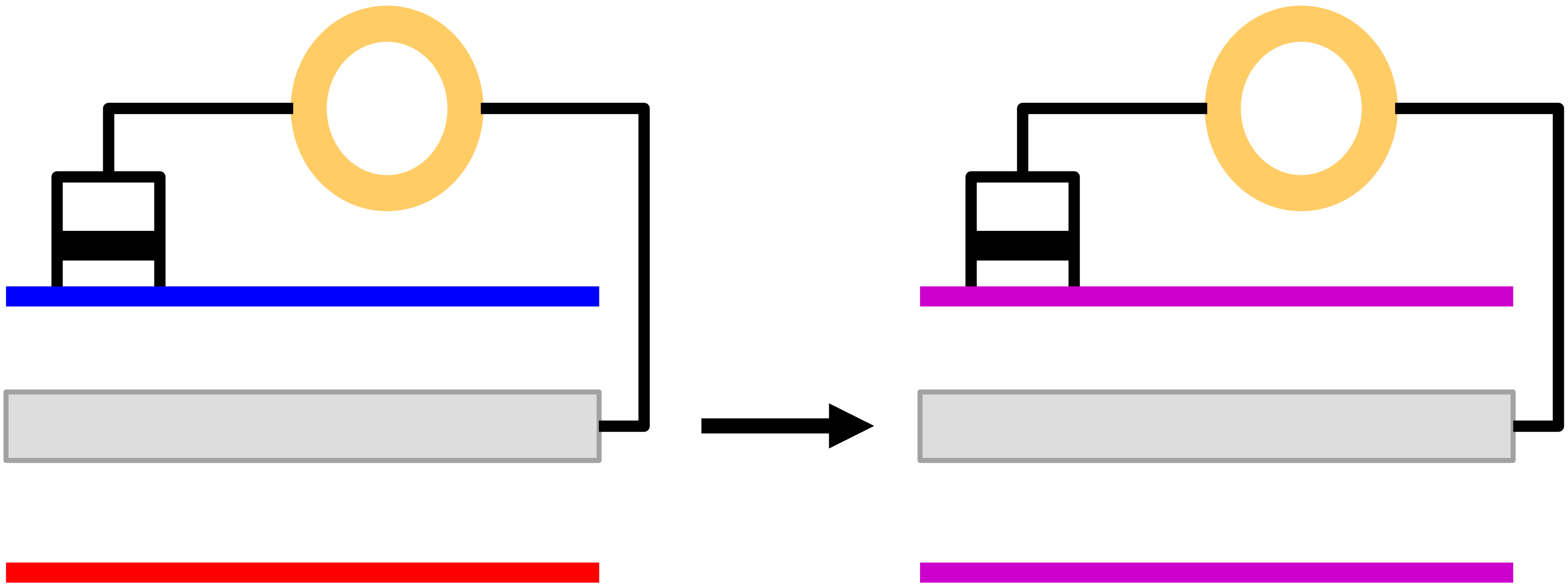
**(But the wheel moves backwards)**



# The Stirling engine and entropy

**With the Stirling engine we can see how energy that is clumped together can be used to do work**

But after this energy is used to do work it is dispersed, and it cannot be used back again



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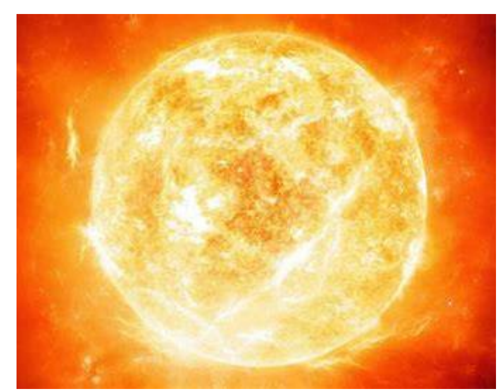
# The Stirling engine and entropy

**With the Stirling engine we can see how energy that is clumped together can be used to do work**

But after this energy is used to do work it is dispersed, and it cannot be used back again

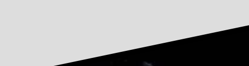
And this happens with everything:

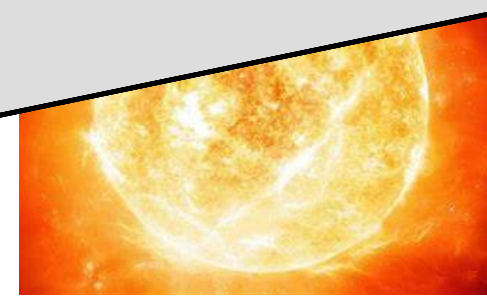


# The Stirling engine and entropy

With the Stirling engin

**And this may be the reason why the universe ends!! (Check the heat death of the universe)**

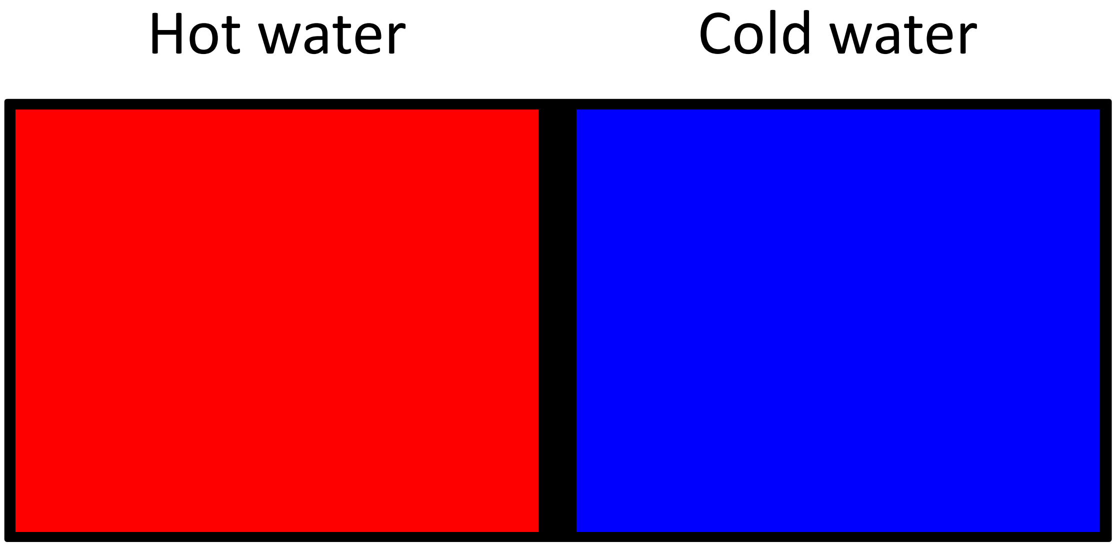




# Why is entropy always increasing?

**Entropy is always increasing because it is always the most likely situation from an statistical point of view**

Imagine the following situation:



# Why is entropy always increasing?

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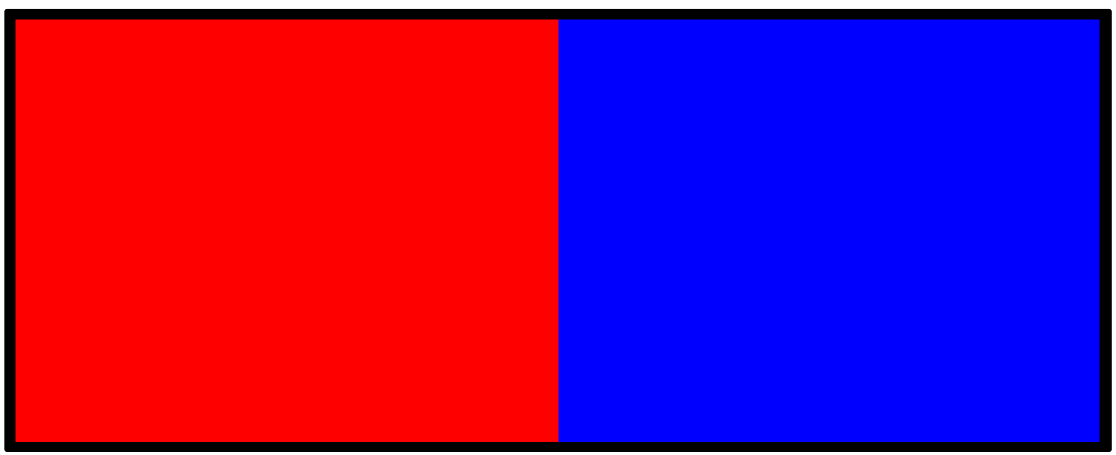
Imagine the following situation:

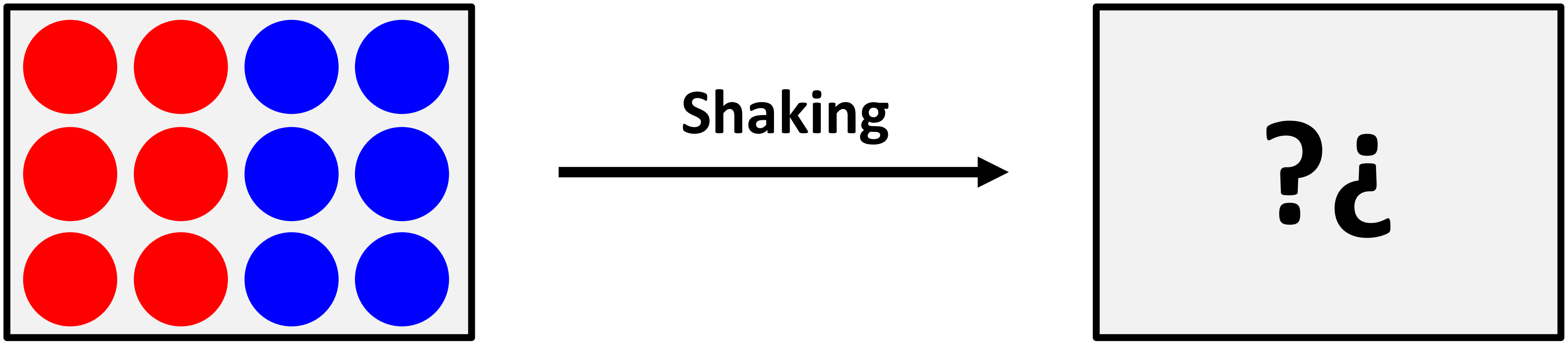
Hot water Cold water



# Why is entropy always increasing?

**Entropy is always increasing because it is always the most likely situation from an statistical point of view**

Since atoms have a lot of freedom of movement, this situation is equivalent to have ping pong balls of different colors in a box and shaking that box.



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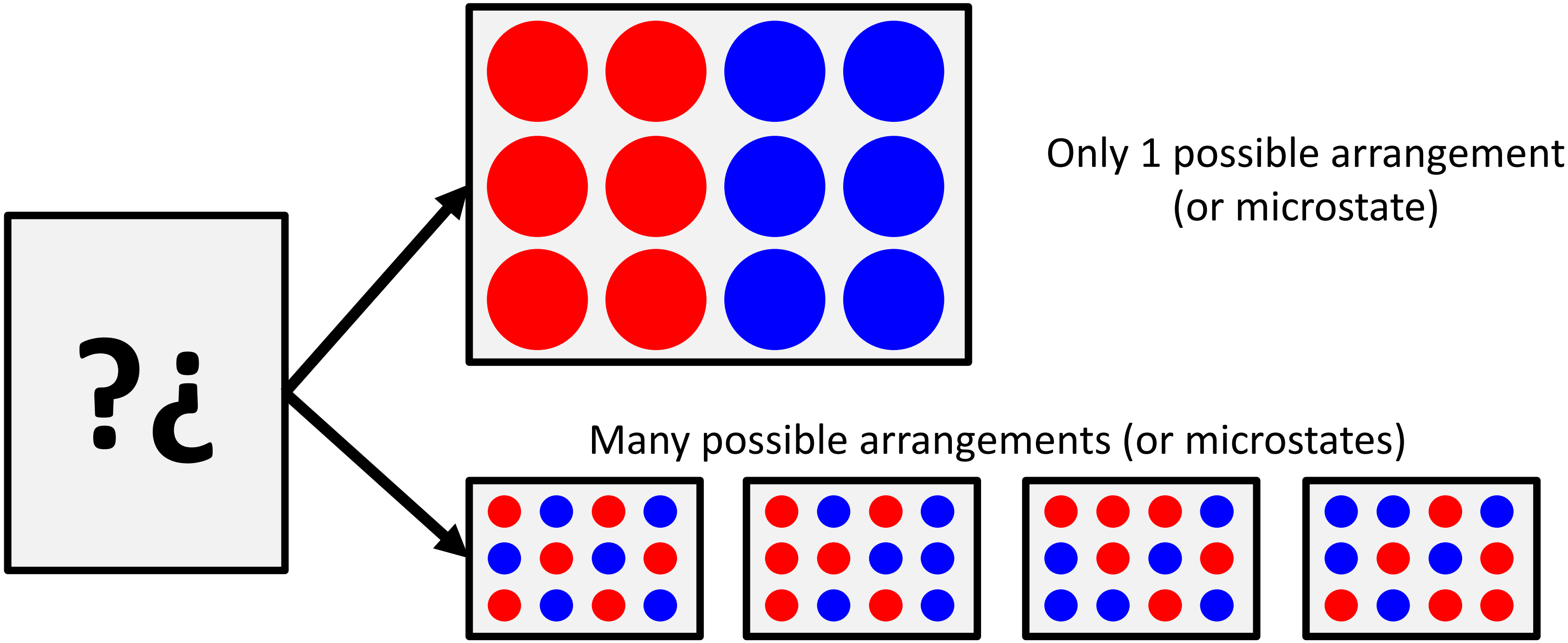


# Why is entropy always increasing?

**Entropy is always increasing because it is always the most likely situation from an statistical point of view**

Also, keep in mind that molecules can clash with each other, then transfering part of their energy to other molecules

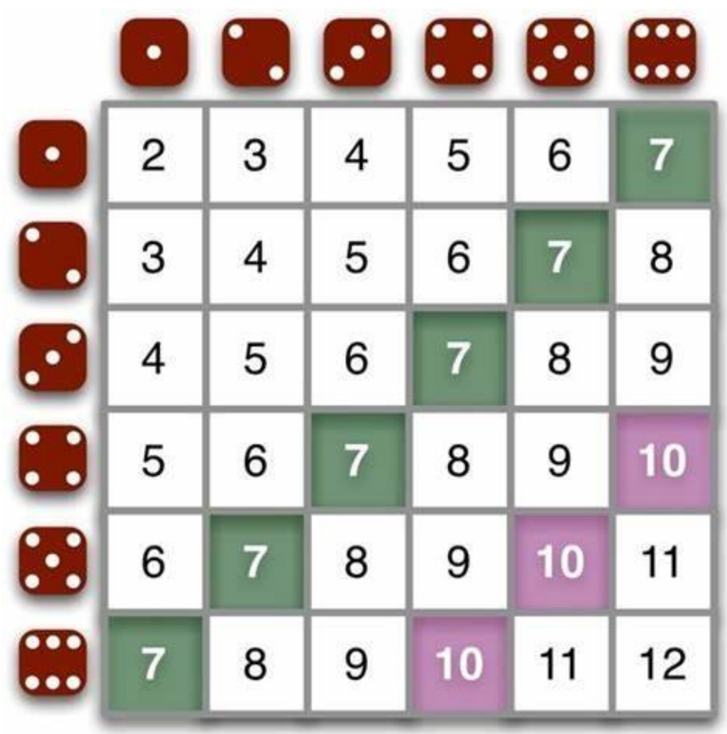
# Why is entropy always increasing?

**Entropy is always increasing because it is always the most likely situation from an statistical point of view**

It is something similar to what happens with the probabilities of having a number when rolling a dice

The number you get is the macrostate

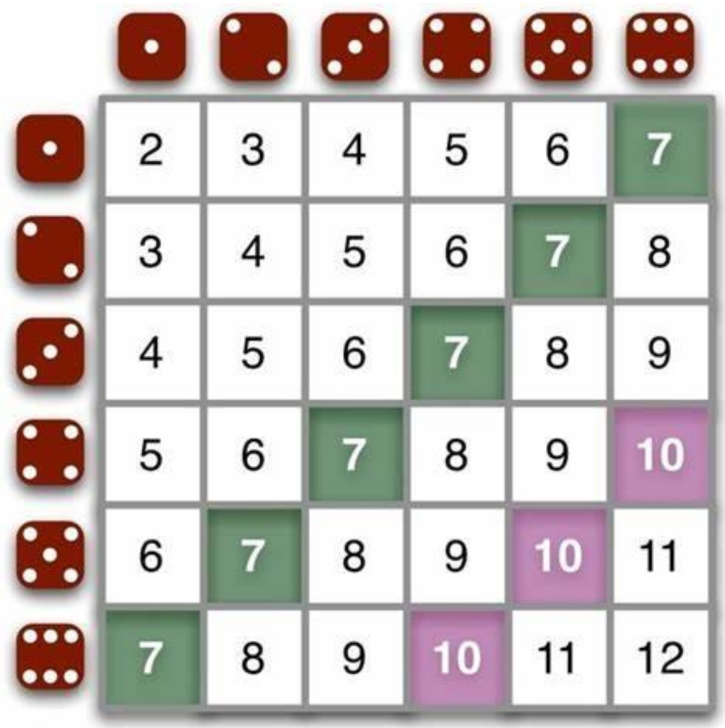
Each combination of dices is a microstate




| Number | Probability |
|---|---|
| **2** | 1/36 |
| **3** | 2/36 |
| **4** | 3/36 |
| **5** | 4/36 |
| **6** | 5/36 |
| **7** | 6/36 |
| **8** | 5/36 |
| **9** | 4/36 |
| **10** | 3/36 |
| **11** | 2/36 |
| **12** | 1/36 |

# Why is entropy always increasing?

## Some questions for you




1. What number is the most likely when rolling two dice? Why?

2. How many microstates are available for that number?

3. What number is the most unlikely when rolling two dice? Why?

4. How many microstates are available for that number?

# Why is entropy always increasing?

**Think about this the next time you play Catan**

# The Stirling engine

**This part of the class was inspired by this youtube video by Steve Mould: https://www.youtube.com/watch?v=w2iTCm0xpDc&t=261s**

If you like science divulgation I really recommend you his channel


A better description of entropy

# The Gibbs free energy equation

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# Enthalpy

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**At constant pressure, the change in enthalpy (ΔH) equals heat**

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But I prefer to think of it this way:

**Chemical bonds contain energy**

**In chemical reactions, bonds are destroyed and made**

**At constant pressure, ΔH is the difference in energy between the broken bonds and the made bonds**

# Enthalpy

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# Bond energy and enthalpy

**Chemical bonds are related to an amount of energy called bond energy, but they don't literally contain this bond energy**

At constant pressure:

**When bonds are created, energy is released as heat**

**When bonds are broken, energy is taken as heat**

# Bond energy and enthalpy

**Chemical bonds are related to energy called bond energy, but they don't literally contain this bond energy**

At constant pressure:

**When bonds are created, energy is released as heat**

$$\Delta H < 0$$

**When bonds are broken, energy is taken as heat**

$$\Delta H > 0$$

# Bond energy and enthalpy

**Chemical bonds are related to energy called bond energy, but they don't literally contain this bond energy**

At constant pressure:

**When bonds are created, energy is released as heat**

**$\Delta H < 0$**

**Processes with $\Delta H < 0$ are <u>exothermic</u>**

**When bonds are broken, energy is taken as heat**

**$\Delta H > 0$**

**Processes with $\Delta H > 0$ are <u>endothermic</u>**

# Bond energy and enthalpy

**Chemical bonds are related to energy called bond energy, but they don't literally contain this bond energy**

At constant pressure:

**The energy that is released when a bond is made is the <u>bond energy</u>**

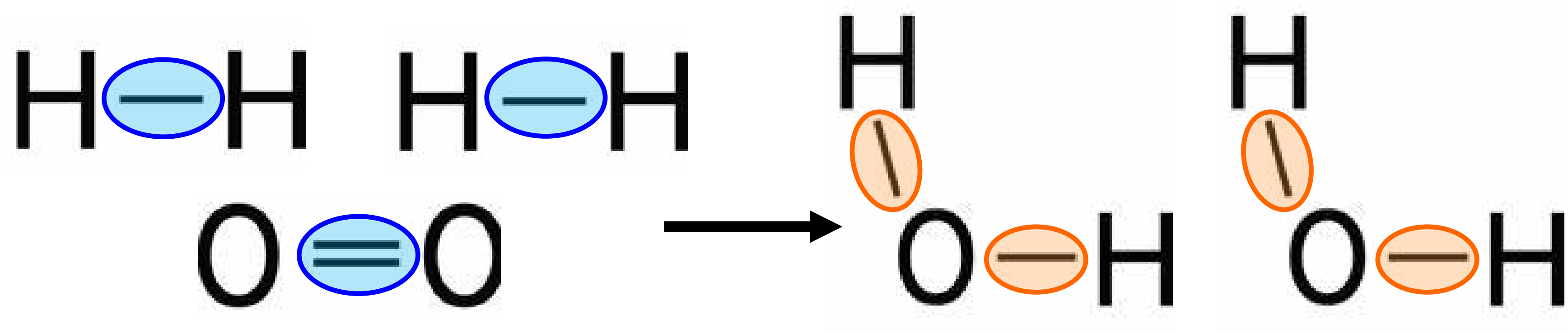
**The energy you have to give to break a bond is the <u>bond energy</u>**

# Bond energy and enthalpy

Let's see a couple of examples: $2H_2 + O_2 \rightarrow 2H_2O$

**Broken bonds: ΔH > 0**

**Created bonds: ΔH < 0**




Bond energy $H_2$ = 432 kJ/mol
Bond energy $O_2$ = 495 kJ/mol

Bond energy $H_2O$ = 467 kJ/mol

**At constant pressure, what is the ΔH of this process?**

# Bond energy and enthalpy

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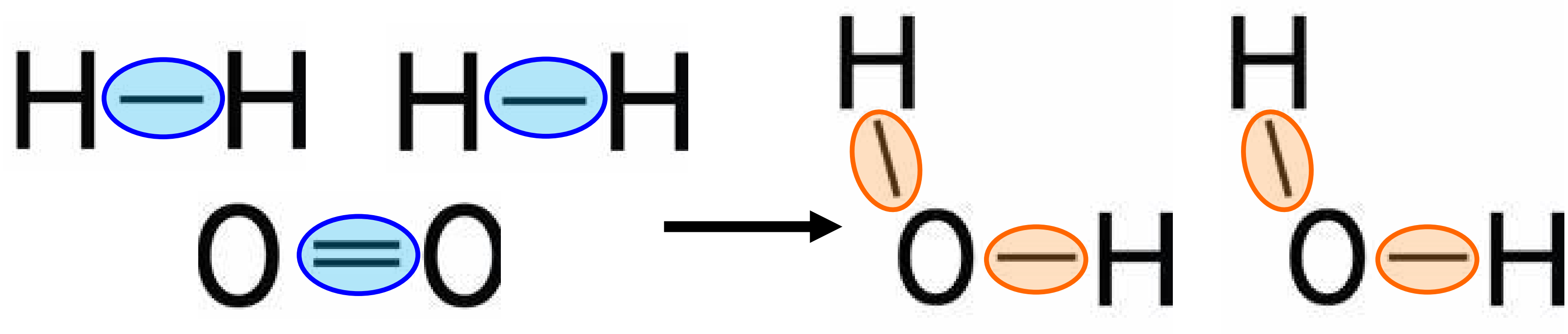


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$$\Delta H = (432 \text{ kJ/mol}*2 + 495 \text{ kJ/mol}) - (467 \text{ kJ/mol}*4)$$

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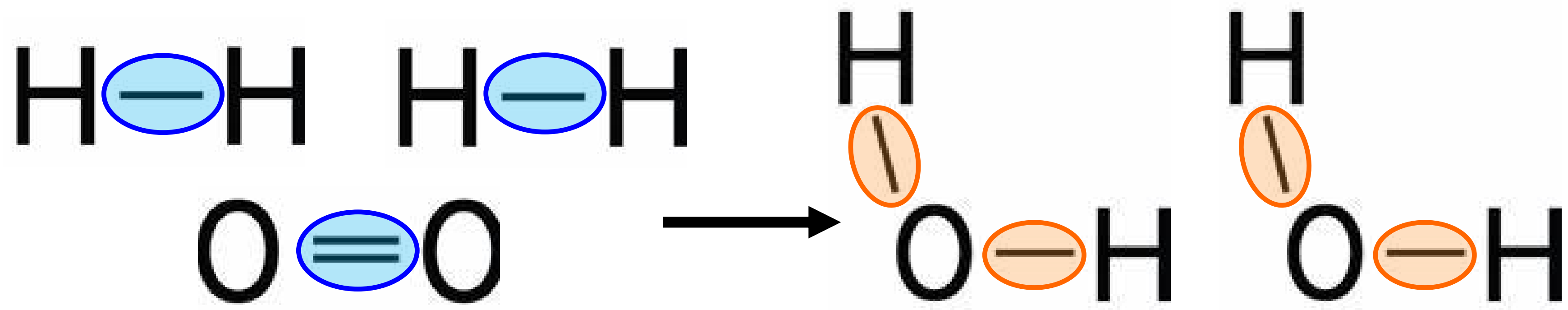


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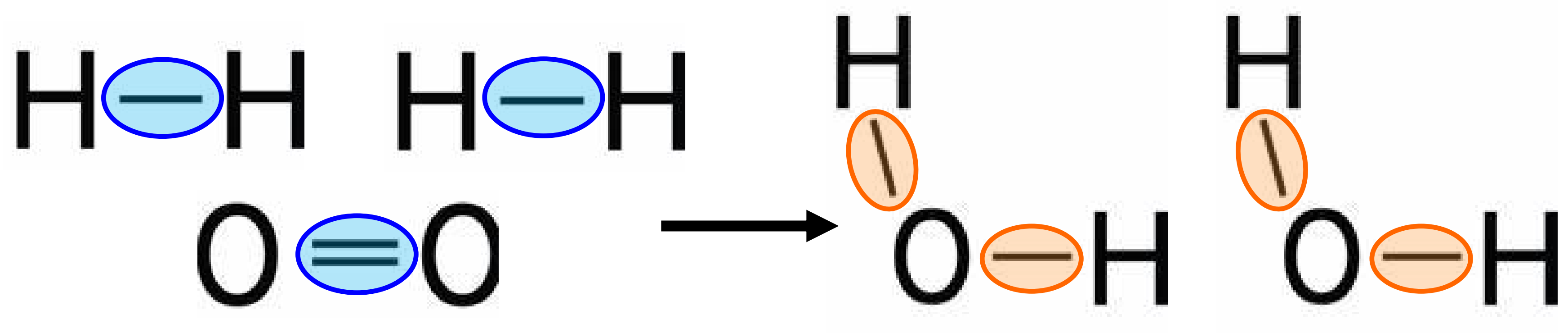



Bond energy $H_2$ = 432 kJ/mol
Bond energy $O_2$ = 495 kJ/mol

Bond energy $H_2O$ = 467 kJ/mol

ΔH = -469 kJ/mol

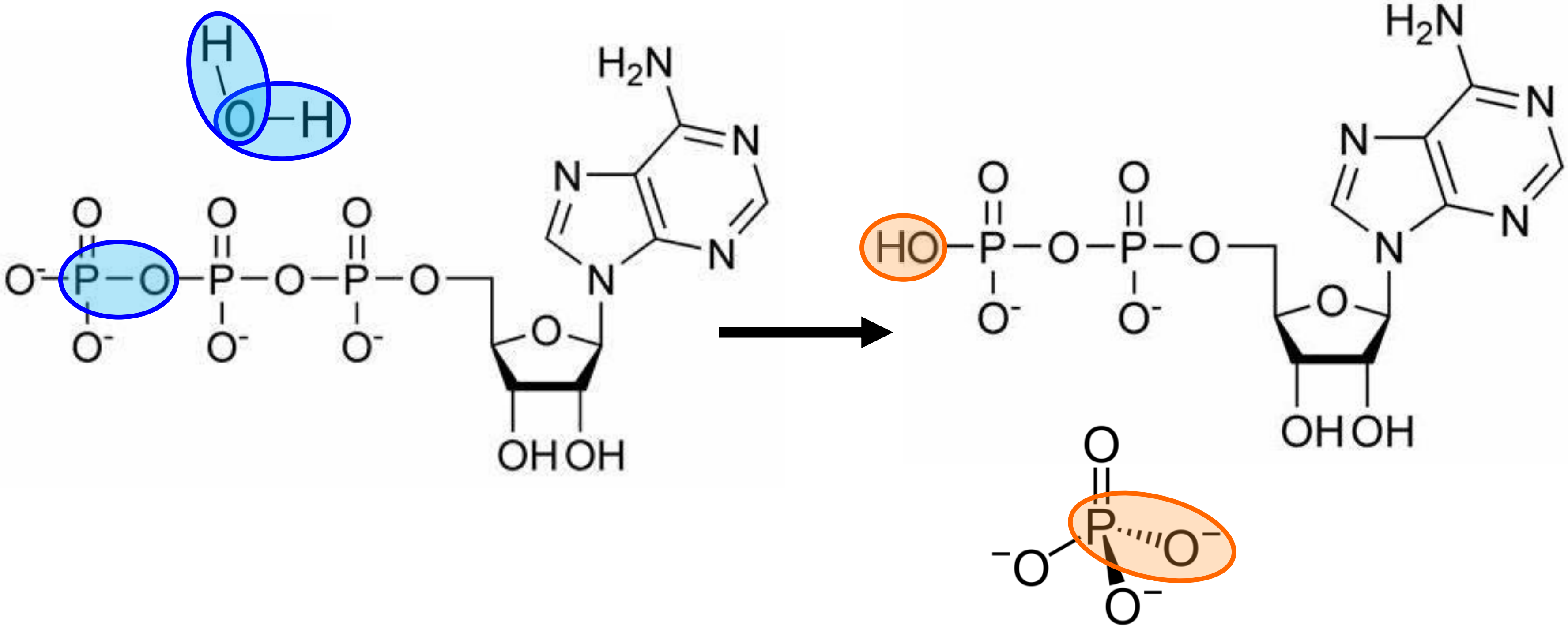
It is an exothermic process, this is how rocket fuel works!

# Bond energy and enthalpy

Let's see a couple of examples: ATP hydrolysis

**Broken bonds: ΔH > 0**

**Created bonds: ΔH < 0**

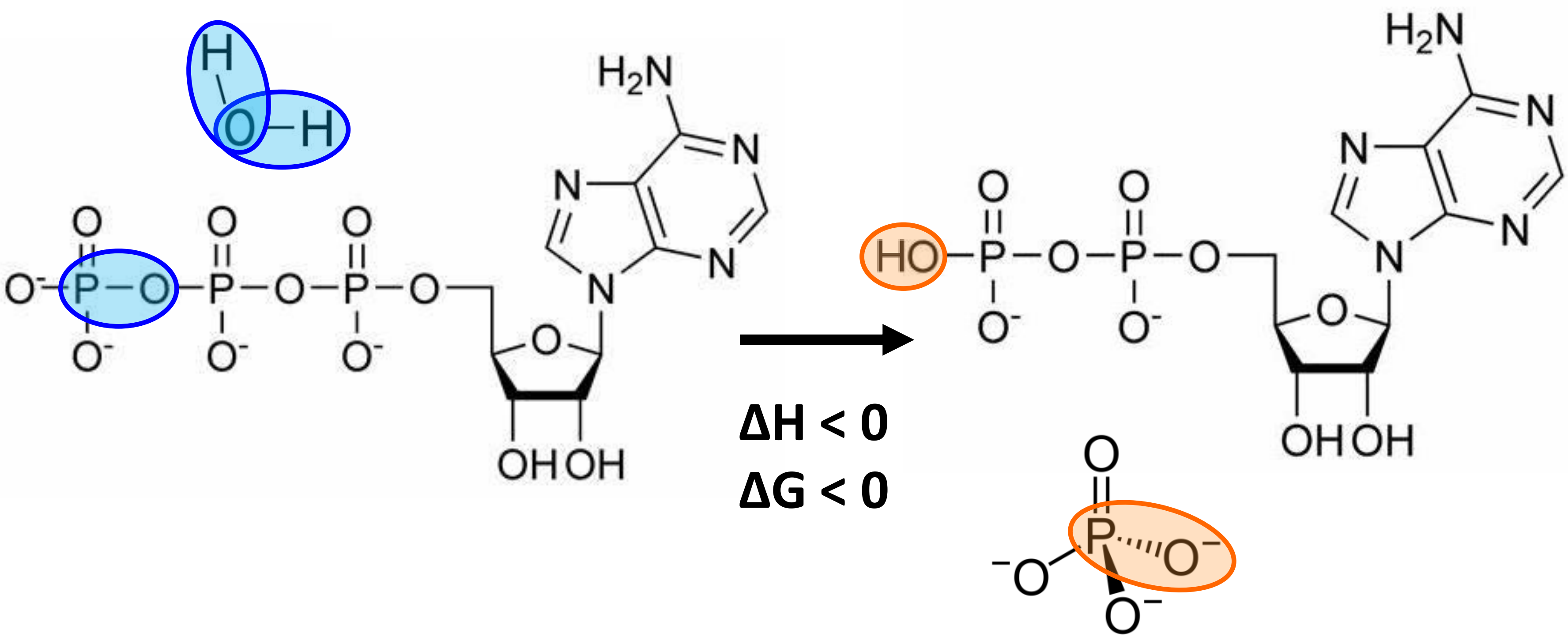


# Bond energy and enthalpy

Let's see a couple of examples: ATP hydrolysis

**Broken bonds: ΔH > 0**
**The broken bonds have low bond energy (ATP mostly, not water)**

**Created bonds: ΔH < 0**
**The created bonds have high bond energy**



# Enthalpy

$$\Delta G = \Delta H - T \cdot \Delta S$$

When bonds are created, energy is released as heat

$\Delta H < 0$

Processes with $\Delta H < 0$ favor spontaneity ($\Delta G < 0$)

When bonds are broken, energy is taken as heat

$\Delta H > 0$

Processes with $\Delta H > 0$ oppose to spontaneity ($\Delta G > 0$)

# Enthalpy

**Try to solve the following exercises without doing calculations, just thinking:**

1. Consider two complementary molecules of single stranded DNA inside the cell nucleus. If they hybridize, will this process increase or decrease the enthalpy of the DNA molecules?

2. Imagine a protein with a lot of alpha helices:
   - Does it has hydrogen bonds?
   - What happens if we increase the temperature of the protein?
   - What is the $\Delta H$ of this process?

# Enthalpy

**Try to solve the following exercises without doing calculations, just thinking:**

1. Consider two complementary molecules of single stranded DNA inside the cell nucleus. If they hybridize, will this process increase or decrease the enthalpy of the DNA molecules?

**Bonds are being made and no bonds are broken. Therefore, the only option is that $\Delta H < 0$**

# Enthalpy

**Try to solve the following exercises without doing calculations, just thinking:**

2. Imagine a protein with a lot of alpha helices:
   - Does it has hydrogen bonds?
   - What happens if we increase the temperature of the protein?
   - What is the $\Delta H$ of this process?

**If we focus on the protein only, bonds are broken and no new bonds are made. Therefore, the only option is that $\Delta H > 0$.**

# The Gibbs free energy equation

$$\Delta G = \Delta H - T \cdot \Delta S$$

**Try to solve the following exercises without doing calculations, just thinking:**

1. Consider a block of ice and a glass of liquid water:
   - What is the $\Delta H$ for going from solid ice to liquid water?
   - What is the $\Delta S$ for going from solid ice to liquid water?
   - Under what conditions becomes spontaneous going from solid ice to liquid water?

2. Consider two water molecules floating in vaccum, if they create a hydrogen bond between themselves:
   - What is the $\Delta H$ of the process?
   - What is the $\Delta S$ of the process?
   - What value is larger in absolut values? $|\Delta H|$ or $|T \cdot \Delta S|$?

# The Gibbs free energy equation

$$\Delta G = \Delta H - T \cdot \Delta S$$

When creating bonds:

**ΔS opposes to it**

**ΔH favors it**

When breaking bonds:

**ΔS favors it**

**ΔH opposes to it**

# The Gibbs free energy equation

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   - What is the ΔH for going from solid ice to liquid water?
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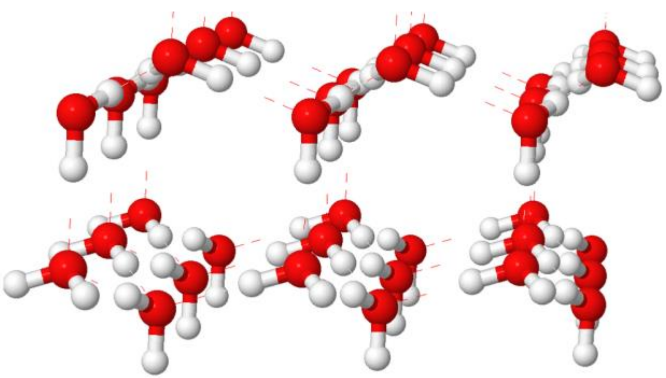
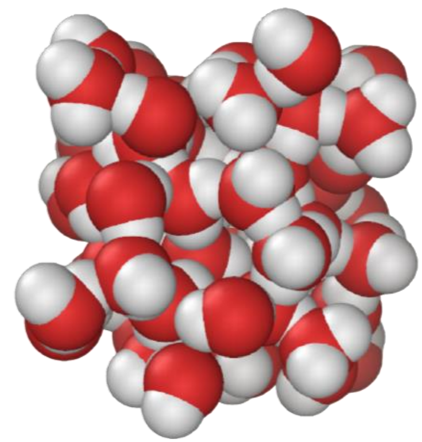


2 HB/molecule

$\Delta H > 0$

$\Delta S > 0$

$\longrightarrow$

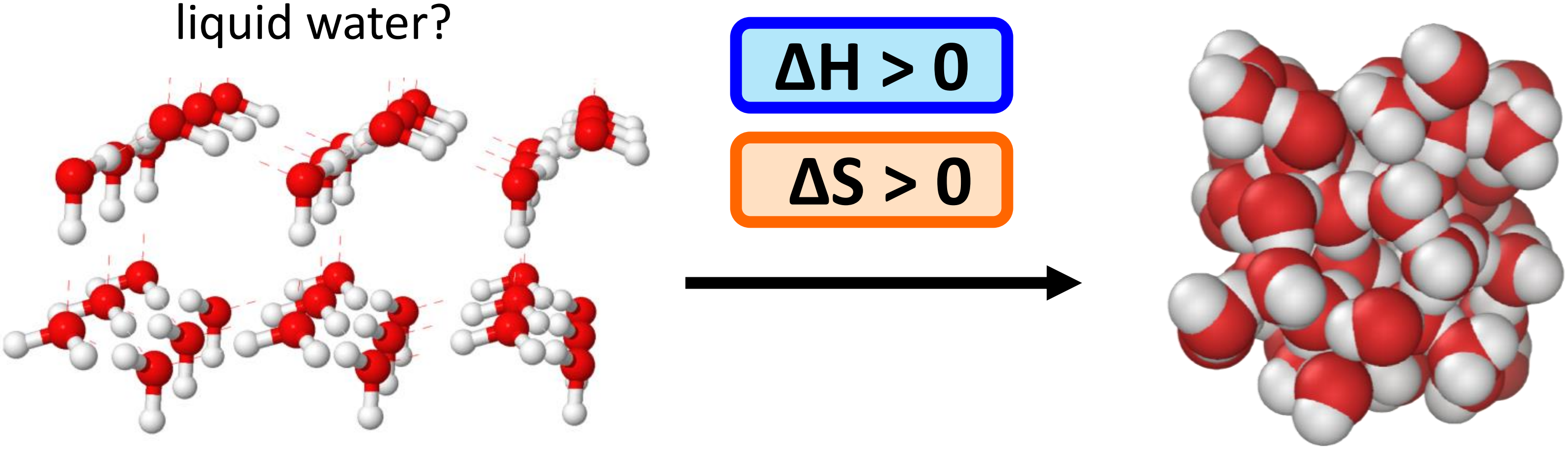


1.5 HB/molecule

# The Gibbs free energy equation

$$\Delta G = \Delta H - T \cdot \Delta S$$

1. Consider a block of ice and a glass of liquid water:
   - What is the ΔH for going from solid ice to liquid water?
   - What is the ΔS for going from solid ice to liquid water?
   - Under what conditions becomes spontaneous going from solid ice to liquid water?

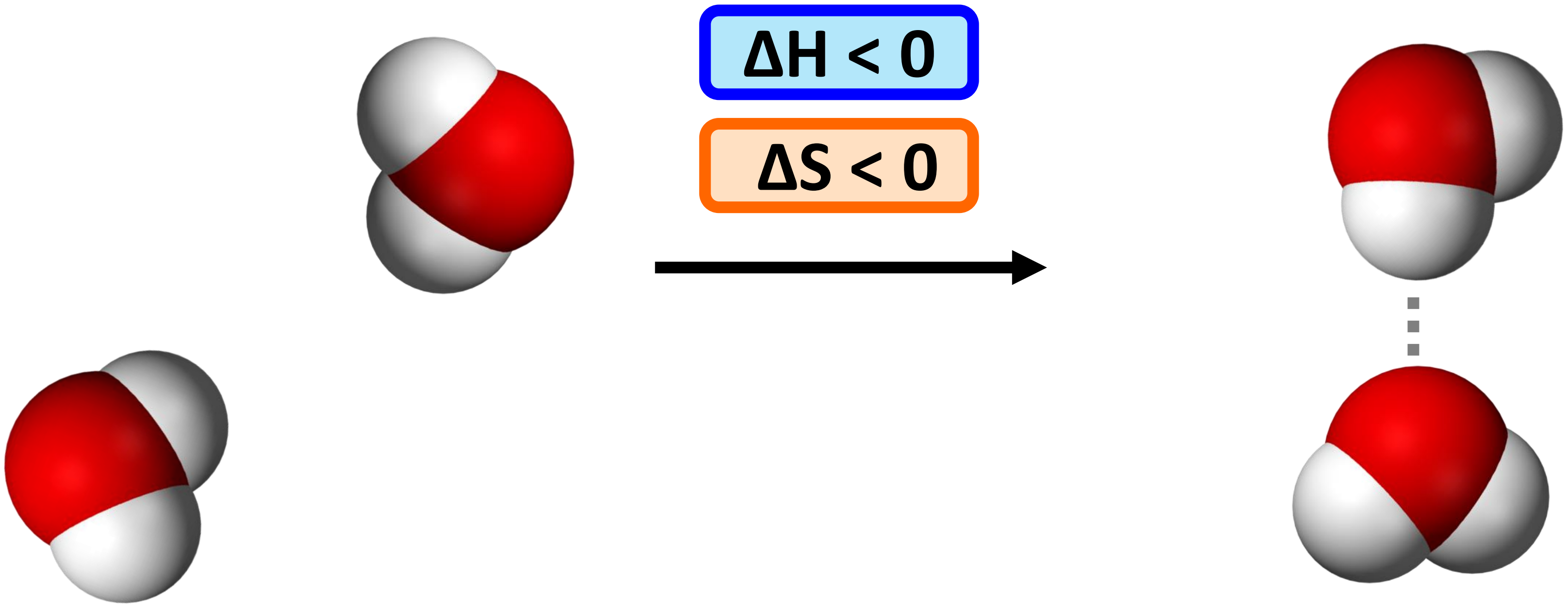



**At 273K, T·ΔS becomes as important as ΔH. Above 273K, the system favors entropy over enthalpy.**

# The Gibbs free energy equation

$$\Delta G = \Delta H - T \cdot \Delta S$$

2. Consider two water molecules floating in vaccum, if they create a hydrogen bond between themselves:
    - What is the ΔH of the process?
    - What is the ΔS of the process?
    - What value is larger in absolut values? |ΔH| or |T·ΔS|?



# The Gibbs free energy equation

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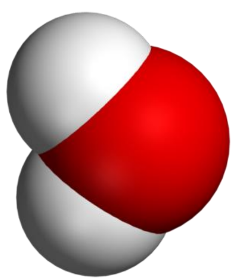
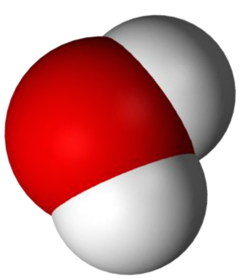
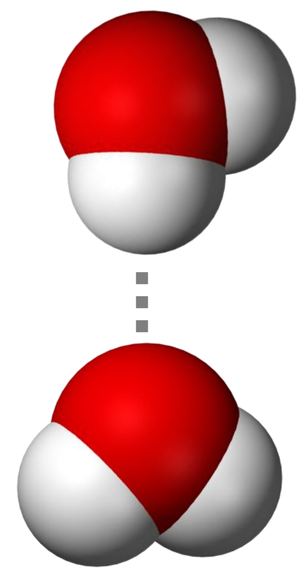




$\Delta H < 0$

$\Delta S < 0$



**When hydrogen bonds are made it is because ΔH is more important than T·ΔS, but at higher temperatures hydrogen bonds are broken**

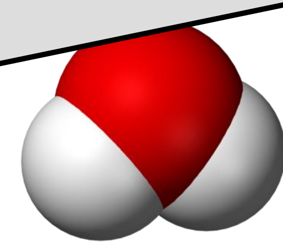
# The Gibbs free energy equation

$\Delta G$

**<u>Temperature</u> is what determines which of the two terms is more relevant!**

ΔS,

...ratures hydrogen
bonds are broken



# Some videos for you to study

A better description of entropy – YouTube
https://www.youtube.com/watch?v=w2iTCm0xpDc

What is entropy? - Jeff Phillips – YouTube
https://www.youtube.com/watch?v=YM-uykVfq_E

Enthalpy: Crash Course Chemistry #18 – YouTube
https://www.youtube.com/watch?v=SV7U4yAXL5I&t=385s

Lecture 03, concept 12: Phase transitions from entropy-enthalpy balance – YouTube
https://www.youtube.com/watch?v=NITMgwZgohI&list=PLuIpgNT2hMwTyjpKVevMHUofykrXFtNVW&index=12

Lecture 03, concept 15: Hydrogen bond formation in water interpreted with entropy/enthalpy – YouTube
https://www.youtube.com/watch?v=CR7rfTyNpdo&list=PLuIpgNT2hMwTyjpKVevMHUofykrXFtNVW&index=15