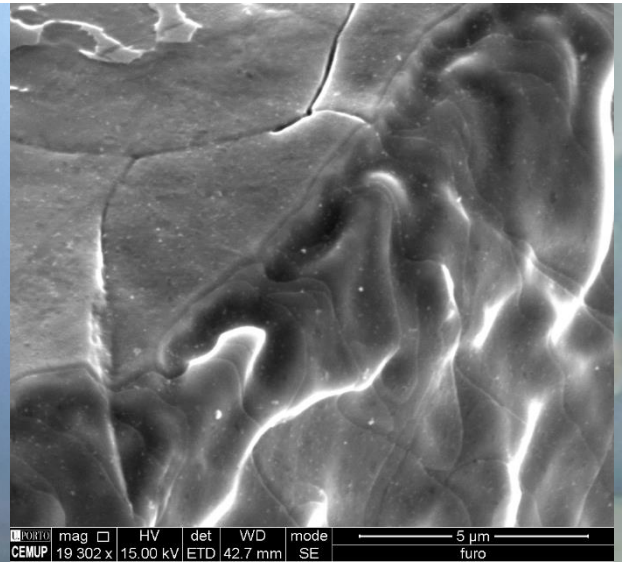
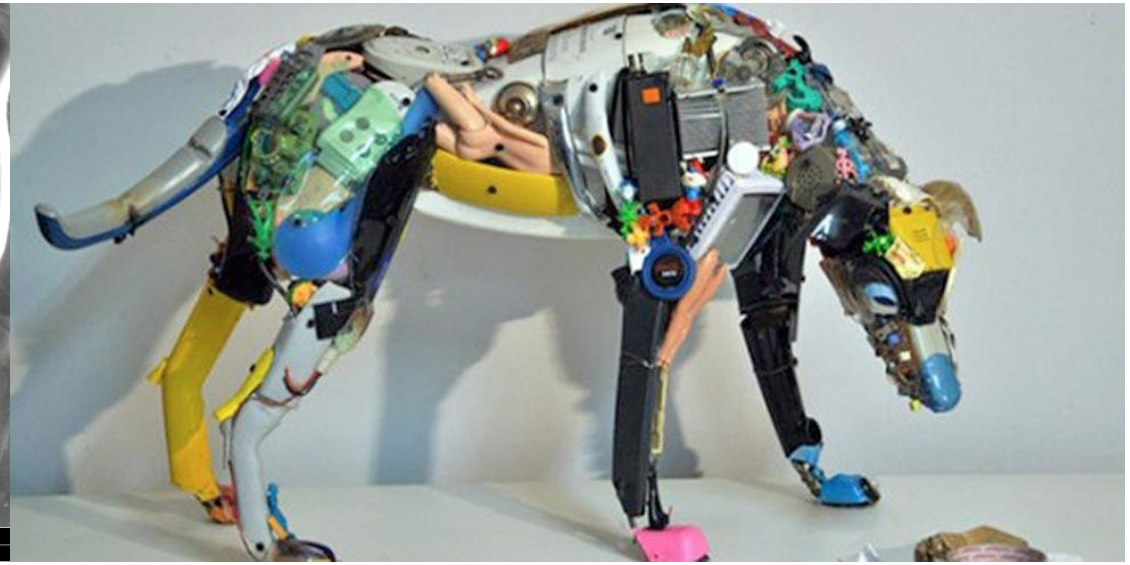
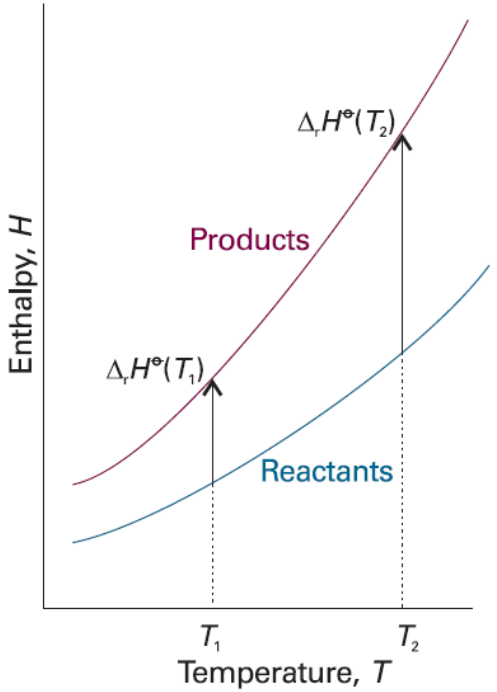
Physical Chemistry

... iremos explorar, refletir, aprender ?..

Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.







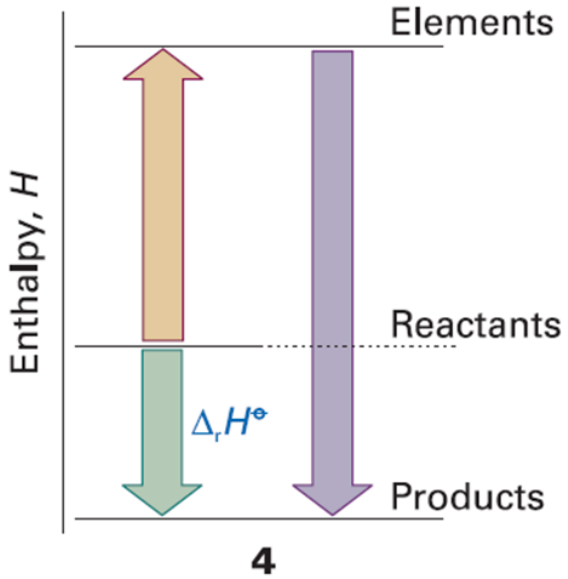
Hess's law

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus$$

Kirchhoff's law

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus \mathrm{d}T$$

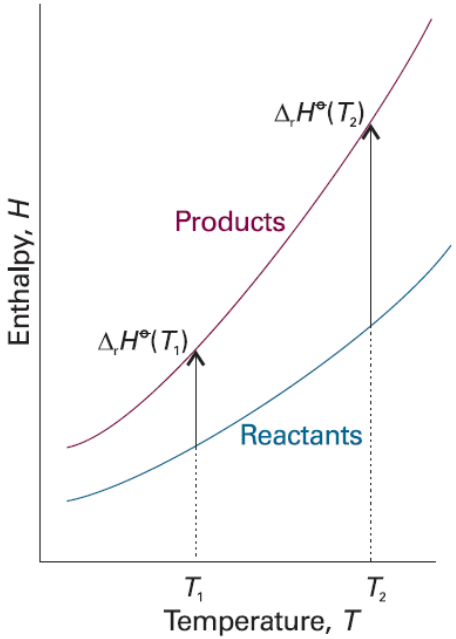
$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,\mathrm{m}}^\ominus - \sum_{\text{Reactants}} \nu C_{p,\mathrm{m}}^\ominus$$



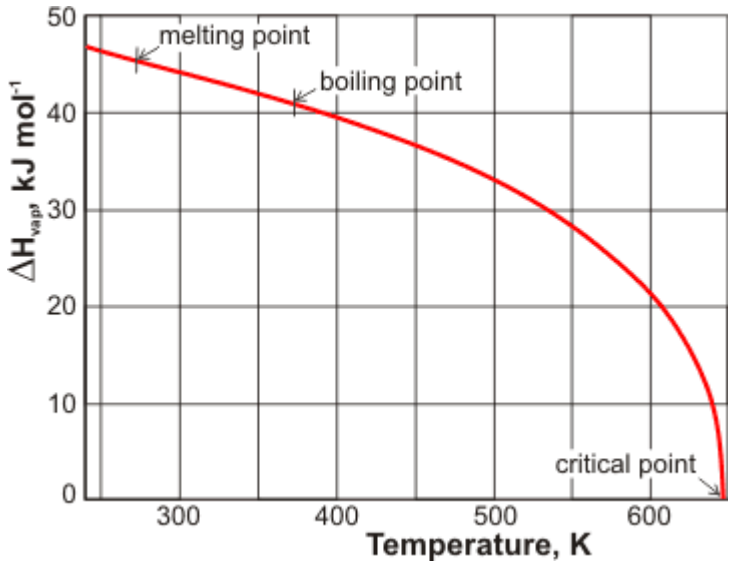
H (*V*, *T*, n)

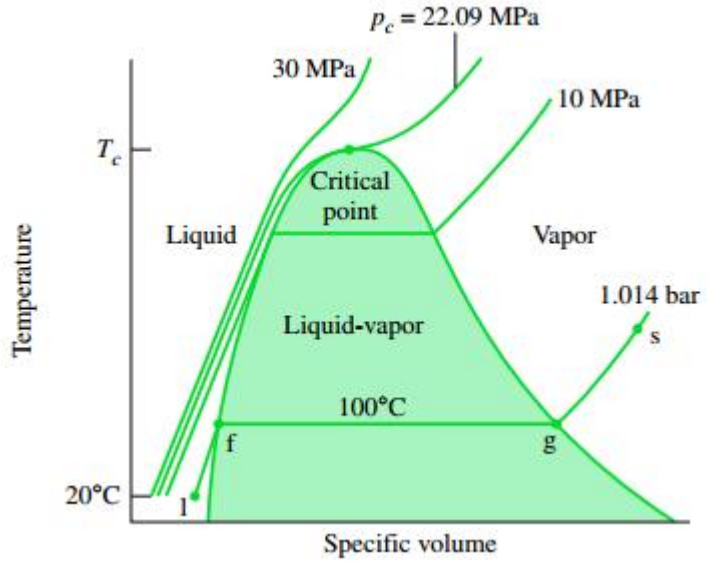
Kirchhoff's law

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus \mathrm{d}T$$



Water

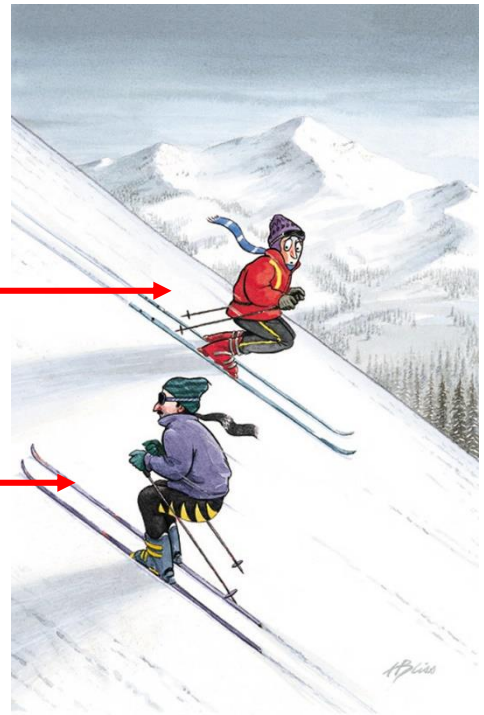


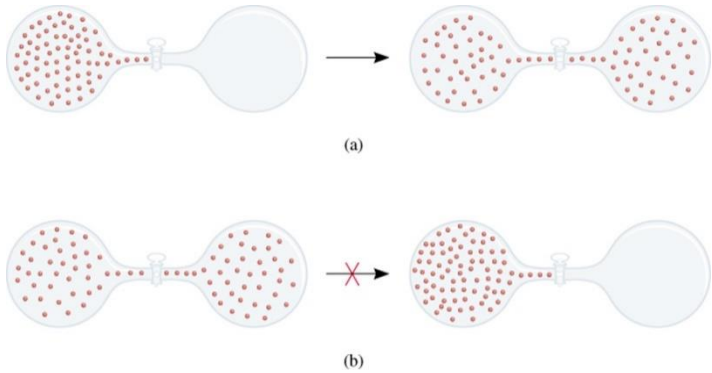


Spontaneous Physical and Chemical Processes !!?

spontaneous

nonspontaneous





spontaneous

nonspontaneous

Spontaneous Physical and Chemical Processes !!?

Second Law of thermodynamics

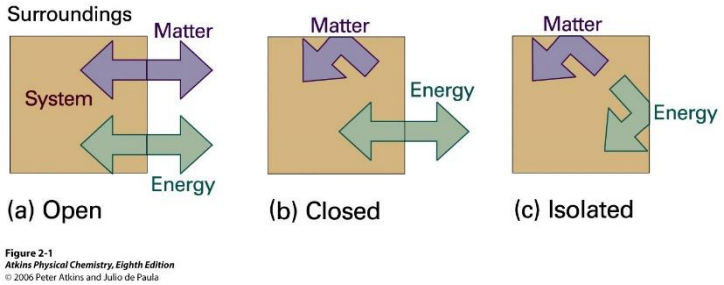


Figure 2-1
Atkins Physical Chemistry, Eighth Edition

The entropy of an isolated system never decreases

The entropy of an isolated system increases in the course of a spontaneous change:
$\Delta S_{tot} > 0$

Spontaneous Physical and Chemical Processes !!?

Second Law of thermodynamics

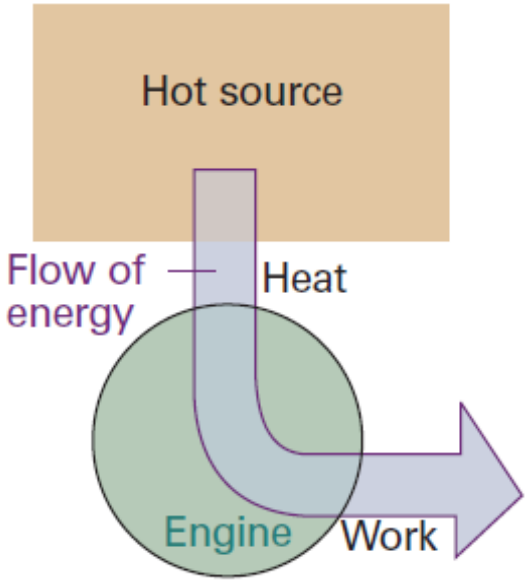


Fig. 3.1 The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change. The process is not in conflict with the First Law because energy is conserved.

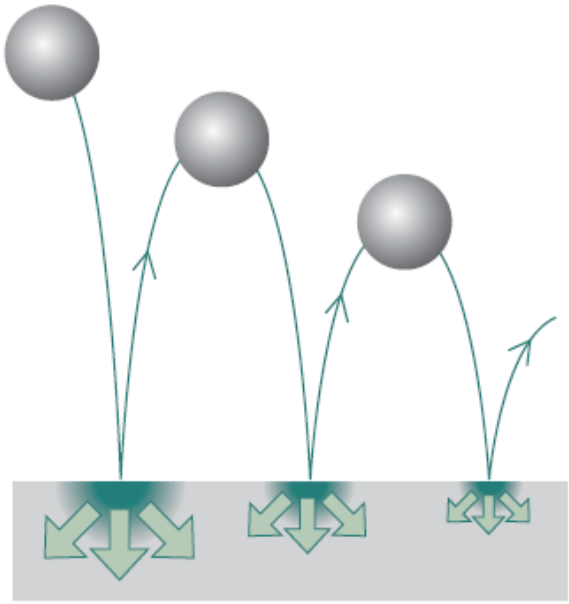


Fig. 3.2 The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a macroscopic scale.

Spontaneous Physical and Chemical Processes !!?

Second Law of thermodynamics

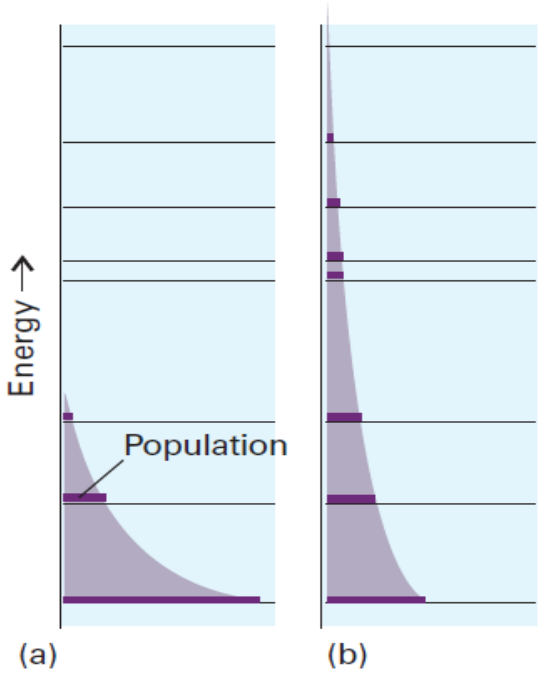
Second Law of thermodynamics: **the entropy of an isolated system never decreases**

State function: **entropy, *S***

$$N_i = \frac{N e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

Where, ***W*** is the number of *microstates*,

$$S = k \ln W$$



$T_1 > T_2$

Spontaneous Physical and Chemical Processes !!?

Second Principle of Thermodynamics

The entropy of the **universe** increases in a spontaneous process and remains unchanged in an equilibrium process.

Spontaneous process:

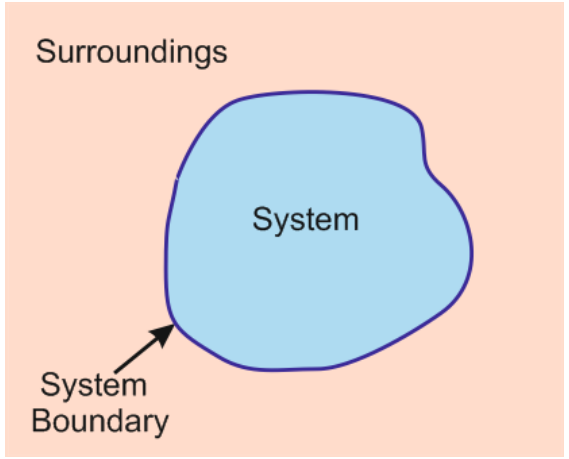
$$dS_{univ} = dS_{sys} + dS_{surr} > 0$$

Increase of energy dispersal

Equilibrium:

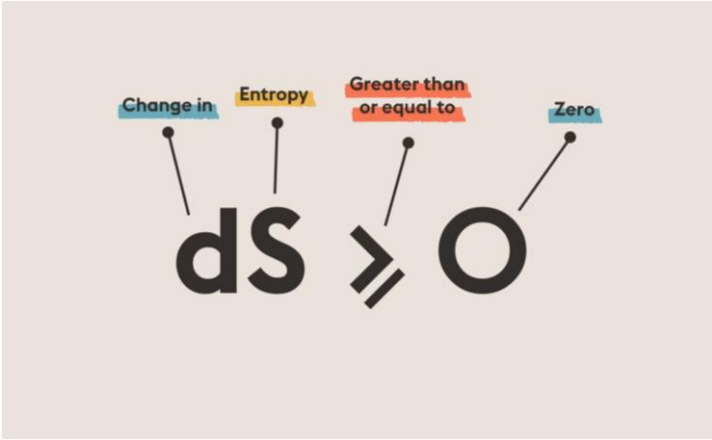
$$dS_{univ} = 0$$

Keep the energy dispersal



Spontaneous Physical and Chemical Processes !!?

Second Principle of Thermodynamics **… entropy?**

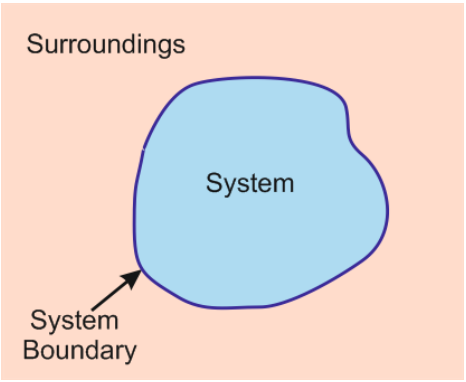


Second Law of Thermodynamics
says that the amount of disorder in a thermodynamic system always increases.

Spontaneous Physical and Chemical Processes !!?

Second Principle of Thermodynamics

The entropy of the **universe** increases in a spontaneous process and remains unchanged in an equilibrium process.

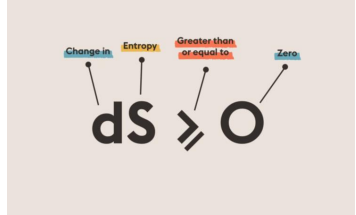


Entropy (*S*)

…. is a measure of the **randomness or energy disorder** of a system.

…. is a measure of the **number of microscopic configurations** that a thermodynamic system can have;

…. is not a measure of disorder, nor is **it a measure of energy dispersal**



Second Law of Thermodynamics says that the amount of disorder in a thermodynamic system always increases.

Spontaneous Physical and Chemical Processes !!?

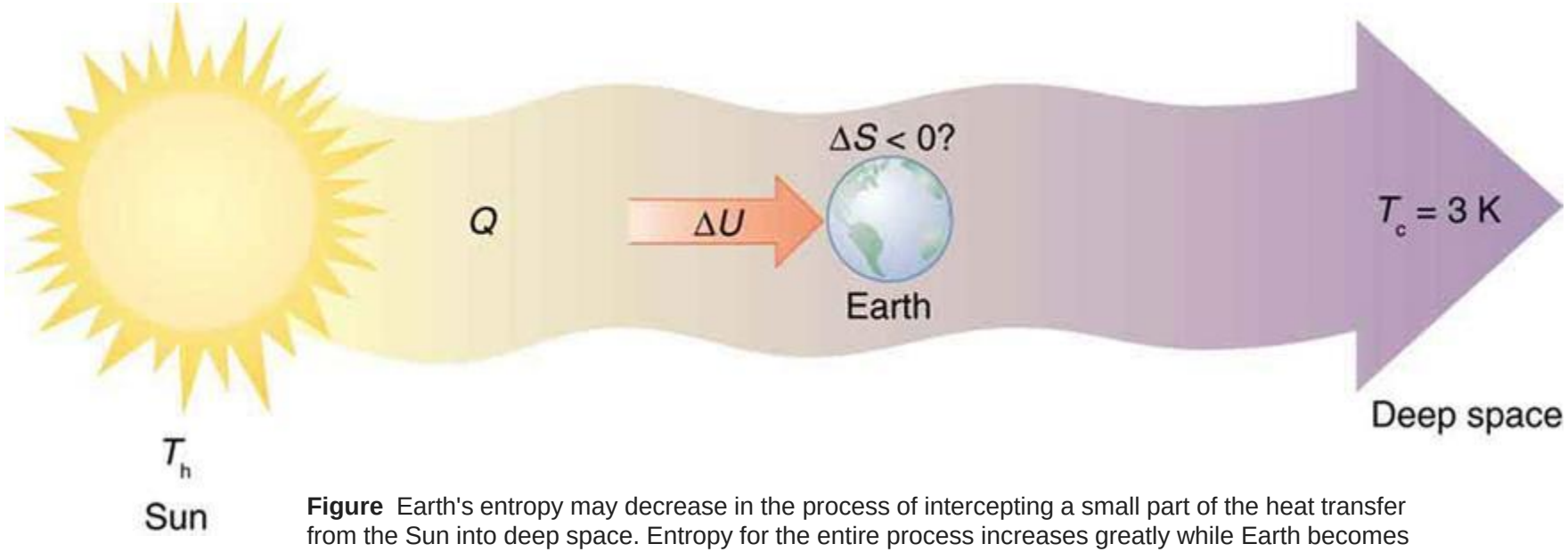
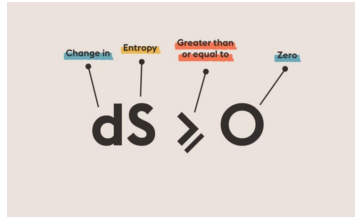


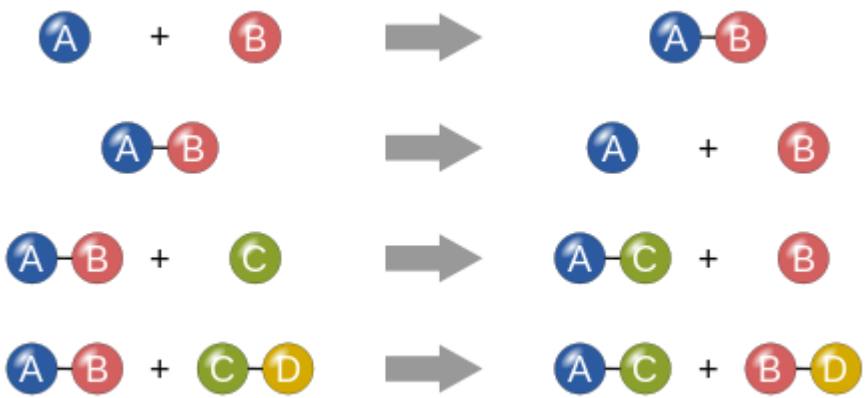
Figure Earth's entropy may decrease in the process of intercepting a small part of the heat transfer from the Sun into deep space. Entropy for the entire process increases greatly while Earth becomes more structured with living systems and stored energy in various forms.

Spontaneous Physical and Chemical Processes !!?



Second Law of Thermodynamics says that the amount of disorder in a thermodynamic system always increases.

Change of Entropy in the system!



$\Delta s_{sys} < 0$

$\Delta s_{sys} > 0$

$\Delta s_{sys} \sim 0$

$\Delta s_{sys} \sim 0$

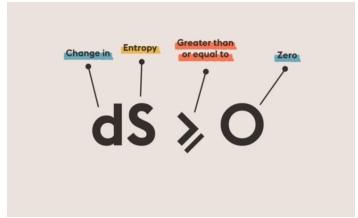
Spontaneous process:

Increase of energy dispersal

Equilibrium:

$dS_{univ} = 0$

Keep the energy dispersal



Second Law of Thermodynamics says that the amount of disorder in a thermodynamic system always increases.

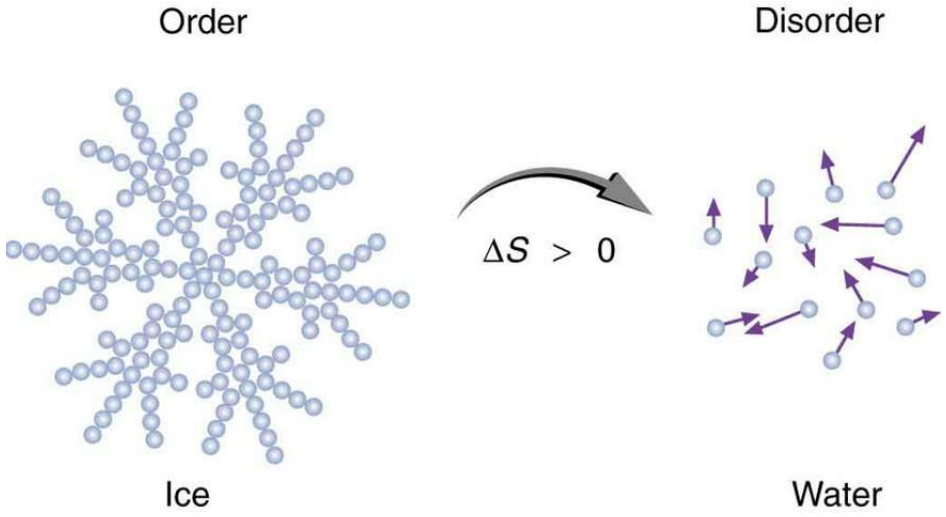
Spontaneous Physical and Chemical Processes !!?

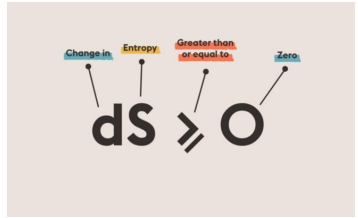
ΔH_{sys} **endothermic**

T_{fus} = 0.0 ˚C

$$dS_{sys} = - dS_{surr}$$

$$dS_{surr} = - dH_{sys} / T_{fus}$$



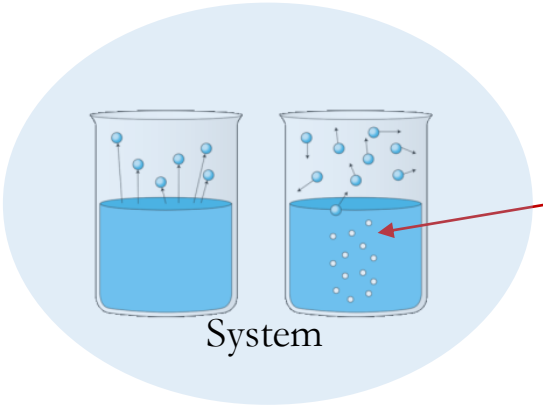


Second Law of Thermodynamics says that the amount of disorder in a thermodynamic system always increases.

Spontaneous Physical and Chemical Processes !!?

For any substance, the **solid** state is more ordered than the **liquid** state and the liquid state is more ordered than **gas** state

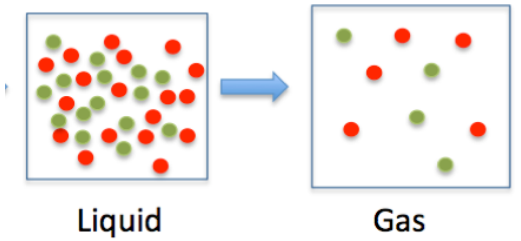
$H_2O\,(i) \longrightarrow H_2O(g) \qquad \Delta H_{sys} = +44\ kJmol^{-1}$



$dS_{surr} < 0 \quad ....= - dH_{sys} / T$

$- \Delta H_{sys} = - 44\ kJmol^{-1}$

Surrounding

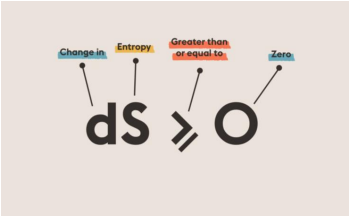


$\Delta s_{sys} > 0$

$dS_{univ} = dS_{sys} + dS_{surr} > 0$

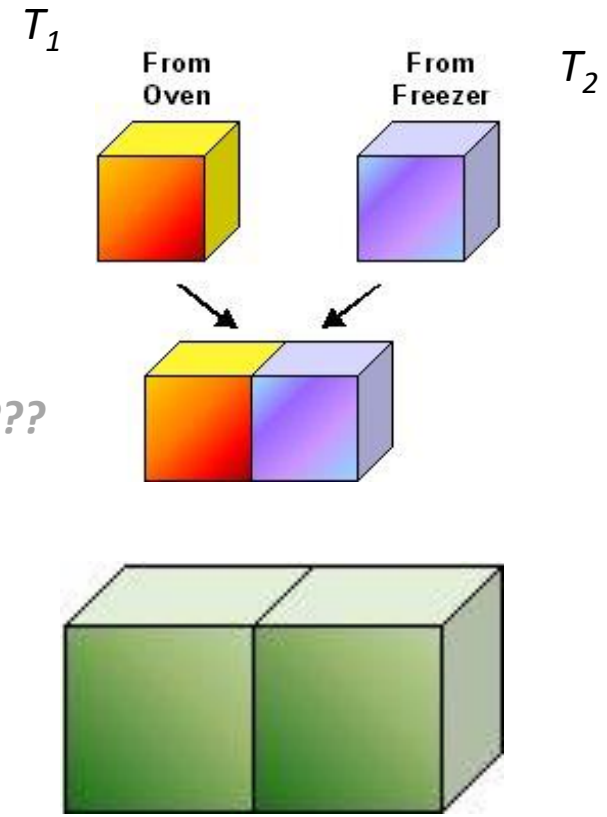
$dS_{sys} > \quad dH_{sys} / T$

Spontaneous Physical and Chemical Processes !!?

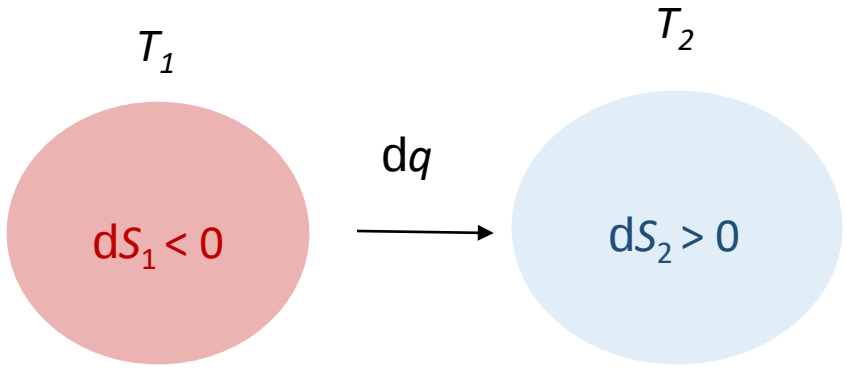


Second Law of Thermodynamics says that the amount of disorder in a thermodynamic system always increases.

Second Principle of Thermodynamics



Heat transfer ????



$dS_1 = dq / T_1$

$dS_2 = - dq / T_2$

$dS_{univ} = dS_1 + dS_2 > 0$

$- dq / T_2 > - dq / T_1$

$dS_2 > - dS_1$

$T_1 > T_2$