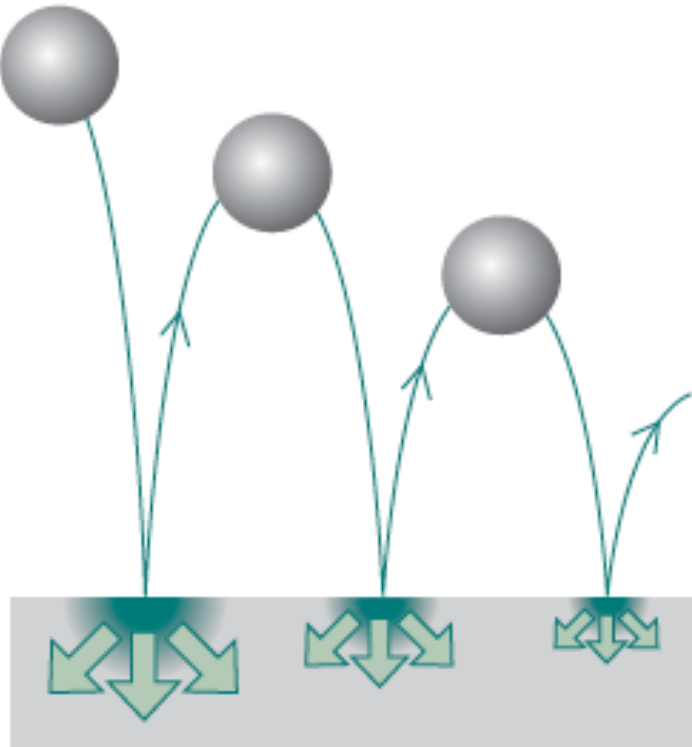# Qual a direção de um processo espontâneo?

O que conduz à dispersão da energia total do sistema

ENTROPY (S)

The entropy of an isolated system increases in the course of a spontaneous change:

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

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

Thermodynamically irreversible processes (like cooling to the temperature of the surroundings and the free expansion of gases) are spontaneous processes, and hence must be accompanied by an increase in total entropy.

A. Aguiar-Ricardo

ENTROPY (S)

The thermodynamic definition of entropy

$$dS = \frac{dq_{rev}}{T}$$

$$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$

A. Aguiar-Ricardo

Entropy changes accompanying specific processes

- ## Expansion of a perfect gas

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{1}{T} \int_i^f dq_{rev} = \frac{q_{rev}}{T}$$

During a reversible isothermal expansion of a perfect gas

$$\Delta U = q + w \quad \text{and} \quad \Delta U = 0$$

$$\Rightarrow q_{rev} = -w_{rev}$$

$$q_{rev} = -w_{rev} = nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = \frac{1}{T} nRT \ln\left(\frac{V_f}{V_i}\right) = nR \ln\left(\frac{V_f}{V_i}\right)$$

A. Aguiar-Ricardo

- **Phase transition**

$$\Delta_{trs} S = \frac{q_{trs}}{T_{trs}}$$

At constant pressure

$$q_{trs} = \Delta_{trs} H$$

$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$

A. Aguiar-Ricardo

IQF

If the phase transition is exothermic ($\Delta_{trs}H < 0$, as in freezing or condensing), then the entropy change is negative.

This decrease in entropy is consistent with localization of matter and energy that accompanies the formation of a solid from a liquid or a liquid from a gas.

If the transition is endothermic ($\Delta_{trs}H > 0$, as in melting and vaporization), then the entropy change is positive.

This increase in entropy is consistent with dispersal of energy and matter in the system.

A. Aguiar-Ricardo

- ## **Heating**

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T}$$

We shall be particularly interested in the entropy change when the system is subjected to constant pressure (such as from the atmosphere) during the heating, thus:

$$dq_{rev} = C_p \, dT$$

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p \, dT}{T}$$

Special notes:

- If Cp is independent of temperature within the temperature range of interest, Cp can be taken outside of the integral

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p \, dT}{T} = S(T_i) + C_p \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_p \ln \frac{T_f}{T_i}$$

- The same expression applies at constant volume, but with C_p replaced by C_v.

A. Aguiar-Ricardo

A note on good practice It is sensible to proceed as generally as possible before inserting numerical data so that, if required, the formula can be used for other data and to avoid rounding errors.

Calculate the entropy change when argon at 25 ºC and 1.00 bar in a container of volume 0.500 dm^3 is allowed to expand to 1.000 dm^3 and is simultaneously heated to 100 ºC.
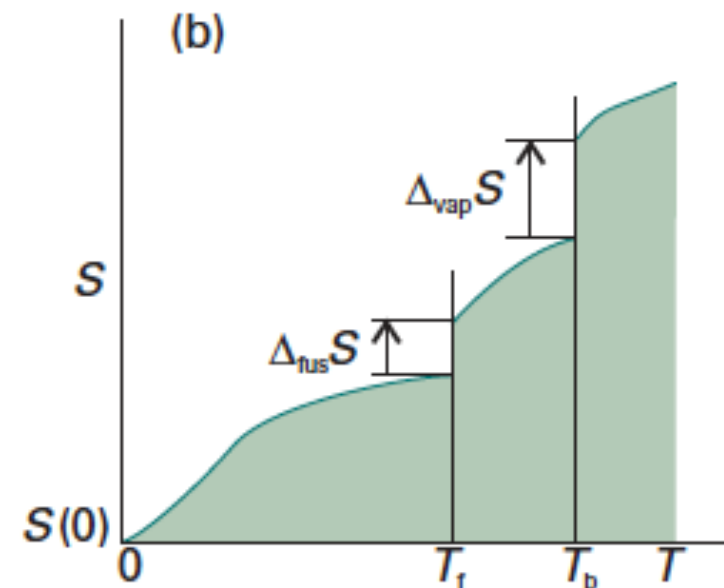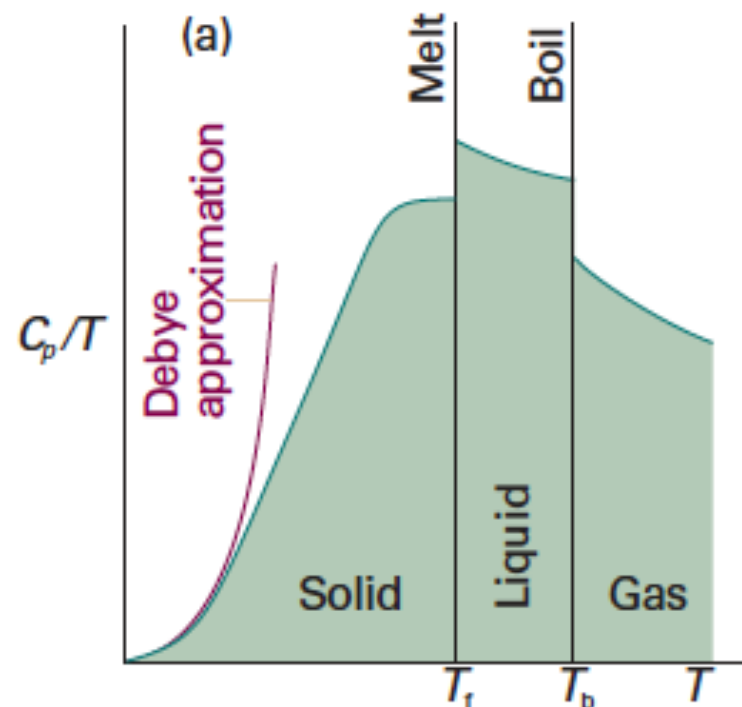(Sol. +0.173 J K^{-1})

Calculate the entropy change when the same initial sample is compressed to 0.0500 dm^3 and cooled to −25 ºC.

(Sol. -0.44 J K^{-1})

• The measurement of entropy

The entropy of a system at a temperature T is related to its entropy at T = 0 by measuring its heat capacity C_p at different temperatures and evaluating the integral in the following equation:

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p\,(sol)\,dT}{T} + \frac{\Delta_{fus}H}{T_{fus}}$$
$$+ \int_{T_f}^{T_b} \frac{C_p\,(liq)\,dT}{T} + \frac{\Delta_{vap}H}{T_b} +$$
$$\int_{T_b}^{T} \frac{C_p\,(gas)\,dT}{T}$$

A. Aguiar-Ricardo

The Third Law of thermodynamics

The Nernst heat theorem

The experimental observation that turns out to be consistent with the view that the entropy of a regular array of molecules is zero at T = 0 is summarized by the Nernst heat theorem:

The **entropy change** accompanying any physical or chemical transformation approaches **zero** as the **temperature** approaches **zero**:

$$\Delta S \rightarrow 0 \text{ as } T \rightarrow 0$$

provided all the substances involved are **perfectly crystalline**.

The entropy of all perfect crystalline substances is zero at T = 0.

A. Aguiar-Ricardo

IQF

Calculate de standard reaction entropy for the reaction:

$$H_2 (g) + 1/2 \, O_2 (g) \rightarrow H_2O (l) \qquad \text{at 25 ºC}$$
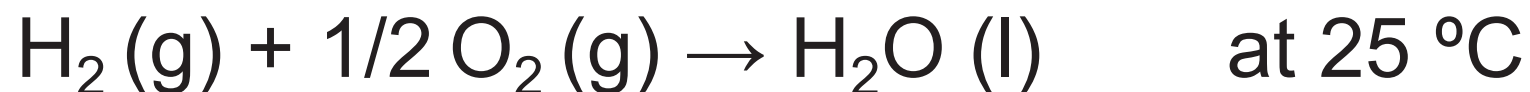
Calculate the standard reaction entropy for the combustion of methane to carbon dioxide and liquid water at 25 ºC.

A note on good practice Do not make the mistake of setting the standard molar entropies of elements equal to zero: they have non-zero values (provided $T >$ 0), as we have already discussed.

    A. Aguiar-Ricardo