

Spontaneous Process

A spontaneous process happens by itself without any outside help. Once it starts, it keeps going on its own.

1. Everyday Examples:

- **Ice Melting:** If you take an ice cube out of the freezer and leave it at room temperature, it melts into water. You don't need to do anything; it happens on its own.
- **Ball Rolling Down a Hill:** If you place a ball at the top of a hill and let go, it will roll down by itself without you pushing it.

2. Characteristics:

- These processes tend to increase disorder or randomness in the system. In scientific terms, we say they increase entropy.
- They usually move towards a more stable state (like water at room temperature is more stable than ice).

Nonspontaneous Process

A nonspontaneous process does not happen by itself. It requires continuous input of energy or effort to occur.

1. Everyday Examples:

- **Freezing Water into Ice:** To freeze water into ice, you need to put it in the freezer, which uses energy to keep it cold.
- **Pushing a Ball Uphill:** If you want to move a ball up a hill, you have to push it all the way up. It won't go up on its own.

2. Characteristics:

- These processes tend to decrease disorder or randomness in the system, meaning they decrease entropy.
- They require energy input to go against natural tendencies (like making water into ice).

Entropy

All spontaneous processes share a common trait: an increase in **entropy**.

Entropy

Entropy, denoted by the symbol **S**, is a measure of molecular randomness or disorder.

Imagine your room. If your room is messy, with clothes and books scattered everywhere, it has **high entropy** because it's **very disordered**. If your room is neat and everything is in its place, it has **low entropy** because it's **well-ordered**.

How Does Entropy Work in Chemistry?

1. Particles and Movement:

- In chemistry, we often talk about molecules and atoms. The more ways these tiny particles can move around and arrange themselves, the higher the entropy.
- For example, in a solid, particles are tightly packed and can't move much, so the entropy is low. In a gas, particles can move freely and spread out, so the entropy is high.

2. Changes in Entropy:

- When ice melts into water, the water molecules can move around more freely than in solid ice, so the entropy increases.
- When water boils and turns into steam, the molecules spread out even more, increasing the entropy.

Calculating entropy changes

Standard entropies, S°

Entropy is given the symbol S , and standard entropy (measured at 298 K and a pressure of 1 bar) is given the symbol S° . The units of entropy are $\text{J K}^{-1}\text{mol}^{-1}$.

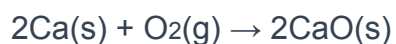
Entropy changes, ΔS°

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

Where Σ (sigma) simply means "the sum of".

Example

Calculate the entropy change of the system for the reaction:



Solution:

The standard entropy values are:

$$S^\circ [\text{Ca(s)}] = 41.40 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ [\text{O}_2(\text{g})] = 205.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ [\text{CaO(s)}] = 39.70 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta S^\circ_{\text{system}} = S^\circ_{\text{products}} - S^\circ_{\text{reactants}}$$

$$= 2 \times S^\circ [\text{CaO(s)}] - \{2 \times S^\circ [\text{Ca(s)}] + S^\circ [\text{O}_2(\text{g})]\}$$

$$= 2 \times 39.70 - ((2 \times 41.40) + 205.0)$$

$$= 79.40 - 287.8$$

$$\Delta S^\circ_{\text{system}} = -208.4 \text{ JK}^{-1} \text{ mol}^{-1}$$

Calculating the entropy change of the surroundings.

An **exothermic reaction** releases heat to the **surroundings**, and that extra heat increases the entropy of the surroundings.

An **endothermic reaction** absorbs heat from the surroundings, and so the entropy of the surroundings decreases.

Total entropy change is the sum of the entropy changes of the system and the surroundings.

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

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T}$$

ΔH is the enthalpy change for the reaction. T is the temperature in Kelvin.

Example:

In the metallurgy of antimony, the pure metal is recovered via different reactions, depending on the composition of the ore. For example, iron is used to reduce antimony in sulfide ores:



Calculate $\Delta S_{\text{surroundings}}$ for the reaction.

Solution:

We use

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T}$$

where

$$T = 25 + 273 = 298 \text{ K}$$

$$\Delta S_{\text{surroundings}} = -\frac{-125\text{kJ}}{298\text{K}} = 0.419 \text{ kJ/K} = +419 \text{ J/K}$$

Free Energy

Another thermodynamic function that helps predict whether a process or reaction will proceed spontaneously is Gibbs's free energy (G).

Gibb's Free Energy

Gibbs's free energy is the energy associated with a chemical reaction that can be used to do work. It combines enthalpy (H), entropy (S), and temperature (T) in a way that helps predict the direction of spontaneous processes.

The formula is $G = H - TS$.

For a process that occurs at constant temperature, the change in free energy (ΔG) is given by the equation

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

where:

- ΔH is the change in enthalpy (heat content).
- T is the absolute temperature (in Kelvin).
- ΔS is the change in entropy (disorder).

Free Energy and Spontaneity

- If $\Delta G < 0$, the process or the reaction is spontaneous (it can happen on its own).
- If $\Delta G > 0$, the process is or the reaction nonspontaneous (it requires energy input to occur).
- If $\Delta G = 0$, the system is or the reaction at equilibrium (no net change occurs).

Applying the equation $\Delta G = \Delta H - T\Delta S$

Example

Calculate the Gibbs free energy change for the decomposition of zinc carbonate at 298 K.



(Values for S in $\text{J K}^{-1} \text{ mol}^{-1}$: $\text{CO}_2(\text{g}) = +213.6$,
 $\text{ZnCO}_3(\text{s}) = +82.4$, $\text{ZnO}(\text{s}) = +43.6$)

Solution

Step 1 Convert the value of ΔH_r to J mol^{-1} :

$$+71.0 \times 1000 = 71\,000 \text{ J mol}^{-1}$$

Step 2 Calculate ΔS_{system} :

$$\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$$

$$= S[\text{ZnO}(\text{s})] + S[\text{CO}_2(\text{g})] - S[\text{ZnCO}_3(\text{s})] = 43.6 + 213.6 - 82.4$$

$$\Delta S_{\text{system}} = +174.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Step 3 Calculate ΔG :

$$\Delta G = \Delta H_{\text{reaction}} - T\Delta S_{\text{system}}$$

$$= 71\,000 - 298 \times (+174.8)$$

$$\Delta G = +18\,909.6 \text{ J mol}^{-1}$$

$$= +18.9 \text{ kJ mol}^{-1} \text{ (to 3 significant figures)}$$

As the value of ΔG is positive, the reaction is not spontaneous at 298 K.