

Thermodynamics: 2nd and 3rd Law

Introduction

While the First Law of Thermodynamics established the principle of energy conservation, it does not explain why certain processes occur spontaneously in one direction but not the reverse. The **Second and Third Laws of Thermodynamics** address this, introducing the concept of **Entropy** and the ultimate criterion for spontaneity: **Gibbs Free Energy**.

This module explores the directionality of change:

- We will define entropy as a measure of disorder or dispersal of energy in a system.
- We will establish the criteria for spontaneity using both the Second Law (the universe's perspective) and Gibbs Free Energy (the system's perspective).

Learning Objectives

By the end of this module, you will be able to:

- **Define** entropy (S) in terms of microscopic disorder and macroscopic heat flow.
- **State** the Second and Third Laws of Thermodynamics.
- **Calculate** the change in Gibbs Free Energy (ΔG) under various conditions.
- **Predict** the spontaneity of a chemical reaction or physical process using the sign of ΔG .
- **Relate** ΔG standard to the equilibrium constant (K).

Key Concepts and Definitions

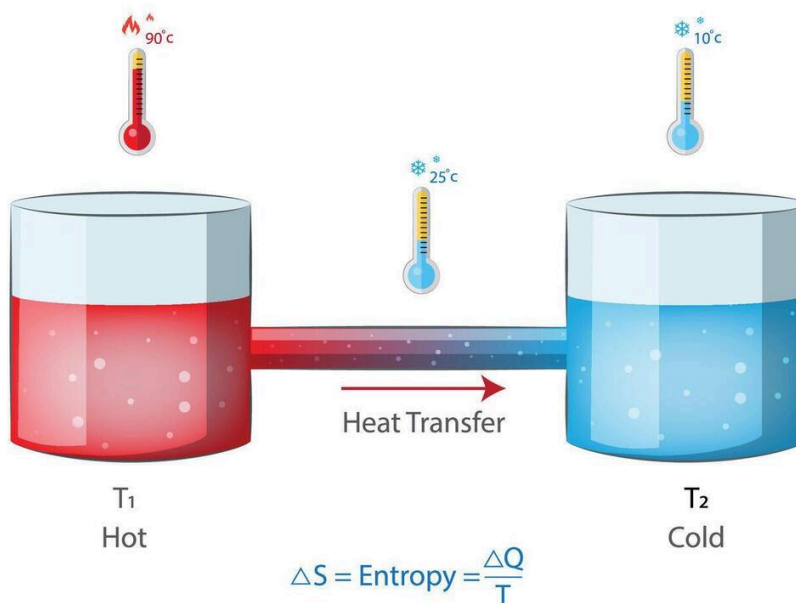
Term	Definition
Entropy (S)	A measure of the dispersal of energy (disorder) in a system at a specific temperature.
Second Law of Thermodynamics	The entropy of the universe always increases for any spontaneous process.
Third Law of Thermodynamics	The entropy of a perfectly crystalline substance at absolute zero (0 K) is zero.
Gibbs Free Energy (ΔG)	The maximum amount of non-PV work a system can perform at constant temperature and pressure. It is the predictor of spontaneity.
Spontaneous Process	A process that occurs naturally without continuous outside intervention (e.g., a ball rolling downhill).

Detailed Discussion

1. The Second Law and Entropy of the Universe

The **Second Law of Thermodynamics** dictates the direction of time and change. It states that for any process to be spontaneous, the total entropy change of the universe must be positive:

SECOND LAW OF THERMODYNAMICS



Equation for Entropy of the Universe: ΔS of the universe = ΔS of the system + ΔS of the surroundings

Spontaneity Criteria (from the perspective of the Universe):

- **Spontaneous:** ΔS of the universe is greater than 0
- **At Equilibrium:** ΔS of the universe equals 0

- **Non-spontaneous:** ΔS of the universe is less than 0 (The reverse process is spontaneous)

The change in entropy of the surroundings (ΔS of the surroundings) is determined by the heat released or absorbed by the system (ΔH of the system) at a given temperature (T):

Entropy of Surroundings Equation:

$$\Delta S \text{ of the surroundings} = - (\Delta H \text{ of the system}) / T$$

- **Exothermic reactions (ΔH is less than 0)** increase the entropy of the surroundings (ΔS of the surroundings is greater than 0).
- **Endothermic reactions (ΔH is greater than 0)** decrease the entropy of the surroundings (ΔS of the surroundings is less than 0).

2. Gibbs Free Energy (ΔG) and Spontaneity

Calculating ΔS of the universe is difficult because it requires tracking the surroundings. Therefore, **Gibbs Free Energy (ΔG)** was developed as a state function that acts as the universal criterion for spontaneity, using only the properties of the system (ΔH of the system and ΔS of the system).

The Gibbs equation combines Enthalpy, Temperature, and Entropy:

Gibbs Free Energy Equation:

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

Where T is the absolute temperature in Kelvin.

Spontaneity Criteria (from the perspective of the System):

- **Spontaneous:** ΔG is less than 0
- **At Equilibrium:** ΔG equals 0
- **Non-spontaneous:** ΔG is greater than 0 (Requires continuous energy input)

3. Gibbs Free Energy and Equilibrium

Under standard conditions, the standard Gibbs Free Energy change (ΔG standard) is related to the **Equilibrium Constant (K)** via the following equation:

Standard Gibbs Free Energy and Equilibrium Constant:

$$\Delta G \text{ standard} = - R * T * \ln K$$

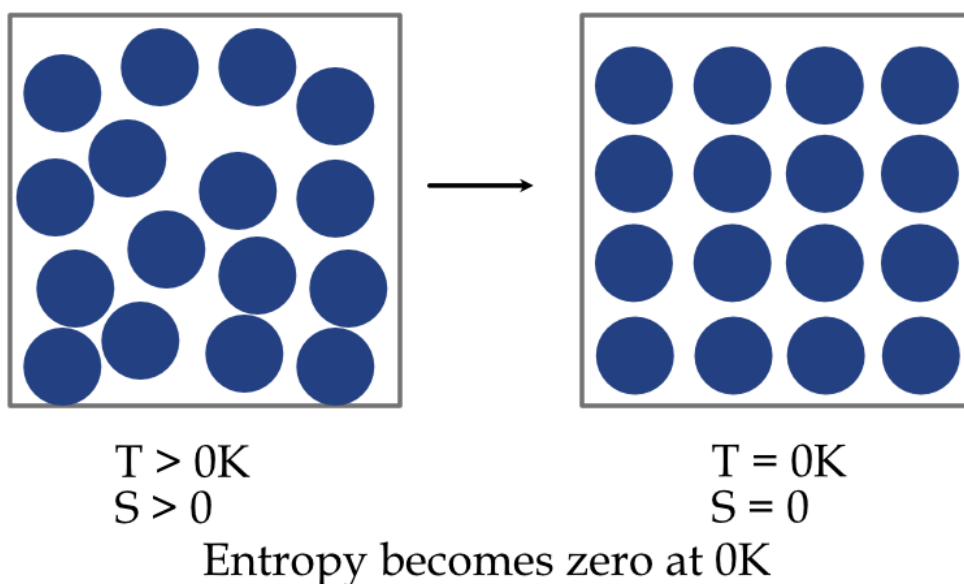
Where R is the ideal gas constant (8.314 J/mol·K).

- If K is greater than 1, then $\ln K$ is positive, ΔG standard is negative, and the reaction is spontaneous (products are favored).
- If K equals 1, then $\ln K$ is zero, ΔG standard is zero, and the system is at equilibrium.
- If K is less than 1, then $\ln K$ is negative, ΔG standard is positive, and the reaction is non-spontaneous (reactants are favored).

4. The Third Law of Thermodynamics

The **Third Law of Thermodynamics** provides a basis for determining absolute entropy values. It states that the entropy of a perfectly crystalline solid at absolute zero (0 K) is zero.

Third Law of Thermodynamics



Third Law Statement: S approaches 0 as T approaches 0 K (for a perfect crystal)

This allows chemists to calculate the absolute entropy (S) for substances at any temperature by measuring the heat capacity and integrating from 0 K up to the temperature of interest. These absolute values are used to calculate the change in entropy for a reaction (ΔS standard for the reaction).

REFERENCES:

Atkins, P. W., de Paula, J., & Keeler, J. (2018). Atkins' Physical Chemistry (11th ed.). Oxford University Press.

Engel, T., & Reid, P. (2020). Physical Chemistry (4th ed.). Pearson.

LibreTexts. (2024). Physical and Theoretical Chemistry: Thermodynamics.

International Union of Pure and Applied Chemistry (IUPAC). (2019). The Gold Book (Compendium of Chemical Terminology).