
Chapter 5

Gibbs free energy

10.1 Calculation the Gibbs free energy values (ΔG) for the following cases:

$\because \Delta G = \int_{P_1}^{P_2} V\,dp$

1- When the size is constant:

$\because \Delta G = V (P_2 - P_1)$

$\Delta G = V\Delta P$

2- When the pressure is constant:

$\because \Delta G = V\Delta P$

ΔG = Zero

3- When volume and pressure (V & P) change:

We can only integrate in the presence of an ideal gas

PV = nRT

$\because V = \frac{nRT}{P}$

$\therefore \Delta G = \int_{P_1}^{P_2} nRT \frac{dP}{P}$

$\Delta G = n\,RT\ \ln \frac{P_2}{P_1}$

$\Delta G = 2.303\ n\ RT \log \frac{P_2}{P_1}$ = (w) <u>Labor Law</u>

$\Delta G = 2.303\ n\ RT \log \frac{V_1}{V_2}$ = <u>Labor law contrary to the sign</u>

Example (2): Calculate the change in Gibbs free energy ΔG for one mole of an ideal gas that expands to ten times its volume at a temperature of (25°C). Is the process spontaneous or not?

$\Delta G = 2.303\ n\ RT \log \frac{V_1}{V_2}$

$= 2.303 \times 1 \times 8.314 \times 298 \log \frac{1}{10}$

$= -(\ \ )$ Joule. Mole^{-1}

$\because (\Delta G = -) \Rightarrow$ the reaction is spontaneous.

The summary of the previous thermodynamic calculations is:

In the first law: w, q, ΔE, ΔH

In the second law: ΔS

In the third law: ΔA, ΔG

Note: Not every reaction with a value of ($\Delta H = +$) is nonspontaneous. It may be spontaneous, and ΔG is what determines whether or not the reaction is spontaneous.

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Question: (What determines the spontaneity of a reaction)? Explain.

ΔG

Where if the value is:

$\Delta G = (-)$, the reaction is spontaneous.

$\Delta G = (+)$, the reaction is *nonspontaneous*.

Free energy (ΔG) is considered a measure of bioenergetics (the energy present within a living body).

H.W: One mole of an ideal gas at 27°C expands isothermally and reversibly from a pressure of 10 atmospheres to a pressure of 1 atmosphere (the pressure decreases as the expansion occurs). Is the process spontaneous or not?

Calculate the following thermodynamic values:

w, q, ΔE, ΔH, ΔA, ΔG, ΔS

10.2 Relating Gibbs Free Energy to Fuel Cells

Fuel cells are devices that convert chemical energy from a fuel (such as hydrogen) and an oxide (such as oxygen) directly into electrical energy. This conversion occurs via an electrochemical reaction.

10.2.1 The primary role of Gibbs free energy:

ΔH: Represents the total chemical energy stored in the bonds. If hydrogen and oxygen react, the enthalpy change (ΔH) represents the total heat released by the reaction.

ΔS: Represents the portion of energy that cannot be converted into useful work but is instead converted into heat due to increased entropy of the system.

Thus, ΔG is the actual portion of energy available to do useful electrical work.

10.2.2 Theoretical Maximum Efficiency of Fuel Cells:

Unlike heat engines that follow the Carnot cycle, whose efficiency is limited by temperature, the theoretical maximum efficiency of a fuel cell is determined directly by the Gibbs free energy.

Electrochemical efficiency (η_e) is the ratio of electrical energy produced to the total chemical energy of the fuel.

η_e = electrical energy produced / total chemical energy

Using Gibbs energy, we can write this equation more precisely:

$\eta_e = \Delta G / \Delta H$

Because ΔG represents the maximum electrical work that can be obtained, and ΔH represents the total energy available.

Example (3):

Hydrogen and oxygen reaction: $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

- Enthalpy change (ΔH): −285.83 kJ/mol (total energy)

- Gibbs free energy change (ΔG): −237.13 kJ/mol (energy available for work)

- Theoretical maximum efficiency:

$\eta_e = \Delta G / \Delta H$

$=285.83/ 237.13 \approx 0.829$ or 82.9%

This result tells us that the theoretical maximum efficiency of a hydrogen fuel cell is approximately 83%, meaning that 17% of the energy will inevitably be lost as heat.

Summary

- Gibbs free energy is the energy available to do useful work in a chemical reaction.

- It is used in fuel cells to determine the theoretical maximum efficiency because it represents the maximum amount of chemical energy that can be converted into electricity.

- Efficiency is calculated by dividing the change in Gibbs energy (ΔG) by the change in enthalpy (ΔH).

- Unlike heat engines, which are subject to the limitations of the Carnot cycle, fuel cells exhibit much higher theoretical efficiencies because they are not limited by operating temperatures.

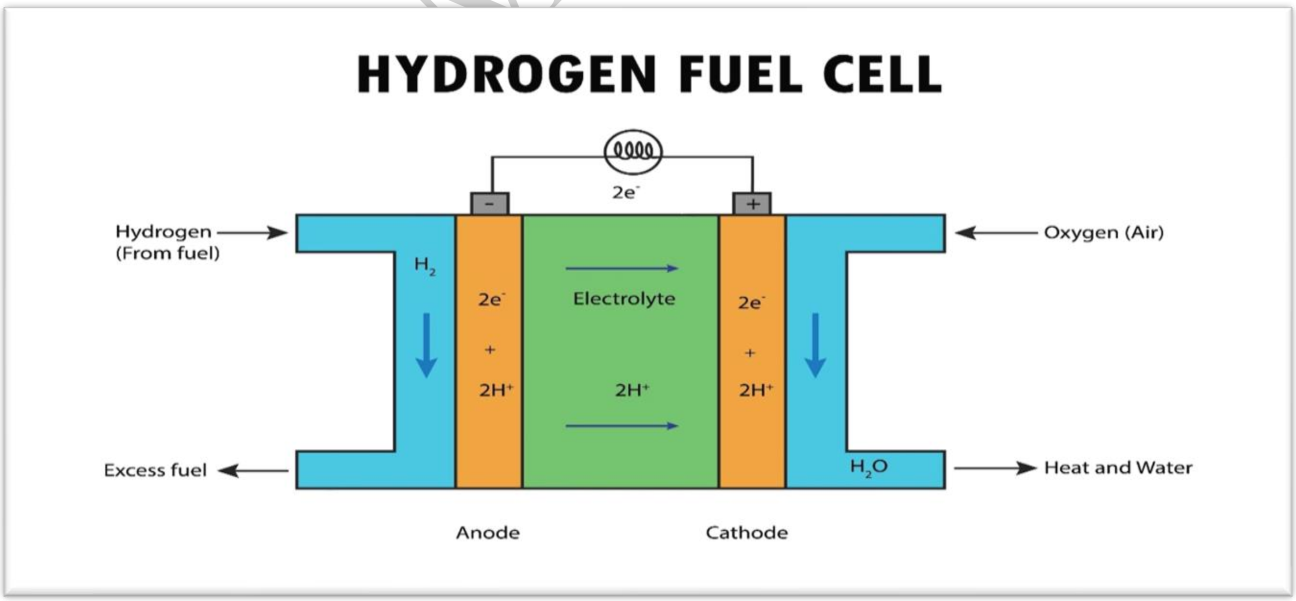
Understanding this concept provides insight into the physical limits of fuel cell performance and guides research efforts to design systems that approach this theoretical efficiency.

10.3 Why are fuel cells more efficient than heat engines?

One of the most important advantages of fuel cells in the field of renewable energy is their high efficiency, compared to conventional heat engines. The scientific reason behind this lies in their ability to overcome the limitations of the Carnot cycle, unlike heat engines, which are subject to limitations, as explained in Chapter 4.

10.3.1 Fuel Cells: Direct Energy Conversion

Unlike heat engines, a fuel cell is not a heat engine. It is an electrochemical device that directly converts the chemical energy of a fuel into electrical energy through an electrochemical reaction.



10.3.2 How does the fuel Cells work?

In a hydrogen fuel cell, hydrogen and oxygen are fed into the cell, where the ions react at the electrodes to produce water. The electrons in this process produce an electric current.

10.3.3 Bypassing Limitations:

Since a fuel cell does not rely on a thermal cycle (i.e., it does not use heat as an intermediate stage to produce work), it is not subject to the limitations of the Carnot cycle. It converts chemical energy directly into electricity, avoiding the significant heat loss associated with the thermal cycle.

10.3.4 Theoretical Efficiency:

The theoretical maximum efficiency of a fuel cell is determined by the Gibbs free energy (ΔG), which represents the maximum useful energy that can be obtained from the reaction.

$$\eta_e = \Delta G / \Delta H$$

ΔH: Total chemical energy of the fuel.

ΔG: Maximum energy that can be converted into electricity.

This principle allows fuel cells to achieve theoretical efficiencies much higher than those of heat engines, which can reach 80-85% for a hydrogen fuel cell.

Table: Comparison between Heat Engines and Fuel Cells

Property	Heat Engines	Fuel Cells
Principle of Operation	Thermal cycle (heat → work)	Electrochemical reaction (chemistry → electricity)
Limitations	Subject to Carnot cycle limitations	Bypasses Carnot cycle limitations
Theoretical Efficiency	Limited by temperature difference	Reaches 85% or more
Primary Losses	Significant heat loss due to the cycle	Losses due to internal resistance and other factors

Conclusion: Fuel cells outperform heat engines in efficiency because they don't rely on the inefficient principle of converting heat into work. Instead, they convert chemical energy directly into electricity, bypassing the physical limitations of the Carnot cycle and offering a promising solution for generating clean energy.