Chapter 4

The second and third laws of thermodynamics

9.1 The third law of thermodynamics

It depends entirely on the second law, but the difference between them is that in the second law:

If we have a heating process:

$$\Delta S = \int_{T_1}^{T_2} \begin{matrix} C_P \\ C_V \end{matrix} \frac{dT}{T}$$

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} C_P \frac{dT}{T} = \int_{T_1}^{T_2} C_P \; d \ln T$$

The third law: It is known as (an attempt to measure the absolute value of entropy S).

$$\mathbf{S_0^T}$$

Definition of the third law: It states that: The entropy of all crystalline materials at absolute zero is equal to zero.

(Zero = − 273 C° = (0°K))

S_0 at 0°K = Zero

9.1.1 Why is S_0 at 0°K equal to zero?

At absolute zero, crystalline materials (frozen solids) have a single conformation, i.e.

($\Omega = 1$).

$\because S = K \ln \Omega \Rightarrow S = K \ln 1 \Rightarrow S = 0$

Where:

Ω: is the number of arrangements and probability.

K: the molecular Boltzmann gas constant.

$K = \frac{R}{N}$

Boltzmann's constant (the number of molecules in one mole).

Avogadro's number = N

R = mole

* If the material is amorphous, it has more than one conformation ($S \neq 0$) and is greater than zero.

∴ Only for crystalline materials ($S = 0$).

9.2 Applications of the Third Law of Thermodynamics in Renewable Energy:

This law establishes an absolute reference point for entropy. If we know that the entropy at absolute zero is zero, we can calculate the absolute entropy of any substance at any higher temperature. This enables us to accurately calculate entropy changes in chemical reactions.

These concepts are vital for the design and evaluation of renewable energy systems, especially those that rely on chemical reactions.

1. Green Hydrogen Systems

The electrolysis of water is the basis for green hydrogen production. Engineers use the third law of thermodynamics to calculate the theoretical requirements for this process.

The law helps determine the absolute entropy of the reactants (water) and the products (hydrogen and oxygen).

This allows us to calculate the entropy change (ΔS) for the reaction.

Once ΔS and ΔH (enthalpy) are known, we can calculate the minimum electrical energy required for the reaction, which is equivalent to the Gibbs free energy (ΔG).

This calculation is essential for determining the maximum theoretical efficiency of an electrolyze.

2. Fuel Cells

As discussed earlier, the Gibbs free energy is used to determine the maximum theoretical efficiency of a fuel cell.

from the third law, ΔS can be accurately calculated from absolute entropy tables, leading to a highly accurate calculation of ΔG.

The maximum efficiency of a fuel cell is the ratio of ΔG to ΔH.

This helps understand that some of the chemical energy must be converted to heat (due to entropy) for the reaction to proceed spontaneously, which explains why the theoretical efficiency of a fuel cell is not 100%.

3. Battery Development

Batteries rely on electrochemical reactions to store and release energy.

The Gibbs free energy is used to determine the theoretical voltage of a battery.

The third law helps calculate ΔS for the internal reactions of a battery, allowing for accurate determination of ΔG, and hence the voltage it can produce. This is critical for designing high-voltage batteries with stable performance.

Summary

1- The third law of thermodynamics is not just a theoretical concept; it is a fundamental tool in engineering. It establishes a reference point for entropy, allowing accurate calculations of entropy change and Gibbs free energy.

2- These accurate calculations enable us to determine the maximum efficiency and minimum power required to operate renewable energy systems.

3- It is used in the design and optimization of fuel cells, hydrogen production systems, and batteries, contributing to more efficient and high-performance renewable energy systems.

Chapter 5

Gibbs free energy

9.3 Gibbs free energy definition

is a physical quantity defined as the maximum amount of useful energy that can be obtained from a chemical reaction. Its value depends on enthalpy, temperature, and entropy.

In short, the third law provides us with a tool to calculate the value of entropy, which in turn is used in the Gibbs free energy equation:

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

Without the ability to accurately calculate the change in entropy (ΔS)

we cannot accurately calculate the change in Gibbs free energy (ΔG).

Therefore, the third law of thermodynamics is an important foundation that enables us to utilize Gibbs free energy effectively.

The summary of the three laws of thermodynamics is (Gibbs free energy)

When $\Delta S = 0$, the process is reversible.

$\Delta S > 0$, the process is irreversible (spontaneous).

9.4 Free energy properties (A and G) ΔA and ΔG

1- State function property.

2- Global properties (i.e., they depend on the quantity of the system; they increase with increasing energy and decrease with decreasing energy).

$G = E + PV - TS$

$\because A = E - TS$

$\therefore G = A + PV$ or $\Delta G = \Delta A + P\Delta V$

ΔG = Free energy at constant pressure (which is the most important).

ΔA = Free energy at constant volume.

$\Delta G > \Delta A$ by $P\Delta V$

With the same relationship between ΔH and ΔE

$\Delta G = \Delta A + P\Delta V$… …………**The first law of free energy**

$\Delta H = \Delta E + P\Delta V$

** Free energy (ΔG) is called the free energy of G and is a measure or standard of spontaneity or equilibrium.

$G = E + P\Delta V - T\Delta S$

$G = H - TS$

$\Delta G = \Delta H - T\Delta S$ .... **The second law of free energy**

The sign for ΔG is determined by ΔS and ΔH as follows:

1) $T\Delta S > \Delta H \Rightarrow \Delta G = (-)$ ($A \rightarrow P$ **The reaction is spontaneous and irreversible**)

2) $T\Delta S = \Delta H \Rightarrow \Delta G = 0$ ($A \rightleftharpoons P$ **Non-spontaneous and reversible equilibrium reaction)**

3) $\Delta H > T\Delta S$

Or $T\Delta S < \Delta H$

$\Longrightarrow \Delta G = (+)$

No reaction occurs

$A \not\rightarrow P$

Example (1): Does the evaporation of gasoline at 100°C occur spontaneously or not, given that the heat of vaporization of gasoline is 7340 kcal/mol and the change in entropy (ΔS) is 20.8 K^{-1} mol^{-1}?

What is the normal boiling point of gasoline?

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

$= 7340 - 373 \times 20.8$

$= -418 \text{ cal. mol}^{-1}\text{. K}^{-1}$

$\therefore \Delta G = (-)$

∴ The process is automatic.

So, gasoline can be vaporized at (100°C).

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B) $\because \Delta G = \Delta H - T\Delta S$

Note: At the boiling point, this indicates equilibrium, and at the melting point, this indicates equilibrium ($\Delta G = 0$).

$0 = \Delta H - T\Delta S$

$\therefore T = \frac{\Delta H}{\Delta S} = \frac{7340}{20.8}$

$= 353^\circ \text{ K} - 273 = 80\ ^\circ\text{C}$

∴ At 70 °C, benzene does not boil (no vaporization).

That is, ($\Delta G = +$), meaning no N.R. reaction occurs