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Understanding the thermodynamics of gases is fundamental in physics and chemistry, especially when analyzing processes such as gas expansion. One of the key thermodynamic potentials involved in such processes is the Gibbs free energy (G), which provides insight into the spontaneity and equilibrium conditions of reactions and phase changes. Specifically, calculating the change in molar Gibbs energy during an isothermal expansion of a perfect gas is crucial for designing efficient engines, understanding natural phenomena, and optimizing industrial processes. This article delves into the detailed methodology to compute the change in molar Gibbs energy during an isothermal expansion, explaining the underlying principles, step-by-step calculations, and practical applications.

Understanding Gibbs Free Energy and Perfect Gases

Before diving into the calculation, it's essential to grasp the concepts of Gibbs free energy and perfect gases.

What Is Gibbs Free Energy?

Gibbs free energy (G) is a thermodynamic potential defined as:

$$ G = H - TS $$

where:
- H is the enthalpy,
- T is the absolute temperature,
- S is the entropy.

Gibbs free energy indicates the maximum reversible work that can be obtained from a thermodynamic system at constant temperature and pressure. A process is spontaneous if the change in Gibbs free energy, ΔG, is negative.

Properties of a Perfect Gas

A perfect (ideal) gas follows the ideal gas law:

$$ PV = nRT $$

where:
- P is the pressure,
- V is the volume,
- n is the number of moles,
- R is the universal gas constant,
- T is the temperature.

In the context of molar quantities, the ideal gas law simplifies to:

$$P V_m = R T$$

where V_m is the molar volume.

The Thermodynamics of Isothermal Expansion

An isothermal process occurs at constant temperature (T remains unchanged). During such an expansion, the gas does work against external pressure, and energy exchange occurs in the form of heat to maintain temperature.

Key Characteristics of Isothermal Expansion

- The temperature remains constant throughout the process.
- The internal energy of an ideal gas remains unchanged because it depends solely on temperature.
- The work done by the gas during expansion is given by:

$$W = nRT \ln \left(\frac{V_f}{V_i} \right)$$

where:
- V_i and V_f are the initial and final volumes, respectively.

- Since the internal energy change ΔU for an ideal gas is zero in an isothermal process, the heat added to the system equals the work done:

$$Q = W$$

Calculating the Change in Molar Gibbs Energy: Step-by-Step Guide

The main goal is to find ΔG, the change in molar Gibbs free energy, during an isothermal expansion of a perfect gas from an initial state (P_i, V_i) to a final state (P_f, V_f).

Step 1: Express the Gibbs Free Energy for an Ideal Gas

For an ideal gas, the molar Gibbs free energy at a particular temperature and pressure is:

$$ G = G^\circ(T) + RT \ln \left(\frac{P}{P^\circ} \right) $$

where:
- $ G^\circ(T) $ is the standard molar Gibbs free energy at temperature $ T $,
- $ P^\circ $ is the standard pressure (commonly 1 atm).

Since $ G^\circ(T) $ is constant at fixed $ T $, the change in Gibbs free energy depends only on the pressure change:

$$ \Delta G = G_f - G_i = RT \ln \left(\frac{P_f}{P_i} \right) $$

Key Point: For an ideal gas undergoing an isothermal process, the change in molar Gibbs free energy is directly related to the ratio of the final and initial pressures.

Step 2: Relate Pressures to Volumes

Using the ideal gas law:

$$ P V = RT \Rightarrow P = \frac{RT}{V} $$

Thus, the initial and final pressures are:

$$ P_i = \frac{RT}{V_i} $$
$$ P_f = \frac{RT}{V_f} $$

Substituting into the expression for $ \Delta G $:

$$ \Delta G = RT \ln \left(\frac{\frac{RT}{V_f}}{\frac{RT}{V_i}} \right) = RT \ln \left(\frac{V_i}{V_f} \right) $$

Note the negative sign indicating that an increase in volume (expansion) causes the molar Gibbs energy to decrease.

Final Expression:

$$ \boxed{
\Delta G = RT \ln \left(\frac{V_i}{V_f} \right)
} $$

Practical Applications and Examples

Understanding this calculation has vital applications in various scientific and engineering fields.

Application 1: Gas Expansion in Engines

In internal combustion engines or turbines, gases expand isothermally during certain stages, and calculating the change in Gibbs energy helps evaluate the work potential and efficiency.

Application 2: Chemical Process Optimization

In chemical manufactories involving gases, controlling expansion processes and understanding their thermodynamic feasibility is critical. This calculation guides process design to maximize energy efficiency.

Example Calculation:

Suppose 1 mole of an ideal gas expands isothermally from an initial volume $V_i = 1\, \text{L}$ to a final volume $V_f = 10\, \text{L}$ at $T = 300\, \text{K}$.

Calculate ΔG.

Solution:

Using the formula:

$$\Delta G = RT \ln \left(\frac{V_i}{V_f} \right)$$

Constants:
- $R = 8.314\, \text{J mol}^{-1}\text{K}^{-1}$,
- $T = 300\, \text{K}$,
- $V_i = 1\, \text{L}$,
- $V_f = 10\, \text{L}$.

Calculate:

$$\Delta G = 8.314 \times 300 \times \ln \left(\frac{1}{10} \right)$$
$$\Delta G = 2494.2 \times \ln (0.1)$$
$$\ln (0.1) \approx -2.3026$$
$$\Delta G \approx 2494.2 \times (-2.3026)$$
$$\Delta G \approx -5744\, \text{J}$$

Interpretation:

The negative value indicates the process is spontaneous, and the decrease in molar Gibbs energy signifies the increased entropy and natural tendency to expand.

Important Considerations and Assumptions

When applying this calculation, keep in mind the following:

1. **Ideal Gas Approximation:** The derivation assumes the gas behaves ideally. Deviations occur at high pressures or low temperatures.
2. **Isothermal Conditions:** The temperature remains constant throughout the process, requiring heat exchange with the surroundings.
3. **Reversibility:** The calculation assumes a reversible process; real processes may involve irreversibilities that affect actual energy changes.
4. **Pressure and Volume Relationship:** The relation between pressure and volume hinges on the ideal gas law.

Conclusion

In summary, calculating the change in molar Gibbs energy for a perfect gas during an isothermal expansion involves understanding the fundamental thermodynamic relationships. The key formula:

$$\Delta G = RT \ln \left(\frac{V_i}{V_f} \right)$$

provides a straightforward method to quantify the spontaneity and energy change associated with volume expansion at constant temperature. This knowledge is essential for designing efficient thermodynamic systems, analyzing natural processes, and optimizing industrial operations involving gases.

By mastering this calculation, scientists and engineers can better predict system behavior, improve process efficiencies, and deepen their understanding of fundamental thermodynamic principles.

Frequently Asked Questions

What is the expression for the change in molar Gibbs free energy during an isothermal expansion of a perfect gas?

The change in molar Gibbs free energy, ΔG, during an isothermal expansion from volume V_1 to V_2 is

given by $\Delta G = RT \ln(V_2 / V_1)$, where R is the gas constant and T is the absolute temperature.

How does the change in molar Gibbs energy depend on the initial and final volumes during isothermal expansion?

It depends logarithmically on the ratio of the final to initial volume, expressed as $\Delta G = RT \ln(V_2 / V_1)$. An increase in volume results in a positive ΔG, indicating a non-spontaneous process under constant temperature.

Can you derive the change in Gibbs free energy for an ideal gas expanding isothermally?

Yes. Starting from the fundamental thermodynamic relation, for an ideal gas, $\Delta G = nRT \ln(V_2 / V_1)$. For a molar basis (n=1), it simplifies to $\Delta G = RT \ln(V_2 / V_1)$.

What role does temperature play in the change of Gibbs energy during isothermal expansion?

Since the process is isothermal, the temperature T remains constant, directly influencing ΔG through the product RT. Higher temperatures lead to larger changes in Gibbs energy for the same volume change.

Is the expansion of a perfect gas at constant temperature spontaneous, based on the change in Gibbs energy?

The spontaneity depends on the initial and final volumes. If $V_2 > V_1$, $\Delta G > 0$, indicating non-spontaneous expansion; if $V_2 < V_1$, $\Delta G < 0$, indicating a spontaneous compression. Typically, expansion at constant temperature is spontaneous if external work is done.

How does the concept of chemical potential relate to the change in Gibbs energy during ideal gas expansion?

For an ideal gas, the chemical potential μ is given by $\mu = RT \ln(P/P^0)$. During expansion, as volume increases and pressure decreases, the chemical potential changes, contributing to the overall change in Gibbs energy.

What assumptions are made about the gas when calculating the change in Gibbs free energy during isothermal expansion?

The calculation assumes the gas is ideal (perfect gas), the process is reversible and isothermal, and no phase changes or interactions occur other than those described by ideal gas behavior.

How would the change in Gibbs free energy differ if the gas were not ideal during the isothermal expansion?

For non-ideal gases, interactions between molecules and deviations from ideality would modify the

expression for ΔG, often requiring correction terms from equations of state like Van der Waals, making the change more complex than the simple ideal gas formula.

Can you explain the practical significance of calculating the change in Gibbs free energy for isothermal gas expansion?

Calculating ΔG helps determine whether the process is spontaneous, informs work extraction potential, and aids in designing thermodynamic systems like engines or compressors operating under isothermal conditions.

Additional Resources

Calculate The Change In The Molar Gibbs Energy Of A Perfect Gas When It Expands Isothermally At A Temperature is a fundamental problem in thermodynamics that offers deep insights into the behavior of gases and the principles governing spontaneous processes. Understanding how the molar Gibbs free energy changes during an isothermal expansion of a perfect gas is crucial for chemists, physicists, and engineers involved in designing processes such as chemical reactors, engines, and refrigeration systems. This guide aims to provide a comprehensive and detailed analysis of the calculation involved, including the theoretical background, step-by-step derivation, and practical implications.

Introduction to Gibbs Free Energy in Thermodynamics

Gibbs free energy (G) is a thermodynamic potential that indicates the maximum reversible work that can be performed by a system at constant temperature and pressure. The change in Gibbs energy (ΔG) during a process reveals whether the process is spontaneous (ΔG < 0), at equilibrium (ΔG = 0), or non-spontaneous (ΔG > 0).

For a molar quantity—meaning per mole of substance—the molar Gibbs free energy (G_m) is particularly useful when analyzing phase changes, reactions, or expansions involving gases.

The Context: Isothermal Expansion of a Perfect Gas

In an isothermal process, the temperature (T) remains constant throughout the expansion. For a perfect (ideal) gas, the internal energy (U) depends solely on temperature, and it remains unchanged during an isothermal process because the temperature does not vary.

The process of interest involves a perfect gas expanding from an initial volume V_i to a final volume V_f at constant temperature T. The key question is: how does the molar Gibbs energy change during this process?

Fundamental Concepts and Key Equations

Before diving into the calculation, let's review some essential equations and concepts:

- Ideal Gas Law:
$$ PV = RT $$
where P is pressure, V is volume, R is the universal gas constant, and T is temperature.

- Gibbs Free Energy for an Ideal Gas:
$$ G = G^\circ + RT \ln \left(\frac{P}{P^\circ}\right) $$
Alternatively, in terms of volume:
$$ G = G^\circ + RT \ln \left(\frac{V}{V^\circ}\right) $$

- Change in Gibbs Free Energy (ΔG):
For a process from an initial state (i) to a final state (f):
$$ \Delta G = G_f - G_i $$

- For an ideal gas, the molar Gibbs free energy at a given state:
$$ G(T, P) = G^\circ(T) + RT \ln \left(\frac{P}{P^\circ}\right) $$

Step-by-Step Calculation of the Change in Molar Gibbs Energy

1. Expressing the Initial and Final Gibbs Free Energies

At the initial state:
- Pressure: $ P_i $
- Volume: $ V_i $

At the final state:
- Pressure: $ P_f $
- Volume: $ V_f $

Using the ideal gas law:
$$ P_i V_i = RT $$
$$ P_f V_f = RT $$

Since temperature is constant, the initial and final pressures relate to their respective volumes:
$$ P_i = \frac{RT}{V_i} $$
$$ P_f = \frac{RT}{V_f} $$

The molar Gibbs free energies at these states are:
$$ G_i = G^\circ + RT \ln \left(\frac{P_i}{P^\circ} \right) $$
$$ G_f = G^\circ + RT \ln \left(\frac{P_f}{P^\circ} \right) $$

Subtracting:
$$ \Delta G = G_f - G_i = RT \left[\ln \left(\frac{P_f}{P^\circ} \right) - \ln \left(\frac{P_i}{P^\circ} \right) \right] $$
$$ \Delta G = RT \ln \left(\frac{P_f}{P_i} \right) $$

Expressing in terms of volumes:
$$ \frac{P_f}{P_i} = \frac{\frac{RT}{V_f}}{\frac{RT}{V_i}} = \frac{V_i}{V_f} $$

Thus:
$$\boxed{\Delta G = RT \ln \left(\frac{V_i}{V_f} \right)}$$

Final Expression for the Change in Molar Gibbs Energy

The key result from the derivation is:

The change in molar Gibbs free energy during an isothermal expansion of a perfect gas from volume V_i to V_f is:

$$\boxed{\Delta G = RT \ln \left(\frac{V_i}{V_f} \right)}$$

This clear and elegant formula reveals that:

- If the gas expands ($V_f > V_i$), then $\frac{V_i}{V_f} < 1$, and ΔG is negative, indicating the process is spontaneous.
- If the gas is compressed ($V_f < V_i$), then $\frac{V_i}{V_f} > 1$, and ΔG is positive, indicating the process is non-spontaneous unless external work is done.

Physical Interpretation and Implications

1. Spontaneity of Expansion

Since ΔG becomes negative during expansion, it confirms that an isothermal expansion of a perfect gas is spontaneous when it occurs without external work input. This aligns with the second law of thermodynamics, which states that processes tend to move toward states of lower free energy.

2. Work Done During Expansion

The work W done by the system during an isothermal expansion is:

$$W = nRT \ln \left(\frac{V_f}{V_i} \right)$$

For a molar process ($n=1$), the work is:

$$W = RT \ln \left(\frac{V_f}{V_i} \right)$$

Notice that:

$$
\Delta G = -W
$$

for an ideal gas in an isothermal process, indicating the work done by the system is directly related to the change in Gibbs free energy.

Practical Examples and Applications

Example 1: Calculating Gibbs Energy Change for a Specific Expansion

Suppose 1 mol of an ideal gas expands isothermally from 10 L to 20 L at 300 K. The gas constant $R = 8.314\, \text{J mol}^{-1}\text{K}^{-1}$.

Calculate ΔG:

$$
\Delta G = RT \ln \left(\frac{V_i}{V_f} \right) = 8.314 \times 300 \times \ln \left(\frac{10}{20} \right)
$$

$$
\Delta G \approx 8.314 \times 300 \times \ln(0.5) \approx 8.314 \times 300 \times (-0.6931) \approx -1726\, \text{J}
$$

The negative sign indicates the process is spontaneous, and the system's Gibbs free energy decreases by approximately 1.73 kJ.

Example 2: Implications in Chemical Engineering

In designing turbines or expanders, understanding the change in Gibbs free energy helps optimize energy efficiency during gas expansion processes. Knowing that the free energy decreases during expansion allows engineers to predict the maximum work achievable in turbines operating at constant temperature.

Limitations and Assumptions

While the derivation provides an exact expression for an ideal gas, real gases exhibit deviations due to interactions and finite molecular sizes. In such cases, modifications to the model, such as using the van der Waals equation, are necessary.

Additionally, the process assumes quasi-static (reversible) expansion, which may not always be practical. Real processes often involve irreversibilities, which reduce the work obtainable and alter the Gibbs energy change.

Summary and Key Takeaways

- The change in molar Gibbs free energy during an isothermal expansion of a perfect gas from volume V_i to V_f is:

$$
\boxed{
\Delta G = RT \ln \left(\frac{V_i}{V_f} \right)
}
$$

- The process is spontaneous when the gas expands ($V_f > V_i$), as ΔG is negative.
- The work done by the gas during expansion is:

$$
W = RT \ln \left(\frac{V_f}{V_i} \right)
$$

- The relation $\Delta G = -W$ highlights the fundamental connection between free energy change and work in ideal gas processes.

- Understanding this calculation is essential for thermodynamic analysis and the design of energy systems involving gas expansions.

Final Remarks

The simplicity of the formula underscores the power of thermodynamics in predicting system behavior. Whether analyzing natural processes or designing engineering systems, the calculation of the change in molar Gibbs energy during an isothermal expansion provides a cornerstone for

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