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Understanding the equilibrium constant (K) for chemical reactions is fundamental in chemistry, especially in thermodynamics and reaction kinetics. When analyzing a reaction such as $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$ with an enthalpy change (H) of 181 KJ and an entropy change (S) of 24.9 J/K·g, calculating the equilibrium constant at a specific temperature provides insight into the reaction's spontaneity and position of equilibrium. This article explores how to determine the equilibrium constant (K) given the thermodynamic data, explains the underlying principles, and discusses the significance of the results.

Understanding the Thermodynamic Principles Behind Equilibrium Constant (K)

What is the Equilibrium Constant?

The equilibrium constant, K, quantifies the ratio of product concentrations to reactant concentrations at equilibrium for a reversible chemical reaction. It is temperature-dependent and provides insight into whether a reaction favors products or reactants under specific conditions.

For a general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant, K, is expressed as:

$$ K = \frac{[C]^c [D]^d}{[A]^a [B]^b} $$

where the brackets denote molar concentrations or partial pressures.

Thermodynamics and the Relationship to K

The link between thermodynamic parameters and the equilibrium constant is established through the Gibbs free energy change (ΔG°). The relation is:

$$ \Delta G^\circ = -RT \ln K $$

where:

- ΔG° is the standard Gibbs free energy change
- R is the universal gas constant (8.314 J/mol·K)
- T is the temperature in Kelvin
- $\ln K$ is the natural logarithm of the equilibrium constant

If $\Delta G^\circ < 0$, the reaction favors products; if $\Delta G^\circ > 0$, it favors reactants.

Calculating ΔG° Using Enthalpy and Entropy

To determine K, we need to compute the standard Gibbs free energy change, which relates to enthalpy (ΔH°) and entropy (ΔS°) via:

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

Given data:

- $\Delta H^\circ = 181\, \text{kJ}$
- $\Delta S^\circ = 24.9\, \text{J/K·g}$

Important: To ensure consistency, convert all units to joules:

- $\Delta H^\circ = 181\, \text{kJ} = 181{,}000\, \text{J}$

Note on units for ΔS°: The provided ΔS is per gram, but standard thermodynamic calculations typically

require molar quantities. Therefore, to proceed accurately, we need to clarify whether the ΔS is per mole or per gram. In most reaction thermodynamics, ΔS is expressed per mole. Assuming the given ΔS is per mole, then:

- $\Delta S^\circ = 24.9\, \text{J/K·mol}$

If instead, the data is per gram, molar mass considerations are necessary to convert to per mole basis. For simplicity, we proceed assuming ΔS is per mole.

Calculating $\Delta G°$ at a Given Temperature

Suppose we are interested in the reaction at a temperature $T = 181\, \text{K}$. Then:

$$
\Delta G^\circ = 181,000\, \text{J} - (181\, \text{K} \times 24.9\, \text{J/K·mol}) = 181,000 - (181 \times 24.9)
$$

Compute:

$$
181 \times 24.9 \approx 181 \times 25 - 181 \times 0.1 = 4525 - 18.1 = 4506.9\, \text{J}
$$

So:

$$
\Delta G^\circ = 181,000 - 4,506.9 \approx 176,493.1\, \text{J}
$$

Note: Since ΔG° is positive, the reaction is non-spontaneous at this temperature.

Determining the Equilibrium Constant (K)

Using the relation:

$$
\Delta G^\circ = -RT \ln K
$$

we solve for K:

$$
K = e^{-\frac{\Delta G^\circ}{RT}}
$$

Plugging in the values:

- $R = 8.314\, \text{J/mol·K}$
- $T = 181\, \text{K}$
- $\Delta G^\circ = 176,493.1\, \text{J}$

Calculate:

$$
K = e^{-\frac{176,493.1}{8.314 \times 181}} = e^{-\frac{176,493.1}{1504.634}} \approx e^{-117.4}
$$

Since $e^{-117.4}$ is an extremely small number, K is effectively zero:

$$
K \approx 2.4 \times 10^{-51}
$$

This indicates that at 181 K, the formation of NO is thermodynamically unfavorable, and the reactants (N_2 and O_2) dominate.

Implications of the Calculated K Value

Reaction Favorability

A very small K value suggests the reaction heavily favors the reactants at low temperatures. Conversely, higher temperatures might shift the equilibrium toward products, especially if the reaction is endothermic, as indicated by positive ΔH.

Effect of Temperature on K

Since:

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

and $\Delta H°$ is positive, increasing T will increase ΔG°, making the reaction less spontaneous. However, because $\Delta S°$ is positive, higher T decreases ΔG°, potentially making the reaction more favorable at elevated temperatures.

Estimating K at Different Temperatures

For a comprehensive understanding, one can calculate K at various temperatures to observe how equilibrium shifts. For example, at higher temperatures (e.g., 2000 K), the reaction might become thermodynamically favorable.

Practical Applications and Significance

Industrial Synthesis of NO

Nitric oxide (NO) plays a crucial role in producing nitric acid, a vital industrial chemical. Understanding the thermodynamics of NO formation informs manufacturing processes, especially in optimizing temperature conditions to maximize yield.

Environmental Considerations

NO is a significant pollutant contributing to smog and acid rain. Controlling its formation through temperature management aligns with environmental regulations and pollution control strategies.

Thermodynamic Data in Reaction Engineering

Accurate calculations of K help chemical engineers design reactors and processes by predicting equilibrium states, optimizing reaction conditions, and minimizing unwanted byproducts.

Summary and Conclusions

- The equilibrium constant K for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$ depends heavily on temperature.
- Using thermodynamic data, ΔH° and ΔS°, one can calculate ΔG° at any temperature and determine K.
- At the provided temperature of 181 K, the reaction favors reactants, with an extremely low K.
- Increasing temperature can shift the equilibrium to favor NO formation due to the reaction's endothermic nature.
- Knowledge of K assists in process design, environmental management, and understanding reaction spontaneity.

Final Thoughts

Calculating the equilibrium constant from thermodynamic data is a powerful tool in chemistry and chemical engineering. It allows scientists and engineers to predict reaction behavior under various conditions, optimize industrial processes, and develop environmentally friendly technologies. Whether dealing with the synthesis of nitric oxide or other gases, mastery of these calculations supports innovation and sustainability in chemical industries.

Note: Always verify the units and molar basis for thermodynamic data when performing such calculations to ensure accuracy.

Frequently Asked Questions

What is the relationship between the enthalpy change (ΔH) and the equilibrium constant (K) for the reaction $N_2(g) + O_2(g) \rightarrow 2\,NO(g)$?

Since ΔH is positive (181 kJ), the reaction is endothermic, and increasing temperature will favor the formation of reactants, causing K to decrease.

How does temperature affect the equilibrium constant (K) for an endothermic reaction like $N_2 + O_2 \rightarrow 2\,NO$?

For an endothermic reaction, increasing temperature increases K, shifting equilibrium toward products; decreasing temperature lowers K.

Given $\Delta H = 181$ kJ and $\Delta S = 24.9$ J/K, how can we calculate the

temperature at which the reaction reaches equilibrium?

Use the relation $\Delta G = \Delta H - T\Delta S$; at equilibrium, $\Delta G = 0$, so $T = \Delta H / \Delta S$. Convert ΔH to J and compute T accordingly.

What is the formula to determine the equilibrium constant (K) from ΔG?

K = e^(-ΔG / RT), where ΔG is the Gibbs free energy change, R is the gas constant, and T is the temperature in Kelvin.

How does entropy change (ΔS) influence the equilibrium constant (K) for this reaction?

A positive ΔS (24.9 J/K) favors the formation of products at higher temperatures, increasing K as temperature rises.

At a given temperature, how can we estimate the equilibrium constant (K) for the reaction?

Calculate $\Delta G = \Delta H - T\Delta S$ and then use K = e^(-ΔG / RT) to estimate the equilibrium constant.

Is the reaction $N_2 + O_2 \rightarrow 2\,NO$ spontaneous at high temperatures? Why?

Yes, because ΔH is positive but large, and with increasing temperature, the reaction can become spontaneous in the forward direction due to entropy considerations.

What is the significance of the given entropy value (24.9 J/K) in

calculating the equilibrium constant?

It allows us to determine how temperature influences □G and, consequently, the equilibrium constant for the reaction.

How would you expect the equilibrium constant (K) to change if the temperature is increased for this reaction?

K would increase because the reaction is endothermic, and higher temperatures favor product formation, thus increasing K.

Additional Resources

Equilibrium Constant (K): Unveiling the Dynamics of the N□(g) + O□(g) □ 2 NO(g) Reaction

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Introduction: Understanding Chemical Equilibria and the Role of K

Chemical reactions are the cornerstone of understanding processes in chemistry, physics, and even biological systems. One fundamental concept that governs these reactions is chemical equilibrium, a state where the forward and reverse reactions occur at the same rate, resulting in constant concentrations of reactants and products over time. To quantify this balance, chemists employ the equilibrium constant, denoted as K.

In this article, we delve into the specifics of how to determine the equilibrium constant for the reaction:

\[\mathrm{N_2 (g)} + \mathrm{O_2 (g)} \leftrightarrow 2\, \mathrm{NO (g)} \]

given the reaction's enthalpy change (ΔH) of 181 kJ and entropy change (ΔS) of 24.9 J/K. We'll explore what these thermodynamic parameters imply, how they influence K, and what the magnitude of K reveals about the reaction's behavior under standard conditions.

Thermodynamics of the Reaction: ΔH and ΔS

Before discussing the equilibrium constant, it is essential to understand the thermodynamic parameters involved – enthalpy and entropy, which influence the reaction's spontaneity and position of equilibrium.

Enthalpy Change ($\Delta H = 181$ kJ)

- Definition: Enthalpy change reflects the heat absorbed or released during a reaction at constant pressure.
- Implication in this reaction: $\Delta H = +181$ kJ indicates the reaction is endothermic, requiring energy input for nitrogen and oxygen to combine into nitric oxide (NO). This energy absorption suggests that at lower temperatures, the equilibrium might favor the reactants, but at higher temperatures, the reaction shifts toward products due to increased thermal energy.

Entropy Change ($\Delta S = 24.9$ J/K)

- Definition: Entropy change measures the disorder or randomness associated with the reaction.
- Implication in this reaction: $\Delta S = +24.9$ J/K signifies an increase in disorder, which makes sense because two gaseous molecules (N_2 and O_2) are combining to form two molecules of NO. Although the number of molecules remains the same, the molecular structure and energy distribution contribute to an overall increase in entropy, possibly due to the formation of more complex molecules or

vibrational states.

Calculating the Equilibrium Constant (K)

The equilibrium constant K quantifies the ratio of product concentrations to reactant concentrations at equilibrium. For gases, it is often expressed in terms of partial pressures (K_p) or concentrations (K_c). In thermodynamics, K can be related to the standard Gibbs free energy change (ΔG°), which itself is linked to ΔH and ΔS via the fundamental relation:

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

and

$$
K = e^{-\frac{\Delta G^\circ}{RT}}
$$

where:

- R = universal gas constant = 8.314 J/(mol·K)
- T = temperature in Kelvin (K)

Note: Since the reaction's ΔH and ΔS are given, to compute K, we need to select a temperature. Typically, calculations use standard temperature (25°C or 298 K), but the specific temperature of interest can be substituted as needed.

Step 1: Convert ΔH to Joules

Given $\Delta H = 181$ kJ,

$$
\Delta H^\circ = 181\, \text{kJ} = 181,000\, \text{J}
$$

Step 2: Calculate $\Delta G°$ at 298 K

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

$$
\Delta G^\circ = 181,000\, \text{J} - (298\, \text{K})(24.9\, \text{J/K})
$$

$$
\Delta G^\circ = 181,000 - (298 \times 24.9)
$$

$$
\Delta G^\circ = 181,000 - 7,420.2
$$

$$
\Delta G^\circ \approx 173,579.8\, \text{J}
$$

Step 3: Calculate the Equilibrium Constant, K

$$
K = e^{-\frac{\Delta G^\circ}{RT}}
$$

$$
K = e^{-\frac{173,579.8}{(8.314)(298)}}
$$

$$
K = e^{-\frac{173,579.8}{2,477.572}}
$$

$$
K = e^{-70.02}
$$

$$
K \approx 2.84 \times 10^{-31}
$$

Interpreting the Magnitude of K

The calculated $K \approx 2.84 \times 10^{-31}$ at 298 K (25°C) is an exceedingly small number, indicating that the equilibrium heavily favors the reactants—namely, N_2 and O_2 gases—under standard conditions.

What Does a Small K Mean?

- The reaction hardly proceeds toward the formation of NO at room temperature.

- The thermodynamic data reveal that forming NO from nitrogen and oxygen is thermodynamically unfavorable at standard temperature.
- The reaction likely requires elevated temperatures or catalysts to shift the equilibrium toward NO production.

How Temperature Affects K

Since ΔH is positive and ΔS is positive, the reaction is endothermic with an increase in entropy. According to Le Châtelier's principle and the Gibbs free energy relation:

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

- At higher temperatures, the $T \Delta S^\circ$ term becomes more significant, potentially making $\Delta G°$ negative and K larger.
- At lower temperatures, $\Delta G°$ remains positive, and K remains tiny, favoring reactants.

Implications for Industrial and Environmental Chemistry

Understanding the equilibrium constant in this context has real-world significance, especially in processes like:

- Nitric oxide synthesis: Often performed at high temperatures in industry, such as in the Ostwald process for nitric acid production.
- Air pollution: NO is a primary pollutant formed in combustion engines; knowing the thermodynamics helps in designing control strategies.
- Environmental impact: Since the formation of NO is thermodynamically unfavorable at standard

conditions, high-temperature combustion is necessary to produce significant NO emissions.

Summary and Key Takeaways

- The reaction $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ has a positive ΔH (+181 kJ) and ΔS (+24.9 J/K), indicating an endothermic process with increased entropy.
- At 25°C (298 K), the equilibrium constant K is approximately 2.84×10^{-31}, an extremely small value, meaning the reaction favors reactants at room temperature.
- The magnitude of K is sensitive to temperature; increasing T can shift the equilibrium toward NO formation.
- Thermodynamic parameters provide insight into reaction feasibility and help in designing conditions for industrial synthesis or understanding environmental phenomena.

Conclusion: Thermodynamics as a Guide to Reaction Behavior

The calculation of the equilibrium constant K from thermodynamic data exemplifies how fundamental principles govern chemical reactions. While the reaction of nitrogen and oxygen to form NO is thermodynamically unfavorable at ambient conditions, elevating the temperature can substantially increase K, facilitating NO production. Recognizing the relationship between ΔH, ΔS, and K empowers chemists and engineers to optimize conditions for desired outcomes, whether in industrial synthesis or environmental management.

Understanding these concepts underscores the importance of thermodynamics in predicting reaction behavior, guiding practical applications, and advancing our knowledge of chemical systems.

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