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Consider The Following Reaction: $2NO_2(g) \rightleftharpoons N_2O_4(g)$. Calculate G at 298 K If The Partial Pressures Of NO_2 And

Understanding the thermodynamics of chemical reactions is essential for predicting the spontaneity and equilibrium behavior of chemical systems. In this context, calculating the Gibbs free energy change (ΔG) for the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ at a specific temperature, such as 298 K, provides valuable insights into whether the reaction favors the formation of N_2O_4 or remains predominantly as NO_2. This article will guide you through the process of calculating ΔG under given partial pressures, elucidate relevant concepts, and discuss the significance of the results.

Understanding the Reaction and Its Thermodynamic Context

The Reaction Overview

The reaction between nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4) is an equilibrium process:

$$ 2 NO_2(g) \rightleftharpoons N_2O_4(g) $$

This reaction is an example of a dynamic equilibrium, where NO_2 and N_2O_4 coexist in varying proportions depending on temperature and pressure conditions.

Significance of Gibbs Free Energy (ΔG)

The Gibbs free energy change (ΔG) determines the spontaneity of the reaction:

- If $\Delta G < 0$, the reaction proceeds spontaneously in the forward direction.
- If $\Delta G > 0$, the reaction favors the reverse process.
- If $\Delta G = 0$, the system is at equilibrium.

At a given temperature, ΔG can be related to the reaction quotient (Q) and

the standard Gibbs free energy change (ΔG°) through:

$$ ΔG = ΔG° + RT \ln Q $$

where:
- R is the universal gas constant (8.314 J mol^{-1} K^{-1}),
- T is the temperature in Kelvin,
- Q is the reaction quotient at the current partial pressures.

Calculating Standard Gibbs Free Energy Change (ΔG°)

Standard Gibbs Free Energy and Equilibrium Constant

The standard Gibbs free energy change (ΔG°) relates to the equilibrium constant (K) at a specific temperature:

$$ ΔG° = -RT \ln K $$

K is the equilibrium constant expressed in terms of partial pressures for gaseous reactions:

$$ K_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2} $$

To find ΔG°, you need the value of K at 298 K, which can often be obtained from thermodynamic tables or literature.

Obtaining Thermodynamic Data

The standard Gibbs free energies of formation (ΔG_f°) for the involved species are typically given or can be found in thermodynamic data sources:

Species	ΔG_f° (kJ/mol)
$NO_2(g)$	+51.3
$N_2O_4(g)$	+97.7

Using these, the standard Gibbs free energy change for the reaction is:

$$ ΔG° = ΔG_f°(N_2O_4) - 2 \times ΔG_f°(NO_2) $$
$$ ΔG° = 97.7 - 2 \times 51.3 = 97.7 - 102.6 = -4.9\, \text{kJ/mol} $$

This negative ΔG° indicates that, under standard conditions, the formation of N_2O_4 from NO_2 is slightly spontaneous.

Calculating the Equilibrium Constant (K) at 298 K

Given ΔG°, the equilibrium constant K can be calculated:

$$ K = e^{-ΔG° / RT} $$

Converting ΔG° into Joules:

$$ ΔG° = -4.9\, \text{kJ/mol} = -4900\, \text{J/mol} $$

Substituting values:

$$ K = e^{-\left(-4900\right) / (8.314 \times 298)} $$
$$ K = e^{4900 / 2477.7} $$
$$ K \approx e^{1.975} $$
$$ K \approx 7.2 $$

Thus, at 298 K, the equilibrium constant K_p is approximately 7.2, indicating that the equilibrium favors N_2O_4.

Calculating the Reaction Quotient (Q) from Partial Pressures

Suppose the partial pressures of NO_2 and N_2O_4 are known or given. For example:

- Partial pressure of NO_2: $P_{NO_2} = 0.5\, \text{atm}$
- Partial pressure of N_2O_4: $P_{N_2O_4} = 0.2\, \text{atm}$

The reaction quotient Q_p is:

$$ Q_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2} $$
$$ Q_p = \frac{0.2}{(0.5)^2} = \frac{0.2}{0.25} = 0.8 $$

Calculating ΔG at 298 K with Partial Pressures

Using the earlier relation:

$$ ΔG = ΔG° + RT \ln Q $$

Substitute known values:

- $ ΔG° = -4900\, \text{J/mol} $
- R = 8.314 J mol^{-1} K^{-1}
- T = 298 K
- $ Q = 0.8 $

Calculate the natural logarithm:

$$ \ln 0.8 \approx -0.223 $$

Calculate RT ln Q:

$$ RT \ln Q = 8.314 \times 298 \times (-0.223) \approx 8.314 \times 298 \times -0.223 $$
$$ \approx 8.314 \times 298 \times -0.223 $$
$$ \approx 8.314 \times (-66.35) $$
$$ \approx -552.2\, \text{J/mol} $$

Finally, ΔG:

$$ ΔG = -4900 + (-552.2) = -5452.2\, \text{J/mol} $$

or approximately:

$$ ΔG \approx -5.45\, \text{kJ/mol} $$

Since ΔG is negative, the reaction favors the formation of N_2O_4 under these partial pressures at 298 K.

Implications of the Calculated ΔG

Reaction Spontaneity

The negative ΔG indicates that, under the specified partial pressures at 298 K, the formation of N_2O_4 is thermodynamically favorable, and the reaction will tend to proceed in the forward direction until equilibrium is established.

Influence of Partial Pressures

Changes in the partial pressures of NO_2 and N_2O_4 can shift the reaction equilibrium:

- Increasing \(P_{NO_2} \) reduces Q, potentially decreasing ΔG and favoring NO_2.
- Increasing \(P_{N_2O_4} \) increases Q, further favoring N_2O_4 formation.

This dynamic underscores the importance of partial pressure control in industrial processes involving nitrogen oxides.

Temperature Dependence

While this calculation is specific to 298 K, the thermodynamic parameters and equilibrium constants vary with temperature, affecting the spontaneity and extent of the reaction.

Additional Considerations and Practical Applications

Industrial Significance

The equilibrium between NO_2 and N_2O_4 is critical in operating processes such as:

- Production of nitric acid.
- NOx removal in pollution control.
- Designing reactors for nitrogen oxide management.

Understanding ΔG helps optimize conditions for desired outcomes, whether minimizing NO_2 emissions or maximizing N_2O_4 formation.

Environmental Implications

Nitrogen oxides are significant pollutants contributing to smog and acid rain. Controlling their interconversion and understanding the thermodynamics aids in developing effective mitigation strategies.

Laboratory and Research Applications

Accurate calculations of ΔG at specific conditions support research in atmospheric chemistry, combustion, and material science, informing models

that predict reaction behavior under varying environmental conditions.

Summary and Key Takeaways

- The reaction between NO_2 and N_2O_4 is reversible and reaches equilibrium depending on conditions.
- The standard Gibbs free energy change (ΔG°) at 298 K indicates a slight spontaneous tendency toward N_2O_4 formation.
- Calculating the equilibrium constant (K) from thermodynamic data provides insight into the reaction's favorability.
- Reaction quotient (Q) derived from partial pressures determines the actual spontaneity under current conditions.
- The sign and magnitude of ΔG inform whether the reaction proceeds forward or backward at specific partial pressures.

Final Remarks

Calculating ΔG at specific conditions is a fundamental skill in chemical thermodynamics, enabling scientists and engineers to predict reaction behavior and optimize processes. By understanding the relationship between partial pressures, thermodynamic parameters, and

Frequently Asked Questions

What is the balanced chemical equation for the reaction involving NO2 and N2O4?

The balanced reaction is 2 NO2(g) ⇌ N2O4(g).

How do you calculate the standard Gibbs free energy change (ΔG°) for the reaction at 298 K?

ΔG° can be calculated using ΔG° = -RT ln K, where R is the gas constant, T is temperature in Kelvin, and K is the equilibrium constant.

What information is needed to determine ΔG at a

specific point in the reaction?

You need the standard Gibbs free energy change (ΔG°) and the reaction quotient Q, which depends on the partial pressures of NO2 and N2O4.

How do partial pressures of NO2 and N2O4 influence the calculation of ΔG?

The partial pressures determine the reaction quotient Q, which is used to find ΔG at non-standard conditions via ΔG = ΔG° + RT ln Q.

What is the expression for the reaction quotient Q in this reaction?

Q = (P_{N2O4}) / (P_{NO2})^2.

If the partial pressure of NO2 is given as 0.5 atm and that of N2O4 as 0.2 atm, how do you compute ΔG at 298 K?

Calculate Q = 0.2 / (0.5)^2 = 0.2 / 0.25 = 0.8. Then, use ΔG = ΔG° + RT ln Q to find ΔG.

What is the significance of the sign of ΔG in this reaction?

A negative ΔG indicates the reaction proceeds spontaneously in the forward direction, while a positive ΔG suggests non-spontaneity.

How can temperature changes affect the Gibbs free energy for this reaction?

Changing temperature alters ΔG, especially if the reaction has enthalpy and entropy components, influencing the spontaneity depending on the signs of ΔH and ΔS.

Additional Resources

Chemical Equilibrium and Gibbs Free Energy: An In-Depth Analysis of the NO_2/N_2O_4 System at 298 K

Introduction

Understanding chemical equilibrium and thermodynamics is fundamental in the

field of physical chemistry. Among the various thermodynamic functions, Gibbs free energy (G) plays a pivotal role in predicting the spontaneity of reactions under constant temperature and pressure. This article delves into a specific reaction— the dimerization of nitrogen dioxide (NO_2) to form dinitrogen tetroxide (N_2O_4)— and explores how to calculate the Gibbs free energy change (ΔG) at 298 K, given partial pressures of the reactants and products.

By examining this reaction through an expert lens, we aim to clarify the underlying principles, offer step-by-step calculations, and provide insights into the thermodynamic behavior of this equilibrium system.

The Reaction and Its Significance

Reaction Under Consideration:

$$ 2\, \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) $$

This equilibrium is a classic example of a reversible gas-phase reaction influenced by temperature, pressure, and entropy considerations. It is an important reaction in industrial chemistry and atmospheric science, as NO_2 and N_2O_4 are involved in nitrogen oxide cycling and pollution phenomena.

Thermodynamic Foundations

Gibbs Free Energy (G): A Brief Overview

Gibbs free energy is defined as:

$$
G = H - TS
$$

where:
- H = enthalpy
- T = temperature
- S = entropy

The change in Gibbs free energy for a reaction (ΔG) indicates whether the reaction proceeds spontaneously:
- $\Delta G < 0$: spontaneous
- $\Delta G = 0$: at equilibrium
- $\Delta G > 0$: non-spontaneous

At equilibrium, the Gibbs free energy of the system is minimized relative to the initial state, and the reaction quotient Q equals the equilibrium constant K.

Calculating ΔG for the NO_2/N_2O_4 System

Step 1: Understanding the Thermodynamic Parameters

To find ΔG at 298 K, we need:

1. Standard Gibbs free energy change (ΔG°): for the reaction at standard conditions.
2. Reaction quotient (Q): based on current partial pressures.
3. Relation between ΔG, ΔG°, and Q:

$$
\Delta G = \Delta G^\circ + RT \ln Q
$$

where:
- R = universal gas constant ($8.314\, \text{J mol}^{-1}\text{K}^{-1}$)
- T = temperature in Kelvin (298 K)
- Q = reaction quotient based on partial pressures

Step 2: Standard Gibbs Free Energy Change (ΔG°)

The standard Gibbs free energy change relates to the equilibrium constant K:

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

The equilibrium constant K for this reaction in terms of partial pressures is:

$$
K_p = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2}
$$

Values of standard Gibbs free energies of formation (ΔG_f°) for NO_2 and N_2O_4 are typically available in thermodynamic tables:

Species	ΔG_f° (kJ/mol)
$NO_2(g)$	+51.3
$N_2O_4(g)$	+97.7

Using these, the standard Gibbs free energy change:

$$
\Delta G^\circ = \sum \nu_i \Delta G_f^\circ (\text{products}) - \sum \nu_j \Delta G_f^\circ (\text{reactants})
$$

For the reaction:

$$
2\, \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)
$$

we have:

$$
\Delta G^\circ = \Delta G_f^\circ (\text{N}_2\text{O}_4) - 2 \times \Delta G_f^\circ (\text{NO}_2)
$$

Plugging in the values:

$$
\Delta G^\circ = 97.7\, \text{kJ/mol} - 2 \times 51.3\, \text{kJ/mol} = 97.7 - 102.6 = -4.9\, \text{kJ/mol}
$$

Converting to Joules:

$$
\Delta G^\circ = -4900\, \text{J/mol}
$$

Step 3: Determining K_p

Using the relation:

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

Rearranged:

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

Plugging in the numbers:

$$
K = e^{-\left(-4900\, \text{J/mol}\right) / (8.314\, \text{J
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$$
\text{mol}^{-1}\text{K}^{-1} \times 298\, \text{K})}
$$

Calculating the denominator:

$$
8.314 \times 298 \approx 2477.7
$$

So:

$$
K = e^{4900 / 2477.7} \approx e^{1.975}
$$

$$
K \approx 7.2
$$

This indicates that at 298 K, the equilibrium favors N_2O_4, but not overwhelmingly so.

Step 4: Incorporating Partial Pressures and Calculating ΔG

Suppose the partial pressures of NO_2 and N_2O_4 are:

- P_{NO_2} = 0.5 atm
- $P_{\text{N}_2\text{O}_4}$ = 0.2 atm

The reaction quotient Q:

$$
Q = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2} = \frac{0.2}{(0.5)^2} = \frac{0.2}{0.25} = 0.8
$$

Now, calculating ΔG:

$$
\Delta G = \Delta G^\circ + RT \ln Q
$$

$$
\Delta G = -4900 + (8.314)(298) \ln 0.8
$$

Calculate RT:

$$
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$$
8.314 \times 298 \approx 2477.7\, \text{J/mol}
$$

Calculate $\ln 0.8$:

$$
\ln 0.8 \approx -0.223
$$

So:

$$
\Delta G \approx -4900 + 2477.7 \times -0.223 \approx -4900 - 553.6 \approx -5453.6\, \text{J/mol}
$$

Since ΔG is negative, the reaction proceeds spontaneously toward the formation of N_2O_4 under these conditions.

Implications and Practical Insights

- The sign and magnitude of ΔG depend critically on the partial pressures of NO_2 and N_2O_4.
- When the partial pressure ratio favors N_2O_4 (i.e., $Q < K$), the reaction tends toward product formation.
- Conversely, if $Q > K$, the reaction favors NO_2, and ΔG becomes positive.
- Adjusting partial pressures can shift the equilibrium, illustrating Le Châtelier's principle.

Additional Considerations

Temperature Dependence

As temperature affects both K and ΔG, the equilibrium position shifts with temperature:

- Increasing temperature generally favors the endothermic direction.
- For the NO_2/N_2O_4 system, the reaction is exothermic, so increasing temperature shifts equilibrium toward NO_2.

Real-World Applications

- Industrial Synthesis: Control of partial pressures to optimize N_2O_4 production.
- Atmospheric Chemistry: Understanding nitrogen oxide cycling in pollution models.

Summary

This comprehensive exploration of the NO_2/N_2O_4 equilibrium at 298 K demonstrates:

- How to derive ΔG° from thermodynamic data.
- The relationship between the equilibrium constant K and standard Gibbs free energy.
- How to calculate the Gibbs free energy change ΔG under non-standard conditions using partial pressures.
- The importance of thermodynamic principles in predicting reaction spontaneity and equilibrium positioning.

By mastering these concepts, chemists and engineers can better manipulate reaction conditions, optimize processes, and interpret atmospheric phenomena with confidence.

In conclusion, the calculation of ΔG for the NO_2/N_2O_4 system provides valuable insights into reaction spontaneity and equilibrium control, serving as a quintessential example of thermodynamic analysis in chemical systems.

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