

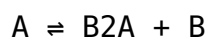
Ch 14 Consider The Reaction Of A To Form B2A <--> B. Kc= 1.8 X 10^-5 At 298K. A Reaction Mixture

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Understanding chemical equilibria is fundamental in the study of chemistry, especially when analyzing reactions that establish a dynamic balance between reactants and products. In this chapter, we focus on the specific reaction where substance A converts into B2A and B, characterized by the equilibrium constant (Kc) of 1.8×10^{-5} at 298 K. Analyzing this reaction involves exploring the reaction mechanism, the significance of the equilibrium constant, the impact of various factors on the equilibrium position, and practical applications in industry and laboratory settings.

Overview of the Reaction System

The reaction under consideration can be represented as:



This indicates that at equilibrium, a certain concentration of reactant A is converted into two products: B2A and B. The low value of the equilibrium constant ($K_c = 1.8 \times 10^{-5}$) suggests that, at 298 K, the reaction heavily favors the reactant side, meaning very little A is converted into B2A and B under standard conditions.

Understanding the Equilibrium Constant (Kc)

Definition and Significance

The equilibrium constant, Kc, expresses the ratio of the concentrations of products to reactants at equilibrium, each raised to the power of their stoichiometric coefficients. For the given reaction:

$$K_c = \frac{[B_2A][B]}{[A]}$$

where:

- [B2A] is the molar concentration of B2A,
- [B] is the molar concentration of B,
- [A] is the molar concentration of A.

A low Kc value indicates the reaction does not proceed significantly toward products, whereas a high

K_c value suggests extensive conversion of reactants into products.

Implications of $K_c = 1.8 \times 10^{-5}$

- The reaction is largely reactant-favored at 298K.
- Only a small proportion of A converts into B₂A and B at equilibrium.
- To shift the equilibrium toward products, external conditions such as temperature, pressure, or concentration must be altered.

Factors Affecting the Equilibrium Position

The position of equilibrium can be influenced by various factors, including concentration, temperature, pressure (for gaseous reactions), and the presence of catalysts. For this specific reaction, key considerations include:

1. Concentration Changes

- Increasing the concentration of A can temporarily shift the equilibrium to produce more B₂A and B.
- Removing B or B₂A as they form can also drive the reaction forward.

2. Temperature Variation

- Since the reaction's K_c is specified at 298 K, changing temperature can significantly impact the equilibrium.
- If the reaction is exothermic or endothermic, Le Châtelier's principle predicts the direction of shift with temperature changes.

3. Catalysts

- Catalysts do not alter the position of equilibrium but speed up the attainment of equilibrium.

Calculating Equilibrium Concentrations in the Reaction Mixture

Suppose we start with a known initial concentration of A, say, 1 mol/L, and no B₂A or B present initially. To analyze how the concentrations change at equilibrium, we can use an ICE (Initial, Change, Equilibrium) table.

Example Calculation

Assuming:

- Initial concentration of A: $[A]_0 = 1.0 \text{ mol/L}$
- Initial concentrations of B2A and B: 0 mol/L

Let x be the amount of A reacted at equilibrium:

Species	Initial (mol/L)	Change (mol/L)	Equilibrium (mol/L)
A	1.0	$-x$	$1.0 - x$
B2A	0	$+x$	x
B	0	$+x$	x

The equilibrium expression:

$$K_c = \frac{[B2A][B]}{[A]} = \frac{x \times x}{(1.0 - x)} = 1.8 \times 10^{-5}$$

Solve for x :

$$x^2 / (1.0 - x) = 1.8 \times 10^{-5}$$

Given the small K_c , x will be very small compared to 1.0, so approximation:

$$x^2 \approx 1.8 \times 10^{-5} \times 1.0$$

$$x \approx \sqrt{(1.8 \times 10^{-5})} \approx 0.00424 \text{ mol/L}$$

Thus:

- $[A]$ at equilibrium $\approx 1.0 - 0.00424 \approx 0.99576 \text{ mol/L}$
- $[B2A] \approx 0.00424 \text{ mol/L}$
- $[B] \approx 0.00424 \text{ mol/L}$

This illustrates that only a tiny fraction of A reacts under these conditions, consistent with the small K_c .

Practical Applications and Industrial Significance

Understanding the equilibrium behavior of reactions with low K_c values is critical in various industrial processes and laboratory applications.

1. Synthesis and Reaction Optimization

- When a reaction has a low K_c , strategies such as increasing reactant concentration, removing products, or adjusting temperature are employed to maximize yield.
- For example, in the production of B2A and B, continuous removal of B and B2A can shift equilibrium toward product formation.

2. Designing Reaction Conditions

- Engineers design reactors and processes that favor the desired reaction pathway.
- For reactions with low K_c , employing techniques such as high-pressure conditions (if gaseous), or using catalysts to lower activation energy, can be effective.

3. Environmental and Safety Considerations

- Reactions that favor reactants minimize waste and reduce environmental impact.
- Understanding equilibrium helps in designing safer processes by controlling reaction conditions to prevent undesired side reactions.

Advanced Topics: Le Châtelier's Principle and Reaction Dynamics

Le Châtelier's principle states that if a system at equilibrium is subjected to a change in concentration, temperature, pressure, or volume, the system adjusts to partially counteract that change.

1. Effect of Temperature

- If the forward or reverse reaction is exothermic, increasing temperature will shift the equilibrium toward the endothermic side.
- Specific enthalpy data is needed to determine the exact shift for this reaction.

2. Reaction Quotient (Q) vs. K_c

- The reaction quotient (Q) helps predict the direction of the reaction's shift when conditions change.
- Comparing Q with K_c determines whether the reaction will proceed forward or reverse to reach equilibrium.

Conclusion and Summary

The reaction $A \rightleftharpoons B$ with a K_c of 1.8×10^{-5} at 298 K exemplifies a predominantly reactant-favored equilibrium. Understanding the factors influencing this equilibrium enables chemists and engineers to manipulate conditions to optimize product yields, design efficient industrial processes, and minimize waste. Analytical calculations, such as ICE tables, provide insights into the extent of reaction under given conditions, guiding practical decision-making. Mastery of equilibrium concepts and their applications is essential for advancing chemical synthesis, environmental management, and process engineering.

Key Takeaways:

- Low K_c indicates a reaction favors reactants at equilibrium.
- Small changes in concentration or temperature can influence the extent of reaction.
- Practical strategies involve manipulating conditions to shift equilibrium toward desired products.
- Analytical tools like ICE tables are essential for predicting equilibrium concentrations.
- Understanding equilibrium behavior is vital for efficient and safe chemical process design.

Further Reading:

- Le Châtelier's Principle and its applications
- Thermodynamics of chemical reactions
- Industrial synthesis of chemical compounds
- Catalysis and reaction kinetics

Frequently Asked Questions

What does the equilibrium constant K_c of 1.8×10^{-5} indicate about the reaction $A \rightleftharpoons B_2A + B$ at 298K?

It indicates that the reaction favors the reactants, with a very low concentration of products at equilibrium, meaning the formation of B_2A and B is not favored under these conditions.

How can the equilibrium expression for the reaction $A \rightleftharpoons B_2A + B$ be written based on the given reaction?

The equilibrium expression is $K_c = [B_2A][B] / [A]$, where $[B_2A]$, $[B]$, and $[A]$ are the molar concentrations of the respective species at equilibrium.

If the initial concentration of A is high, how will the equilibrium position shift given the small K_c value?

Since K_c is very small, even with high initial concentration of A , the reaction will favor remaining mostly as reactant A , with minimal formation of B_2A and B at equilibrium.

What is the significance of temperature (298K) in determining the value of K_c for this reaction?

Temperature affects the equilibrium constant; at 298K, the given K_c value reflects the equilibrium state specific to this temperature, and changing the temperature could alter the equilibrium position.

How would you experimentally determine the concentrations of B_2A and B at equilibrium for this reaction?

You could analyze the reaction mixture using techniques like UV-Vis spectroscopy, NMR, or

chromatography to measure the concentrations of B₂A and B at equilibrium.

What does the small value of K_c suggest about the rate of the forward and reverse reactions for this process?

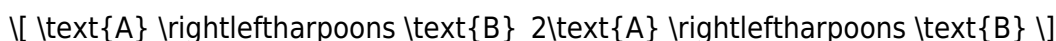
A small K_c suggests that the reverse reaction (breakdown of B₂A and B into A) is likely faster or more favored than the forward reaction, resulting in low product concentrations at equilibrium.

Additional Resources

In-Depth Analysis of the Equilibrium Reaction: $A \rightleftharpoons B_2A \rightleftharpoons B$ at 298 K with $K_c = 1.8 \times 10^{-5}$

Introduction to the Reaction System

Understanding chemical equilibria is fundamental in chemistry, especially when analyzing reactions involving multiple steps or complex formations. The reaction under consideration:



at 298 K, with an equilibrium constant $(K_c = 1.8 \times 10^{-5})$, presents a fascinating case study. This reaction involves the transformation of species A into a dimeric complex B₂A, which can further dissociate into species B. The low value of (K_c) indicates that, at equilibrium, the reaction heavily favors the reactants, with only a tiny fraction converting into B₂A and B under standard conditions.

This analysis aims to dissect this process in detail, exploring the thermodynamics, kinetics, concentration calculations, and practical implications for reaction mixtures. It will serve as a comprehensive guide for chemists dealing with similar equilibrium systems.

Understanding the Reaction Components

Species Involved

- A: The initial reactant species, possibly a monomer or simple molecule.
- B₂A: A dimeric complex formed from two B molecules and one A molecule, indicating possible coordination, associative bonding, or complexation.
- B: A simpler species, likely a monomeric form derived from B₂A.

Note: The exact identities depend on the chemical context, but for this discussion, they represent

general species involved in complex formation and dissociation.

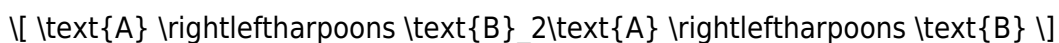
Reaction Pathways

- Formation of B₂A: A molecule of A reacts with B (possibly generated from B₂A dissociation or present initially) to form a bound complex B₂A.
- Dissociation to B: B₂A can dissociate into B molecules, which may be in equilibrium with A and B₂A.

Thermodynamics of the Equilibrium

Equilibrium Constant (K_c) : Definition and Significance

The equilibrium constant (K_c) for the overall process:



can be expressed as:

$$K_c = \frac{[\text{B}]^2}{[\text{A}]}$$

assuming the reactions are reversible and the species are in the same phase (e.g., aqueous or gaseous). Given that the overall (K_c) is (1.8×10^{-5}) , it suggests:

- The formation of B₂A and B from A is thermodynamically unfavorable at 298 K.
- The equilibrium heavily favors A, with minimal amounts of B₂A and B present at equilibrium.

Implication: The system tends to stay predominantly as A under standard conditions, but small quantities of B and B₂A exist, which can be crucial for catalytic or reaction pathway considerations.

Gibbs Free Energy Change (ΔG°)

Using the relation:

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

where:

- $(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$
- $(T = 298 \text{ K})$
- $(K_c = 1.8 \times 10^{-5})$

Calculations:

$$\ln K_c = \ln (1.8 \times 10^{-5}) \approx -10.928$$

\]

\[

$$\Delta G^\circ = - (8.314)(298)(-10.928) \approx 27,099 \text{ J/mol} \approx 27.1 \text{ kJ/mol}$$

\]

Interpretation: The positive ΔG° indicates that the formation of B₂A and B from A is non-spontaneous under standard conditions, aligning with the low K_c .

Concentration Calculations at Equilibrium

Initial Conditions and Assumptions

- Assume an initial concentration of A: $[A]_0$.
- No initial B or B₂A present unless specified.
- The system reaches equilibrium where small amounts of B₂A and B form.

Deriving Equilibrium Concentrations

Let:

- x = concentration of B₂A formed at equilibrium.
- y = concentration of B at equilibrium.

From the reaction scheme, and assuming the dominant pathway involves A converting into B₂A and B, the equilibrium expressions are:

$$K_c = \frac{[B]^2}{[A]}$$

Given the stoichiometry, if x mol of B₂A forms, then:

- $[A]_{eq} = [A]_0 - x$ (assuming each B₂A consumes 1 A)
- $[B]_{eq} = 2x$ (since each B₂A produces 2 B molecules)

Substituting into the K_c expression:

\[

$$K_c = \frac{(2x)^2}{[A]_0 - x} = \frac{4x^2}{[A]_0 - x}$$

\]

Given the small K_c , x is expected to be very small relative to $[A]_0$, allowing approximation:

\[

$$K_c \approx \frac{4x^2}{[A]_0}$$

\]

Rearranged:

$$x \approx \frac{1}{2} \sqrt{K_c \times [A]_0}$$

Example Calculation:

If $[A]_0 = 1 \text{ M}$,

$$x \approx \frac{1}{2} \sqrt{1.8 \times 10^{-5} \times 1} \approx \frac{1}{2} \times 0.00424 \approx 0.00212 \text{ M}$$

Thus:

- $[A]_{eq} \approx 1 - 0.00212 \approx 0.99788 \text{ M}$
- $[B]_{eq} \approx 2 \times 0.00212 \approx 0.00424 \text{ M}$
- $[B_2A]_{eq} \approx 0.00212 \text{ M}$

This demonstrates that at equilibrium, the concentrations of B and B₂A are negligible compared to A, confirming the reaction's unfavorable nature under these conditions.

Kinetics and Rate Considerations

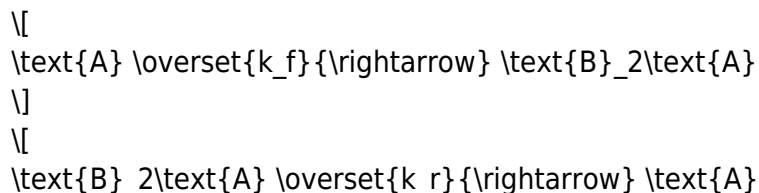
Reaction Rates and Activation Energies

While thermodynamics tells us about the favorability, kinetics dictate how quickly equilibrium is established. For this system:

- The forward and reverse rate constants (k_f and k_r) influence the rate at which A converts to B₂A and B.
- The high activation energy barrier, if present, will slow down the approach to equilibrium, especially given the low K_c .

Rate Law Expressions

Assuming the simplest case where:



\]

and similar for the dissociation into B, the rates are:

\[

$$\text{Forward rate} = k_f [A]$$

\]

\[

$$\text{Reverse rate} = k_r [B_2A]$$

\]

At equilibrium:

\[

$$k_f [A]_{eq} = k_r [B_2A]_{eq}$$

\]

which leads to:

\[

$$K_c = \frac{k_f}{k_r}$$

\]

Given the low K_c , k_f is much smaller than k_r , implying the formation of B_2A is kinetically hindered and thermodynamically unfavorable under standard conditions.

Impact of Temperature and External Conditions

Temperature Dependence of K_c

Using the Van't Hoff equation:

\[

$$\frac{d \ln K_c}{dT} = \frac{\Delta H^\circ}{RT^2}$$

\]

- If $\Delta H^\circ > 0$ (endothermic formation), increasing temperature will increase K_c , favoring product formation.
- For this system, empirical data would be necessary to determine ΔH° , but given the low K_c at 298 K, higher temperatures might shift equilibrium slightly toward B_2A and B.

Practical implication: Elevated temperatures could be used to increase the formation of B_2A , provided the reaction pathway remains accessible.

Le Châtelier's Principle

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