THERMODYNAMICS, KINETICS AND MECHANISM OF ABSORPTION OF A MIXTURE OF GASES CONSISTING OF SULFUR OXIDES INTO ALKALINE SOLUTIONS

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ТЕРМОДИНАМИКА, КИНЕТИКА И МЕХАНИЗМ АБСОРБЦИИ СМЕСИ ГАЗОВ, СОСТОЯЩЕЙ ОКСИДОВ СЕРЫ, В ЩЕЛОЧНЫЕ РАСТВОРЫ

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ABSTRACT

In the article, the thermodynamics, kinetics and mechanism of absorption of a mixture of sulfurous gases in alkaline solutions are considered. The result of thermodynamic analysis showed that the value of Gibbs energy of absorption of sulfur dioxide and trioxide into sodium hydroxide solution under standard conditions was negative. It was determined that the limiting step is the absorption of sulfur dioxide, and ways to increase the partial pressure of the gas were proposed to increase the reaction yield.

АННОТАЦИЯ

В статье рассмотрены термодинамика, кинетика и механизм абсорбции смеси сернистых газов в щелочных растворах. Результат термодинамического анализа показал, что значение энергии Гиббса поглощения диоксида и триоксида серы раствором гидроксида натрия в стандартных условиях было отрицательным. Установлено, что лимитирующей стадией является поглощение диоксида серы, и предложены пути увеличения парциального давления газа для увеличения выхода реакции.

Keywords: sulfur dioxide, sulfur trioxide, absorption, alkaline medium, thermodynamics, kinetics, mechanism.

Ключевые слова: диоксид серы, триоксид серы, абсорбция, щелочная среда, термодинамика, кинетика, механизм.

The process of absorption of SO_2 and SO_3 in an alkaline environment has a wide range of practical applications, from the removal of pollutants in flue gas streams to the production of various chemicals. This process plays a crucial role in reducing air pollution and ensuring the sustainability of industrial processes. The method of gas chromatography was used to determine the composition of gases in the air, and the method of High-Performance Liquid Chromatography was used to determine the purity of the liquid absorbent. In the research, sodium hydroxide was used as a substance that creates an alkaline environment. In order to conduct a thermodynamic analysis of the reactions in the solution system, it is necessary to calculate the standard Gibbs free energy change (ΔG°) and the equilibrium constant (K) at a certain temperature [1-5]. The equations for ΔG° and K are:

$$\Delta G° = -RT\ln K \quad (1)$$

Where: R is the universal gas constant (8.314 J/mol*K), T is the temperature in Kelvin, lnK is the natural logarithm of the equilibrium constant.

The chemical processes involved in each gas component were thermodynamically analyzed [6-7]:

1. $SO_2 + 2NaOH = Na_2SO_3 + H_2O$

The standard Gibbs free energy change for this reaction can be calculated using the values of the standard Gibbs free energy of formation (ΔGf °) of the reactants and products:

$$\Delta G° = \Delta Gf°(Na_2SO_3) + \Delta Gf°(H_2O) - \Delta Gf°(SO_2) - 2\Delta Gf°(NaOH) \quad (2)$$

ΔGf° values at 298 K: $\Delta Gf°(Na_2SO_3)$ = -1095.8 kJ/mol, $\Delta Gf°(H_2O)$ = -237.2 kJ/mol, $\Delta Gf°(SO_2)$ = -300.4 kJ/mol and ΔGf°(NaOH) = -470.1 kJ/mol. If these values are replaced in the equation: ΔG° = -40.8 kJ/mol.

The equilibrium constant at 298 K can be calculated from the value of ΔG° using the following equation [8-9]:

$$K = e^{-\Delta G°/RT} \quad (3)$$

Substituting the values gives: $K = 7.03 \cdot 10^6$

2. $SO_3 + 2NaOH = Na_2SO_4 + H_2O$

The standard Gibbs free energy change for this reaction can be calculated using the previous equation:

$$\Delta G° = \Delta Gf°(Na_2SO_4) + \Delta Gf°(H_2O) - \Delta Gf°(SO_3) - 2\Delta Gf°(NaOH) \quad (4)$$

ΔGf° values at 298 K: $\Delta Gf°(Na_2SO_4)$ = -1385.1 kJ/mol, $\Delta Gf°(H_2O)$ = -237.2 kJ/mol, $\Delta Gf°(SO_3)$ = -371.1 kJ/mol and ΔGf°(NaOH) = -470.1 kJ/mol. Substituting these values into the equation, we get: ΔG° = -36.6 kJ/mol.

The equilibrium constant at 298 K can be calculated from the value of ΔG° using the previous equation: $K = 2.46 \cdot 10^6$

Negative values of ΔG° in both reactions indicate that the reactions are thermodynamically favorable and occur spontaneously [10].

The absorption of sulfur oxides such as sulfur dioxide (SO_2) and sulfur trioxide (SO_3) in alkaline media involves complex chemical reactions that occur in two stages. The first stage is the physical absorption of gas into the liquid phase, and then the chemical reaction of the absorbed gas with sodium hydroxide solution results in the formation of soluble sulfite or sulfate [11].

The absorption mechanism of sulfur oxides in an alkaline environment is usually described by the following equations:

a. $SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$

$H_2SO_3(aq) + 2NaOH(aq) \rightarrow Na_2SO_3(aq) + 2H_2O(l)$

b. $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

The first equation shows the equilibrium between sulfur dioxide gas and water to form sulphitic acid, which then reacts with sodium hydroxide to form sodium sulphite and water in the second equation [12]. Similarly, the third equation shows the formation of sulfuric acid from sulfur trioxide and water, which in the fourth equation reacts with sodium hydroxide to form sodium sulfate and water. The kinetics of the gas absorption process depends on various factors, for example,

the gas concentration in the air, the temperature and pressure of the system, and the properties of the liquid absorbent. The rate of absorption is also affected by the reaction rate of chemical reactions that can be determined experimentally.

In alkaline environments, the rate of absorption of sulfur oxides generally follows first-order kinetics, where the rate of absorption is proportional to the concentration of the gas in the air. The rate constant, k, depends on various factors, such as the absorptivity of the liquid, the temperature, and the partial pressure of the gas [13].

The negative values of $\Delta G°$ in both reactions after absorption of SO_2 and SO_3 gases in alkaline solutions indicate that the reactions are thermodynamically favorable and spontaneous.

The overall efficiency of the absorption process depends on the pH level of the alkaline solution, the concentration of the alkaline solution, and the surface area of the liquid gas absorption. Increasing the pH and concentration of an alkaline solution can increase absorption efficiency by increasing the rate of chemical reactions. The use of high-surface-area liquid gas absorbers, such as sprays or packed tower tanks, can also increase the efficiency of the absorption process by increasing the gas-liquid contact area.

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