

Comparison of Measuring Methods for the Equilibrium Constant of SO₃ and NH₃ Reaction

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Abstract

During the selective catalytic reduction (SCR) process for sulfur-containing coal combustion flue gas, the reaction between SO₃ in the flue gas and NH₃ added in SCR device will generate ammonium bisulfate (ABS) and ammonium sulphate (AS). Due to the high viscosity and corrosiveness of ABS liquid, the reaction product is harmful to the flue gas purification system. In order to predict the amount of ABS and AS production in flue gas, it is necessary to obtain the reaction equilibrium constant through experimental measurement. In this paper, the non-contact measuring method and the high-temperature isothermal condensation measuring method for reaction equilibrium constant measurement are compared theoretically. The comparison results indicate that non-contact measurement is more suitable for measuring low product concentration, while high-temperature isothermal condensation method is suitable for measuring high product concentration.

Keywords

SCR; Ammonium Bisulfate; ABS; Ammonium Sulphate; Equilibrium Constant.

1. Introduction

Sulfur-containing coal combustion flue gas contains a certain concentration of SO₂, among which some SO₂ will be converted into SO₃ [1]. The presence of SO₃ in the flue gas will generate ammonium bisulfate (ABS) and ammonium sulphate (AS) when the reducing agent NH₃ is injected during the selective catalytic reduction (SCR) process. Liquid ABS is a viscous and corrosive substance that can block the SCR catalyst [2-4], air preheater [5, 6], electrostatic precipitators [7] and other device, which is harmful to the flue gas purification system. In order to accurately predict the production of ABS, the equilibrium constant of SO₃ and NH₃ reaction is necessary. At present, the physical property data of ABS and AS in gaseous state is scarce, so it is hardly to calculate the equilibrium constant of gaseous reaction by theoretical calculation. Therefore, the equilibrium constant can only be calculated by measuring the concentration of each component after the reaction.

In terms of gas phase reaction measurement, non-contact measurement [8] and chemical analysis measurement [9] are both commonly used. The detection process using non-contact measurement methods (such as Fourier transform infrared spectra, FTIR spectra) is the most straightforward, which can avoid measurement errors caused by long measurement processes. However, in actual measurement, the complexity of gas composition will affect the accuracy of quantitative measurement. Chemical analysis methods have relatively more measurement steps and are most widely used. This measuring method usually samples and cools the gas at the reactor outlet down to the required temperature for measurement, and then absorbs the target component by an absorbent and measures

it through concentration measurement (such as based on solution conductivity and light absorbance value).

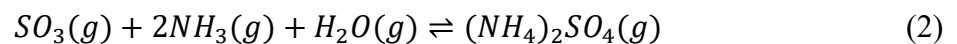
The conventional sampling-cooling measurement scheme has drawbacks. Due to the extremely fast reaction between SO_3 and NH_3 to generate ABS and AS [10], during the sampling and cooling process, temperature changes will cause reaction balance being destroyed. It will continue to generate product. The measured amount of product after cooling is not equal to the equilibrium amount at the reactor temperature, which leads to measurement errors. Therefore, it is necessary to ensure the experimental accuracy and effectiveness of the reaction equilibrium constant measurement.

In order to accurately measure the equilibrium constant of the reaction between SO_3 and NH_3 , a measuring method of high-temperature isothermal condensation was proposed and compared with the non-contact measuring method. It is expected to provide a reference for solving the difficulty in measuring the equilibrium constant of the reaction between SO_3 and NH_3 .

2. Reaction Mechanism and Equilibrium Constants

2.1 Page Numbers

ABS and AS can be generated by both ternary and binary formation reactions [11], where the ternary formation reaction balance equations are as follows:



The equilibrium constant of ABS ternary formation corresponding to ternary formation reaction balance is as follow:

$$K_{ABS(g)-Ter,T} = \frac{\frac{p_{ABS(g)}}{p^\ominus}}{\frac{p_{SO_3(g)}}{p^\ominus} \cdot \frac{p_{NH_3(g)}}{p^\ominus} \cdot \frac{p_{H_2O(g)}}{p^\ominus}} \quad (3)$$

The equilibrium constant of AS ternary formation corresponding to ternary formation reaction is as follow:

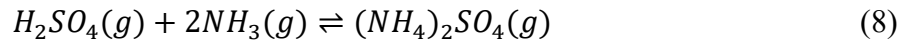
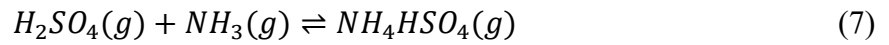
$$K_{AS(g)-Ter,T} = \frac{\frac{p_{AS(g)}}{p^\ominus}}{\frac{p_{SO_3(g)}}{p^\ominus} \cdot \left(\frac{p_{NH_3(g)}}{p^\ominus}\right)^2 \cdot \frac{p_{H_2O(g)}}{p^\ominus}} \quad (4)$$

In the flue gas, SO_3 can react with water vapor to generate sulfuric acid vapor [12], the reaction balance equation and its equilibrium constant are as follows:



$$K_{H_2SO_4(g),T} = \frac{\frac{p_{H_2SO_4(g)}^e}{p^\ominus}}{\frac{p_{SO_3(g)}}{p^\ominus} \cdot \frac{p_{H_2O(g)}}{p^\ominus}} \quad (6)$$

In the presence of sulfuric acid vapor, ABS and AS can also be generated by binary formation reactions [13], the reaction balance equations are as follows:



The equilibrium constant of ABS binary formation corresponding to binary formation reaction is as follow:

$$K_{ABS(g)-B,T} = \frac{\frac{p_{ABS(g)}}{p^\ominus}}{\frac{p_{SO_3(g)}}{p^\ominus} \cdot \frac{p_{NH_3(g)}}{p^\ominus}} \quad (9)$$

The equilibrium constant of AS binary formation corresponding to binary formation reaction is as follow:

$$K_{AS(g)-Bi,T} = \frac{\frac{p_{AS(g)}}{p^\ominus}}{\frac{p_{SO_3(g)}}{p^\ominus} \cdot \left(\frac{p_{NH_3(g)}}{p^\ominus}\right)^2} \quad (10)$$

The schematic diagram of the variables at the inlet and outlet under low concentration feed is shown in Figure 1.

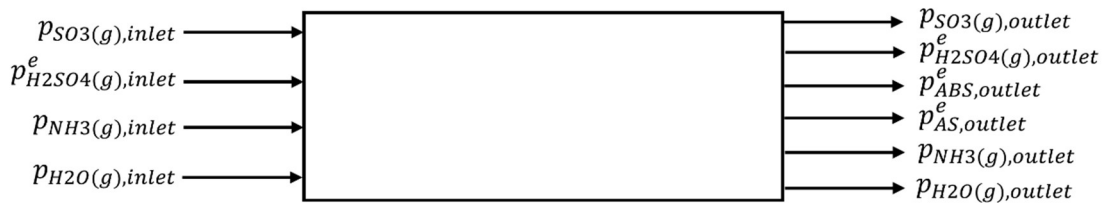
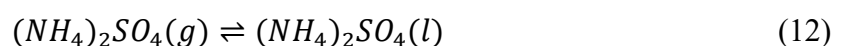
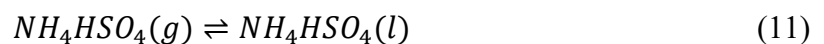


Figure 1. Variables at the inlet and outlet of the reactor under low concentration feed

During the experiment, SO₃ in the inlet feed is generated by evaporation and decomposition of the dilute sulfuric acid solution. The partial pressure of SO₃ and H₂SO₄ at the inlet can be obtained through the sulfuric acid decomposition balance equation. To calculate the equilibrium constant of the ABS/AS formation reaction, the concentration of each component at the outlet needs to be measured.

When the feed concentration is high, the concentration of ABS and AS generated in the reaction is also high. When the gaseous product reaches saturation, liquid product will precipitate. The gaseous and liquid products will eventually reach condensation balance [14], and the condensation balance equations are as follows:



The equilibrium constants of ABS and AS are as follows:

$$K_{ABS(g-l),T} = \frac{1}{p_{ABS,T}^*/p^\ominus} \quad (13)$$

$$K_{AS(g-l),T} = \frac{1}{p_{AS,T}^*/p^\ominus} \quad (14)$$

Since the condensation equilibrium constant is a function of temperature, it can be seen that the saturated vapor pressure $p_{ABS,T}^*$ and $p_{AS,T}^*$ of gaseous ABS and AS are constants at a fixed temperature.

When the gas-phase product reach saturation and precipitate condensed product, the schematic diagram of the variables at the inlet and outlet is shown in Figure 2.



Figure 2. Variables at the inlet and outlet of the reactor under high concentration feed

3. Measuring Methods Comparison

3.1 Non-contact Measuring Method

Among the non-contact measurement methods, quantitative analysis using spectroscopy is commonly used, such as Fourier transform infrared spectra (FTIR spectra) and Tunable Diode Laser Absorption Spectroscopy (TDSLAS). The basis for quantitative spectral analysis is Lambert Beer's law [15]: When a beam of light passes through the sample, the intensity of light absorption is proportional to the concentration of each component in the sample and the absorption optical path length. Therefore, this method can be used to measure the concentration of various substances in the reaction. Due to the fact that the characteristic absorption spectra of ABS and AS are not commonly used, it is difficult to directly measure the concentration of ABS and AS. In this article, the generation of ABS/AS is calculated by measuring the raw material consumption obtained from changes in the concentration of reactants at the inlet and outlet.

The schematic diagram of non-contact measurement device is shown in Figure 3.

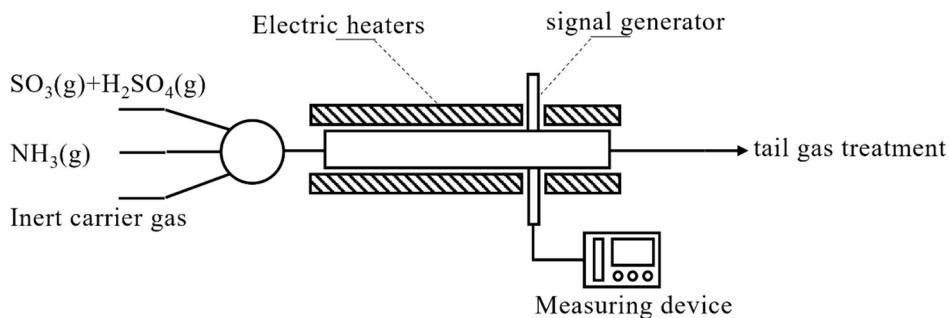


Figure 3. Schematic diagram of non-contact measurement device

3.1.1 No Condensation Balance Condition

Under low concentration feed condition, it only consists of gaseous product without condensation balance and corresponding condensed product.

The SO₃ in the inlet feed is generated by evaporation and decomposition of the dilute sulfuric acid solution. At the inlet of the reaction tube, SO₃ and H₂SO₄ reach a sulfuric acid decomposition balance, and their partial pressures are $p_{SO_3(g),inlet}$ and $p_{H_2SO_4(g),inlet}^e$. The H₂SO₄ can be regarded as hydrated SO₃, and both SO₃ and H₂SO₄ entering the reactor come from dilute sulfuric acid. So, the total amount of SO₃ is determined by SO₃ conservation equation:

$$p_{SO_3(g),outlet} = p_{SO_3(g),inlet} + p_{H_2SO_4(g),inlet}^e - p_{ABS,outlet}^e - p_{AS,outlet}^e - p_{H_2SO_4(g),outlet}^e \quad (15)$$

Similarly, the NH₃ conservation equation is:

$$p_{NH_3(g),outlet} = p_{NH_3(g),inlet} - p_{ABS,outlet}^e - 2 \cdot p_{AS,outlet}^e \quad (16)$$

From the above, it can be seen that the SO₃ partial pressure $p_{SO_3(g),inlet}$, NH₃ partial pressure $p_{NH_3(g),inlet}$, water vapor partial pressure $p_{H_2O(g),inlet}$ and sulfuric acid partial pressure $p_{H_2SO_4(g),inlet}^e$ at the reaction inlet are known quantities.

Assuming that under non-contact measuring method, the SO₃ partial pressure $p_{SO_3(g),outlet}$, NH₃ partial pressure $p_{NH_3(g),outlet}$, water vapor partial pressure $p_{H_2O(g),outlet}$ and sulfuric acid partial pressure $p_{H_2SO_4(g),outlet}^e$ at the reaction outlet are measurable items.

The remaining unknown items are gaseous ABS partial pressure $p_{ABS,outlet}^e$ and gaseous AS partial pressure $p_{AS,outlet}^e$.

After solving the two material conservation equations Eq. (15) and Eq. (16) together, the equilibrium constant K^\ominus can be calculated by the obtained unknown quantities being substituted into the equilibrium constant formulas of ABS/AS ternary/binary formation.

3.1.2 Condition with Condensation Balance

When the inlet feed concentration is high, the concentration of the product will also be high. When it reaches saturation vapor pressure, condensed product will be generated in the reaction tube.

The molar flow rates of condensed ABS and AS are $n_{ABS(l),outlet}$ and $n_{AS(l),outlet}$, respectively, the saturated vapor pressure of the outlet gaseous ABS and AS is $p_{ABS,T}^*$ and $p_{AS,T}^*$. As being illustrated above, the saturated vapor pressure $p_{ABS,T}^*$ and $p_{AS,T}^*$ of gaseous ABS and AS are constants at a fixed temperature.

The relationship between the partial pressure $p_{ABS/AS(g),outlet}^*$ (saturated) of gaseous ABS/AS and its molar flow rate $n_{ABS/AS(g),outlet}$ in gaseous form at the outlet is as follows:

$$p_{ABS/AS(g),outlet}^* \cdot q_V = n_{ABS/AS(g),outlet} \cdot RT \quad (17)$$

With the relation equation of partial pressure and molar flow rate, the SO₃ conservation equation is as follows:

$$p_{SO_3(g),outlet} = p_{SO_3(g),inlet} + p_{H_2SO_4(g),inlet}^e - p_{ABS,outlet}^* - \frac{n_{ABS(l),outlet} \cdot RT}{q_V} - p_{AS,outlet}^* - \frac{n_{AS(l),outlet} \cdot RT}{q_V} - p_{H_2SO_4(g),outlet}^e \quad (18)$$

And the NH₃ conservation equation is as follows:

$$p_{NH_3(g),outlet} = p_{NH_3(g),inlet} - p_{ABS,outlet}^* - \frac{n_{ABS(l),outlet} \cdot RT}{q_v} - 2 \cdot p_{AS,outlet}^* - 2 \cdot \frac{n_{AS(l),outlet} \cdot RT}{q_v} \quad (19)$$

The same to the condition without condensation balance, the SO₃ partial pressure $p_{SO_3(g),inlet}$, NH₃ partial pressure $p_{NH_3(g),inlet}$, water vapor partial pressure $p_{H_2O(g),inlet}$ and sulfuric acid partial pressure $p_{H_2SO_4(g),inlet}^e$ at the reaction inlet are known quantities. The SO₃ partial pressure $p_{SO_3(g),outlet}$, NH₃ partial pressure $p_{NH_3(g),outlet}$, water vapor partial pressure $p_{H_2O(g),outlet}$ and sulfuric acid partial pressure $p_{H_2SO_4(g),outlet}^e$ at the reaction outlet are measurable items.

The remaining unknown items are gaseous ABS saturated partial vapor pressure $p_{ABS,T}^*$ and gaseous AS saturated partial vapor pressure $p_{AS,T}^*$, molar flow rate of condensed ABS $n_{ABS(l),outlet}$ and molar flow rate of condensed AS $n_{AS(l),outlet}$.

Since there are only two equations (SO₃ conservation equation and NH₃ conservation equation), the number of unknown variables is greater than the number of equations, so the equation is not solvable. As mentioned above, it is difficult to directly measure the concentration of ABS and AS, the generation of ABS/AS is calculated by measuring the raw material consumption obtained from changes in the concentration of reactants at the inlet and outlet.

So, when the feed concentration is high and the gaseous product reaches saturation to generate condensed product, only the total amount of gaseous product and condensed product can be calculated, and the amount of product presented in condensed forms (such as aerosols) cannot be measured separately. Therefore, it is impossible to distinguish the amount between gaseous product and condensed product. In addition, when condensed product is generated, product deposition on the detection window of measuring device can also affect the measurement effectiveness of non-contact measuring method.

Based on the above analysis, it can be concluded that: When at the low concentration feed without generating condensed product condition, non-contact measurement can be conveniently carried out; When the feed concentration is high and condensed product is generated, it is hardly to obtain the correct reaction equilibrium constant by non-contact measurement.

3.2 High-temperature Isothermal Condensation Measuring Method

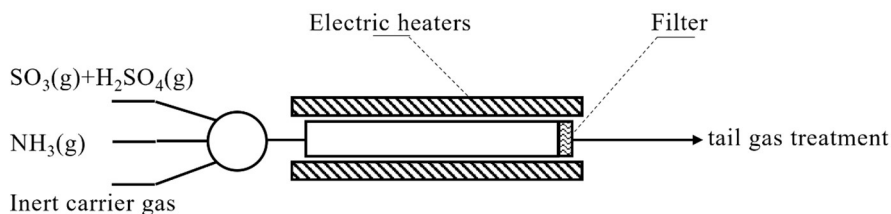


Figure 4. Schematic diagram of high-temperature isothermal condensation measurement device

As can be seen in the schematic diagram of high-temperature isothermal condensation measurement device (Figure 4), the device is equipped with filter and trapping components. When gaseous and condensed products are generated in the reaction tube, the gaseous product can continue to flow out of the reaction tube, while the condensed product is intercepted and captured by filter, thus achieving the separation of gaseous and condensed products. The amount of ABS and AS collected by the filter is $n_{ABS(l),outlet}$ and $n_{AS(l),outlet}$.

The SO₃ conservation equation is the same as non-contact measurement in condition with condensation balance, which is as follows (18).

And the NH₃ conservation equation is also the same as follows (19).

Except for being presented in the form of water vapor, some H₂O molecules exist in the form of H₂SO₄ due to their binding with SO₃. Therefore, water conservation needs to be considered, and its equation is as follows:

$$p_{H_2O(g),outlet} = p_{H_2O(g),inlet} + p_{H_2SO_4(g),inlet}^e - p_{ABS,T}^* - \frac{n_{ABS(l),outlet} \cdot RT}{q_v} - p_{AS,T}^* - \frac{n_{AS(l),outlet} \cdot RT}{q_v} - p_{H_2SO_4(g),outlet}^e \quad (20)$$

The equation at the reaction tube outlet based on the generating equilibrium constant of ABS is as follows:

$$K_{ABS(g)-Ter,T} = \frac{\frac{p_{ABS,T}^*}{p^\ominus}}{\frac{p_{SO_3(g),outlet}}{p^\ominus} \cdot \frac{p_{NH_3(g),outlet}}{p^\ominus} \cdot \frac{p_{H_2O(g),outlet}}{p^\ominus}}{p^\ominus}} \quad (21)$$

Similarly, the equation at the reaction tube outlet based on the generating equilibrium constant of AS is as follows:

$$K_{AS(g)-Ter,T} = \frac{\frac{p_{AS,T}^*}{p^\ominus}}{\frac{p_{SO_3(g),outlet}}{p^\ominus} \cdot \left(\frac{p_{NH_3(g),outlet}}{p^\ominus}\right)^2 \cdot \frac{p_{H_2O(g),outlet}}{p^\ominus}}{p^\ominus}} \quad (22)$$

Based on the known equilibrium constant of sulfuric acid generation, the balance relation at the reaction tube outlet is as follows:

$$K_{H_2SO_4(g),T} = \frac{\frac{p_{H_2SO_4(g),outlet}^e}{p^\ominus}}{\frac{p_{SO_3(g),outlet}}{p^\ominus} \cdot \frac{p_{H_2O(g),outlet}}{p^\ominus}}{p^\ominus}} \quad (23)$$

The high-temperature isothermal condensation measuring method requires taking measurement twice at the same temperature, with different raw material composition ratios for each feed. The known variables in the first measurement are the SO₃ partial pressure $p_{SO_3(g),inlet,1}$, NH₃ partial pressure $p_{NH_3(g),inlet,1}$, water vapor partial pressure $p_{H_2O(g),inlet,1}$ and sulfuric acid partial pressure $p_{H_2SO_4(g),inlet,1}^e$ at the reaction inlet.

The measurable items in the first measurement are the amount of ABS $n_{ABS(l),outlet,1}$ and the amount of AS $n_{AS(l),outlet,1}$ collected by the filter.

The remaining unknown items in the first measurement are gaseous ABS saturated partial vapor pressure $p_{ABS,T}^*$ and gaseous AS saturated partial vapor pressure $p_{AS,T}^*$, the SO₃ partial pressure $p_{SO_3(g),outlet,1}$, NH₃ partial pressure $p_{NH_3(g),outlet,1}$, water vapor partial pressure $p_{H_2O(g),outlet,1}$ and sulfuric acid partial pressure $p_{H_2SO_4(g),outlet,1}^e$ at the reaction outlet.

Then, the second measurement will be carried out to obtain more relation equations. The known variables in the second measurement are the SO₃ partial pressure $p_{SO_3(g),inlet,2}$, NH₃ partial pressure $p_{NH_3(g),inlet,2}$, water vapor partial pressure $p_{H_2O(g),inlet,2}$ and sulfuric acid partial pressure $p_{H_2SO_4(g),inlet,2}^e$ at the reaction inlet.

The measurable items in the second measurement are the amount of ABS $n_{ABS(l),outlet,2}$ and the amount of AS $n_{AS(l),outlet,2}$ collected by the filter.

The remaining unknown items in the second measurement are gaseous ABS saturated partial vapor pressure $p_{ABS,T}^*$ and gaseous AS saturated partial vapor pressure $p_{AS,T}^*$, the SO₃ partial pressure $p_{SO(g),outlet,2}$, NH₃ partial pressure $p_{NH(g),outlet,2}$, water vapor partial pressure $p_{H_2O(g),outlet,2}$ and sulfuric acid partial pressure $p_{H_2SO_4(g),outlet,2}^e$ at the reaction outlet.

By substituting the above variables into Eq. (18)-Eq. (23), a total of 12 equations can be obtained from the two measurements. In the two measurements, the equilibrium constant $K_{ABS(g)-Ter,T}$ and $K_{AS(g)-Ter,T}$ are unknown, but they remain unchanged under the same temperature. Since there are exactly a total of 12 unknown variables mentioned above, they can be calculated by solving 12 equations together.

From the above derivation, it can be inferred that when condensed product is generated, the high-temperature isothermal condensation measuring method can distinguish the amount of condensed product precipitated by separating gaseous and condensed product. For cases where the feed concentration is low and there is no condensed product, the calculation cannot be carried out because the filter inside the reaction tube cannot capture the gaseous product. Therefore, the high-temperature isothermal condensation measurement method is suitable for the case of high feed concentration, which can calculate the equilibrium constant K^e on the basis of the coupling equation.

4. Conclusion

The non-contact measurement can be conveniently carried out when at the low concentration feed without generating condensed product condition; When the feed concentration is high and condensed product is generated, it is hardly to obtain the reaction equilibrium constant by non-contact measurement.

The high-temperature isothermal condensation measuring method can distinguish the amount of condensed product precipitated by separating gaseous and condensed product.

So, the high-temperature isothermal condensation measurement method is suitable for the case of high feed concentration, but is not suitable for the case where the feed concentration is low and there is no condensed product.

It is suggested to combine the non-contact measuring method with the high-temperature isothermal condensation measuring method to achieve greater measurement adaptability.

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