



Experimental determination of equilibrium constant for the complexing reaction of nitric oxide with hexamminecobalt(II) in aqueous solution

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ABSTRACT

Ammonia solution can be used to scrub NO from the flue gases by adding soluble cobalt(II) salts into the aqueous ammonia solutions. The hexamminecobalt(II), $\text{Co}(\text{NH}_3)_6^{2+}$, formed by ammonia binding with Co^{2+} is the active constituent of eliminating NO from the flue gas streams. The hexamminecobalt(II) can combine with NO to form a complex. For the development of this process, the data of the equilibrium constants for the coordination between NO and $\text{Co}(\text{NH}_3)_6^{2+}$ over a range of temperature is very important. Therefore, a series of experiments were performed in a bubble column to investigate the chemical equilibrium. The equilibrium constant was determined in the temperature range of 30.0–80.0 °C under atmospheric pressure at pH 9.14. All experimental data fit the following equation well:

$$K_p = (1.9051 \pm 0.124) \times 10^{-6} \exp\left(\frac{5359.25 \pm 280.13}{T}\right) (\text{bar}^{-1})$$

where the enthalpy and entropy are $\Delta H^\circ = -(44.559 \pm 2.329) \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -(109.50 \pm 7.126) \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

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1. Introduction

Removal of NO_x from the flue gases has recently become very important to comply with the strict environmental emission standards and many processes to remove NO_x by liquid absorbents as well as solid-catalyzed reactions have been proposed. SCR (Selective Catalysis of Reduction) of NO by NH_3 is the best-developed and worldwide used technology for controlling NO_x emissions in fuel combustion from stationary sources [1]. Major concerns about SCR are the deleterious effects that SO_2 , dusts, and water vapor present in the flue gas poison the catalyst, which influences the technology's cost [2]. The high overall operating expenses have prompted a search for alternative methods for controlling NO_x emissions.

It has been suggested that a wet scrubbing combined SO_2/NO_x removal system was one of the best technologies [3]. A wet scrubbing system has an advantage of removing NO_x and SO_2 from the flue gases simultaneously [4–6]. The wet FGD (Flue Gas Desulfurization) system has experienced high SO_2 removal efficiencies, but it is not for NO_x because water insoluble NO is 90–95% of the NO_x present in typical flue gas streams. Additives have to be added to

the scrubbing system either to convert relatively insoluble NO to soluble NO_2 that can then be removed by alkaline absorbents or to bind and activate NO. Many treatments have been reported [7–18] but have not yet been commercialized.

Long [19–25] has proposed a novel technique for the simultaneous elimination of NO and SO_2 from the flue gases by adding soluble cobalt(II) salt into the aqueous ammonia solution. The hexamminecobalt(II) ion produced by NH_3 coordinating with Co^{2+} can not only bind NO but also activate the oxygen molecule. Therefore, NO can be absorbed and oxidized sequentially in the hexamminecobalt(II) ammonia solution. NO is converted into nitrate and nitrite. The existing wet ammonia desulfurization process can be retrofitted for combined removal of SO_2 and NO from the flue gases by such technique.

The equilibrium constant for the coordination between NO and $\text{Co}(\text{NH}_3)_6^{2+}$ is vital for the development of this technological process. In this paper, the thermodynamics of the coordination of molecular NO to $\text{Co}(\text{NH}_3)_6^{2+}$ in an aqueous solution is discussed in the temperature range of 30.0–80.0 °C for the integrity of such a useful process.

2. Theoretical

It is well known that aqueous $\text{Co}(\text{NH}_3)_6^{2+}$ solution absorbs NO but the determination of n in the reaction between NO and

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Nomenclature

a	activity
C	concentration in aqueous phase (mol l^{-1})
H_{PC}	Henry's coefficient (bar mol^{-1})
ΔH°	reaction enthalpy (kJ mol^{-1})
K	equilibrium constant ($\text{l}^{1.5} \text{mol}^{-1.5}$)
K_p	modified equilibrium constant ($\text{bar}^{-1.5}$)
n	stoichiometric factor
p	partial pressure (bar)
R	gas constant, $8.314 \text{ kJ (kmol)}^{-1} \text{ K}^{-1}$
ΔS°	reaction entropy ($\text{J K}^{-1} \text{ mol}^{-1}$)
T	absolute temperature (K)

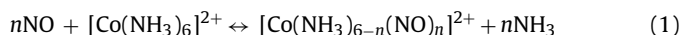
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i component i

Greek symbol

γ^r rational activity coefficient

$\text{Co}(\text{NH}_3)_6^{2+}$ (Eq. (1)) has not been reported in literature.



The thermodynamic equilibrium constant is defined as the following equation:

$$K(T) = \Pi a_i^{v_i} \quad (2)$$

The expression of the equilibrium constant for Eq. (1) can be written as

$$K'(T) = \frac{C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}} C_{\text{NH}_3}^n \gamma_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}^{\gamma} (\gamma_{\text{NH}_3}^{\gamma})^n}{C_{\text{NO}}^n C_{[\text{Co}(\text{NH}_3)_6]^{2+}} (\gamma_{\text{NO}}^{\gamma})^n \gamma_{[\text{Co}(\text{NH}_3)_6]^{2+}}^{\gamma}} \quad (3)$$

Because NH_3 in the solution is sufficient, its concentration can be regarded as invariable when the pH of the solution is maintained constant. So C_{NH_3} in Eq. (3) can be seen as a constant and combined with $K(T)$.

Eq. (3) can be rewritten as

$$K'(T) = \frac{C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}} \gamma_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}^{\gamma}}{C_{\text{NO}}^n C_{[\text{Co}(\text{NH}_3)_6]^{2+}} (\gamma_{\text{NO}}^{\gamma})^n \gamma_{[\text{Co}(\text{NH}_3)_6]^{2+}}^{\gamma}} \quad (4)$$

For diluted ideal solutions, the rational activity coefficient can be neglected, i.e.

$$\gamma_i^r = \frac{a_i}{c_i} = 1 \quad (5)$$

Considering Henry's law, i.e.

$$p_{\text{NO}} = H_{\text{PC}} C_{\text{NO}} \quad (6)$$

The equation for the equilibrium constant has the following form:

$$K(T) = \frac{C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}}{(p_{\text{NO}}^n / H_{\text{PC}}^n C_{[\text{Co}(\text{NH}_3)_6]^{2+}})} = \frac{C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}}{p_{\text{NO}}^n / H_{\text{PC}}^n (C_{[\text{Co}(\text{NH}_3)_6]^{2+}} - C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}})} \quad (7)$$

where $C_{[\text{Co}(\text{NH}_3)_6]^{2+}_0}$ is the initial molar concentration of $\text{Co}(\text{NH}_3)_6^{2+}$, $C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}$ is the equilibrium molar concentration of the NO adduct obtained by graphically integrating

the outlet NO in the tail gas. p_{NO} is the partial pressure of NO in the gas, and H_{PC} is the Henry's constant of NO in water.

The Henry's constant of NO varies considerably with temperature. For practical purposes it may be eliminated by the introduction of the K_p , which is only based on measured variables, i.e.

$$K_p = \frac{K(T)}{H_{\text{PC}}^n} = \frac{C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}}{p_{\text{NO}}^n C_{[\text{Co}(\text{NH}_3)_6]^{2+}}} = \frac{C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}}{p_{\text{NO}}^n [C_{[\text{Co}(\text{NH}_3)_6]^{2+}_0} - C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}]} \quad (8)$$

The equilibrium constant K_p can be calculated from Eq. (8) if $C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}$, $C_{[\text{Co}(\text{NH}_3)_6]^{2+}_0}$ and p_{NO} are obtained.

Eq. (8) can be rewritten as

$$\frac{C_{[\text{Co}(\text{NH}_3)_6]^{2+}_0}}{C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}} - 1 = \frac{1}{p_{\text{NO}}^n K_p} \quad (9)$$

According to Eq. (9), the value of n can be determined from the relation between $1/p_{\text{NO}}$ and $C_{[\text{Co}(\text{NH}_3)_6]^{2+}_0} / C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}} - 1$.

3. Experimental**3.1. Reagents and preparation**

$(\text{NH}_4)_2\text{SO}_4$ (>99%) was obtained from Lingfeng; $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (>99.5%) and ammonia solution (25%) from SCRC; NO (5000 ppm in N_2) and N_2 (>99.99%) from Shanghai Standard Gas Co. Ltd. Deionized water was applied to prepare the solutions.

Firstly, predetermined amounts of $(\text{NH}_4)_2\text{SO}_4$ was dissolved into 150 ml deionized water. Secondly, measured amounts of cobalt sulfate and ammonia were added into the ammonium sulfate solution. $\text{Co}(\text{NH}_3)_6^{2+}$ cation was formed after cobalt sulfate was dissolved into the aqueous solution. Lastly, the solution was diluted with deionized water to the total volume of 250 ml and degassed by evacuating the air over the solution with simultaneous sonification using an ultrasonic cleaner for about 20 min. A pH value of 9.14 was detected with a pH-electrode. For all experiments, 0.013 mol l^{-1} $\text{Co}(\text{NH}_3)_6^{2+}$ aqueous ammonia solutions were used.

3.2. Experimental set-up

Batch experiments were performed in a closed laboratory-scale bubble column of 500 ml to investigate the complexing reaction between NO and hexamminecobalt(II). A schematic diagram of the experiment set-up is shown in Fig. 1. The operation was performed continuously with respect to the gas phase and batchwise to the liquid phase.

3.3. Equilibrium measurements

Equilibrium constants were determined from 30 to 80°C at atmospheric pressure. The temperature was regulated to within $\pm 0.2^\circ\text{C}$ with the use of a jacket through which water from a thermostatic bath was circulated. A $\text{Co}(\text{NH}_3)_6^{2+}$ solution of 250 ml was introduced to the column. A mixture of NO and N_2 with NO concentration ranged from 200 to 800 ppm was bubbled continuously through the solution and the NO concentration in the outlet gas was measured continuously using a gas analyzer (Testo 335, made in Germany) while the inlet concentration was measured via a bypass arrangement beforehand. The gas flow rate was about 700 ml min^{-1} . NO absorption was carried out until equilibrium was reached, i.e. until the NO concentration in the outlet gas became

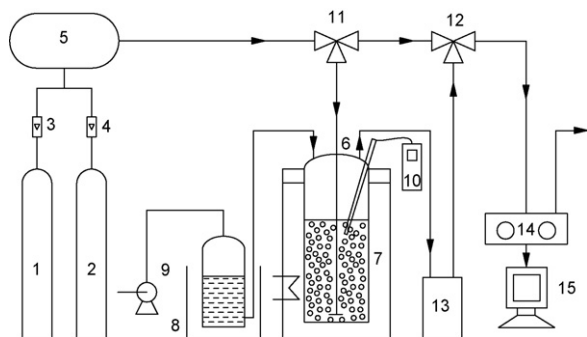
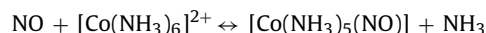


Fig. 1. Schematic diagram of experimental apparatus. 1: NO gas cylinder, 2: N₂ gas cylinder, 3 and 4: mass flow meter, 5: gas mixer, 6: bubble column, 7: water bath, 8: ultrasonic cleaner, 9: pump, 10: pH meter, 11 and 12: triple valve, 13: cooling device, 14: NO analyzer, and 15: computer.

equal to that in the inlet gas. Solubility of NO in water is very low, at about $1.25 \times 10^{-3} \text{ mol l}^{-1} \text{ atm}^{-1}$ at 50 °C. The amount of NO dissolved in the water can be ignored. Therefore, the amount of NO absorbed was determined by graphical integration of the NO concentration in the outlet gas.

4. Results and discussions

A series of experiments have been made to detect the effect of p_{NO} on $C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}}$ at the temperature of 40.0–80.0 °C under atmospheric pressure. A log–log plot of $(C_{[\text{Co}(\text{NH}_3)_6]^{2+}})_0 / C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}} - 1$ vs. $1/p_{\text{NO}}$ from the experiments is shown in Fig. 2. The slope of the lines are 1.01 ± 0.0376 (40.0 °C), 1.08 ± 0.0716 (50.0 °C), 0.99 ± 0.0466 (60.0 °C), 1.10 ± 0.0343 (70.0 °C) and 0.99 ± 0.0491 (80.0 °C), respectively, indicating that the value of n in the reaction shown in Eq. (1) is confirmed to be 1, i.e. the reaction should be:



It is well known that the change in the Gibbs free energy for a reaction is expressed as

$$\Delta G^\circ = -RT \ln K_p \quad (10)$$

Moreover, using the relationship, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, $\ln K_p$ can be expressed in Eq. (11). Thus, if the equilibrium constants for the reaction at different temperatures are known, the standard enthalpic and entropic changes for adsorption can also be estimated

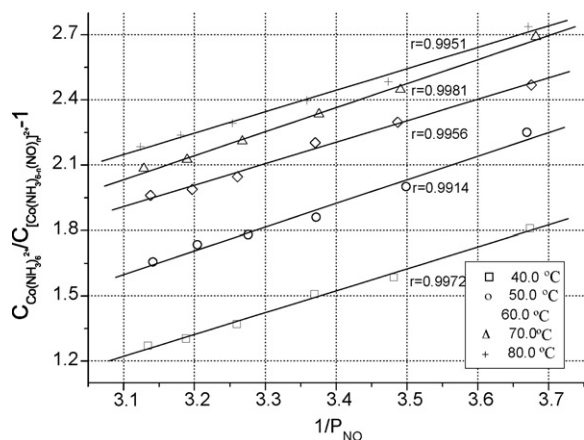


Fig. 2. Log–log plot of $C_{[\text{Co}(\text{NH}_3)_6]^{2+}} / C_{[\text{Co}(\text{NH}_3)_{6-n}(\text{NO})_n]^{2+}} - 1$ vs. $1/p_{\text{NO}}$.

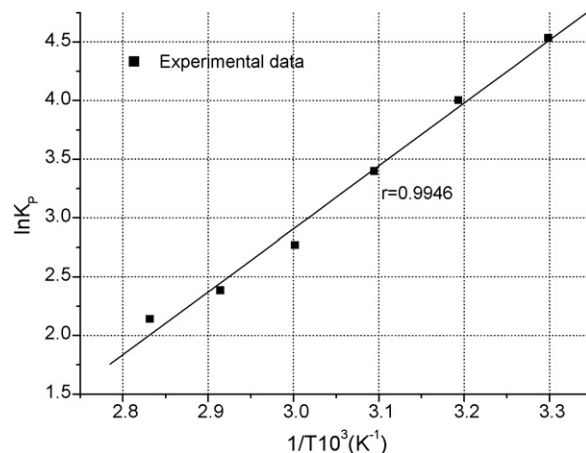


Fig. 3. Van't Hoff plot of equilibrium constants for Eq. (1).

Table 1

Thermodynamic data for reversible NO coordination to cobalt complexes

Temperature (°C)	K_p (bar ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
40.0	51.57		
60.0	18.46	-44.559	-109.50
80.0	7.423		

from the slope and intercept of a linear plot of $\ln K_p$ vs. $1/T$.

$$\ln K_p = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

In terms of Eq. (8), the equilibrium constants K_p for such reaction have been calculated from the experimental results. Fig. 3 represents the Van't Hoff plot of these equilibrium constants. The slope of this plot is $-\Delta H^\circ/R$ and the intercept is $\Delta S^\circ/R$. From the regression of data shown in Fig. 3, the values of K_p obtained in the present work are well correlated by the following equation:

$$\ln K_p = \frac{5359.25}{T} - 13.171 \quad (12)$$

So the expression of K_p , as a function of temperature can be expressed as

$$K_p = (1.9051 \pm 0.1240) \times 10^{-6} \exp\left(\frac{5359.25 \pm 280.1}{T}\right) (\text{bar}^{-1}) \quad (13)$$

Enthalpy and entropy for reaction (1) are $\Delta H^\circ = -(44.559 \pm 2.329) \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -(109.50 \pm 7.126) \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

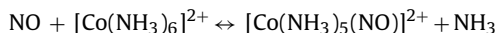
A negative value of ΔH° indicates that the reaction is exothermic in nature and a negative value of ΔG° shows the spontaneous occurrence of the reaction. The binding of gases with metal complexes is characterized by a small negative change in enthalpy and a relatively large change in entropy to compensate for the enthalpy change. This occurs because a gas loses its translational and rotational degree of freedom by coordination. The stability of such reversible complexes is examined by comparing their ΔH° values. The thermodynamic data listed in Table 1 demonstrate that the equilibrium constants decrease with temperature. A high temperature is unfavorable for this complexing reaction.

5. Conclusion

The chemical equilibrium between NO and $\text{Co}(\text{NH}_3)_6^{2+}$ has been studied. The following specific conclusions can be drawn from the

experimental results.

- (1) The equation of the chemical reaction between NO and $\text{Co}(\text{NH}_3)_6^{2+}$ is confirmed as follows:



- (2) The equilibrium constants for the complexing reaction between NO and $\text{Co}(\text{NH}_3)_6^{2+}$ are determined in the temperature range of 30.0–80.0 °C. All experimental data fit the following equation well:

$$K_p = (1.9051 \pm 0.124) \times 10^{-6} \exp\left(\frac{5359.25 \pm 280.13}{T}\right) (\text{bar}^{-1})$$

Temperature is disadvantageous to the complexing reaction between NO and $\text{Co}(\text{NH}_3)_6^{2+}$.

- (3) Thermodynamic parameters such as ΔG° , ΔH° and ΔS° for such reaction have also been obtained from the Van't Hoff plot. A negative value of ΔH° indicates that the reaction is exothermic in nature and negative values of ΔG° show the spontaneous occurrence of the reaction. Negative ΔS° shows the decreased randomness of the coordination reaction system.

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