

# **SUPPORTING INFORMATION (SI)**

## **Determination of Equilibrium Constants for Reactions between Nitric Oxide and Ammoniacal Cobalt(II) Solutions at Temperatures from 298.15 to 309.15 K and pH values between 9.06 and 9.37 under Atmospheric Pressure in a Bubble Column**

*Hesheng Yu<sup>a\*</sup>*

*Zhongchao Tan<sup>a,b,c</sup>*

<sup>a</sup> Department of Mechanical & Mechatronics Engineering

<sup>b</sup> Department of Civil & Environmental Engineering

<sup>c</sup> Waterloo Institute for Sustainable Energy

University of Waterloo

200 University Avenue West, Waterloo, Ontario, Canada N2L 3G1

Phone: (519) 888-4567 ext. 38723; Email: [h48yu@uwaterloo.ca](mailto:h48yu@uwaterloo.ca)

**Table S1.** Step reversible reactions involved in the cobalt (II) – ammonia system

Reaction		$\lg K_n^0$ (n = 1-6)
$Co(H_2O)_6^{2+} + NH_3 \rightleftharpoons Co(NH_3)(H_2O)_5^{2+} + H_2O$	S1	1.99
$Co(NH_3)(H_2O)_5^{2+} + NH_3 \rightleftharpoons Co(NH_3)_2(H_2O)_4^{2+} + H_2O$	S2	1.51
$Co(NH_3)_2(H_2O)_4^{2+} + NH_3 \rightleftharpoons Co(NH_3)_3(H_2O)_3^{2+} + H_2O$	S3	0.93
$Co(NH_3)_3(H_2O)_3^{2+} + NH_3 \rightleftharpoons Co(NH_3)_4(H_2O)_2^{2+} + H_2O$	S4	0.64
$Co(NH_3)_4(H_2O)_2^{2+} + NH_3 \rightleftharpoons Co(NH_3)_5(H_2O)^{2+} + H_2O$	S5	0.06
$Co(NH_3)_5(H_2O)^{2+} + NH_3 \rightleftharpoons Co(NH_3)_6^{2+} + H_2O$	S6	-0.74

**Table S2.** Equilibrium constants at NO = 605 ppm,  $\text{NH}_4\text{NO}_3 = 2 \text{ mol}\cdot\text{L}^{-1}$ ,  $\text{A}=\text{NH}_3$  based  
on ammonia-cobalt(II) analysis

T K	$[\text{Co}]_{\text{T}}$ $\text{mol}\cdot\text{L}^{-1}$	pH	$[\text{NH}_3]$ $\text{mol}\cdot\text{L}^{-1}$	$[\text{CoA}_5\text{N}_2\text{O}_2\text{A}_5\text{Co}^{4+}]$ $\text{mol}\cdot\text{L}^{-1}$	$[\text{CoA}_5^{2+}]$ $\text{mol}\cdot\text{L}^{-1}$	$[\text{CoA}_6^{2+}]$ $\text{mmol}\cdot\text{L}^{-1}$	$a_w$	$K_6$	$10^{-12}$ $K_{\text{NO}}^5$	$10^{-13}$ $K_{\text{NO}}^6$
298.15	0.04	9.35	1.39	1.15E-03	0.0204	7.72	0.98	0.26	3.87	5.89
		9.23	1.06	8.31E-04	0.0198	5.58	0.98		3.01	4.57
	0.05	9.06	0.71	8.98E-04	0.0212	3.89	1.00		2.96	4.50
		9.21	1.01	1.36E-03	0.0241	6.46	0.98		3.37	5.12
304.15	0.04	9.17	1.51	7.21E-04	0.0209	8.03	0.98	0.24	2.78	4.86
		9.21	1.65	6.99E-04	0.0210	8.86	0.98		2.68	4.68
	0.05	9.20	1.61	1.01E-03	0.0261	10.82	0.98		2.53	4.41
309.15	0.04	9.16	2.22	4.99E-04	0.0209	11.77	0.97	0.23	2.19	4.28
	0.05	9.17	2.27	7.17E-04	0.0259	15.02	0.96		2.06	4.03
		9.37	3.59	5.93E-04	0.0222	23.06	0.93		2.15	4.22

**Table S3.** Detailed solution system for each experimental run in **Table S2**

Run	T	V <sub>L</sub>	NH <sub>4</sub> NO <sub>3</sub>	Co(NO <sub>3</sub> ) <sub>2</sub>	ρ	[Co] <sub>T</sub>	pH	[NH <sub>3</sub> ]	a <sub>w</sub>	f <sub>NH3</sub>	[NO] <sub>phy</sub>	[NO] <sub>chem</sub>
	K	mL	g	g	kg·m <sup>-3</sup>	mol·L <sup>-1</sup>		mol·L <sup>-1</sup>			mol·L <sup>-1</sup>	mol·L <sup>-1</sup>
1	298.15	300	48.04	3.4928	1171.78	0.04	9.35	1.39	0.98	1.04	8.25E-07	2.29E-03
2			48.04	3.4937	1171.78		9.23	1.06	0.98	1.02	8.25E-07	1.66E-03
3			48.04	4.3619	1174.67	0.05	9.06	0.71	1	1.00	8.20E-07	1.80E-03
4			48.02	4.364	1174.61		9.21	1.01	0.98	1.02	8.20E-07	2.72E-03
5	304.15		48.03	3.4936	1171.75	0.04	9.17	1.51	0.98	1.04	7.52E-07	1.44E-03
6			48.02	3.4961	1171.72		9.21	1.65	0.98	1.05	7.52E-07	1.40E-03
7			48.03	4.363	1174.64	0.05	9.20	1.61	0.98	1.05	7.47E-07	2.02E-03
8	309.15		48.03	3.492	1171.74	0.04	9.16	2.22	0.97	1.09	6.98E-07	9.98E-04
9			48.03	4.3683	1174.66	0.05	9.17	2.27	0.96	1.09	6.94E-07	1.43E-03
10			48.01	4.3667	1174.59		9.37	3.59	0.93	1.19	6.94E-07	1.19E-03

**Table S3.** Detailed solution system for each experimental run in **Table S2 (continued)**

Run	$[\text{CoA}_5\text{N}_2\text{O}_2\text{A}_5\text{Co}^{4+}]$	$[\text{CoA}_6^{2+}]$	$[\text{CoA}_5^{2+}]$	$[\text{CoA}_4^{2+}]$	$[\text{CoA}_3^{2+}]$	$[\text{CoA}_2^{2+}]$	$[\text{CoA}^{2+}]$	$[\text{Co}^{2+}]$
	$\text{mol}\cdot\text{L}^{-1}$	$\text{mmol}\cdot\text{L}^{-1}$	$\text{mol}\cdot\text{L}^{-1}$	$\text{mmol}\cdot\text{L}^{-1}$	$\text{mmol}\cdot\text{L}^{-1}$	$\text{mmol}\cdot\text{L}^{-1}$	$\text{mmol}\cdot\text{L}^{-1}$	$\text{mmol}\cdot\text{L}^{-1}$
1	1.15E-03	7.72	0.0204	8.56	0.94	0.05	0.00	0.00
2	8.31E-04	5.58	0.0198	11.17	1.66	0.13	0.00	0.00
3	8.98E-04	3.89	0.0212	18.36	4.18	0.49	0.01	0.00
4	1.36E-03	6.46	0.0241	14.28	2.22	0.18	0.00	0.00
5	7.21E-04	8.03	0.0209	8.63	0.94	0.05	0.00	0.00
6	6.99E-04	8.86	0.0210	7.92	0.78	0.04	0.00	0.00
7	1.01E-03	10.82	0.0261	9.98	1.00	0.05	0.00	0.00
8	4.99E-04	11.77	0.0209	5.88	0.43	0.02	0.00	0.00
9	7.17E-04	15.02	0.0259	7.10	0.51	0.02	0.00	0.00
10	5.93E-04	23.06	0.0222	3.40	0.14	0.00	0.00	0.00

## ANALYSIS OF COBALT(II) – AMMONIA SYSTEM

### Before The Introduction of Nitric Oxide

The analysis of the absorbent system before the introduction of nitric oxide is beneficial to the determination of pH value. Based on the equilibria shown in Table S1, the following equations can be given:

$$K_1 = \frac{[Co(NH_3)(H_2O)_5^{2+}]}{[Co(H_2O)_6^{2+}][NH_3]} \cdot \frac{a_w}{f_{NH_3}} \quad S7$$

$$K_2 = \frac{[Co(NH_3)_2(H_2O)_4^{2+}]}{[Co(NH_3)(H_2O)_5^{2+}][NH_3]} \cdot \frac{a_w}{f_{NH_3}} \quad S8$$

$$K_3 = \frac{[Co(NH_3)_3(H_2O)_3^{2+}]}{[Co(NH_3)_2(H_2O)_4^{2+}][NH_3]} \cdot \frac{a_w}{f_{NH_3}} \quad S9$$

$$K_4 = \frac{[Co(NH_3)_4(H_2O)_2^{2+}]}{[Co(NH_3)_3(H_2O)_3^{2+}][NH_3]} \cdot \frac{a_w}{f_{NH_3}} \quad S10$$

$$K_5 = \frac{[Co(NH_3)_5H_2O^{2+}]}{[Co(NH_3)_4(H_2O)_2^{2+}][NH_3]} \cdot \frac{a_w}{f_{NH_3}} \quad S11$$

$$K_6 = \frac{[Co(NH_3)_6^{2+}]}{[Co(NH_3)_5H_2O^{2+}][NH_3]} \cdot \frac{a_w}{f_{NH_3}} \quad S12$$

The concentration of hydrogen ion is described by the pH value measured by an Oakton pH meter,

$$[H^+] = 10^{-pH} \quad S13$$

In the  $NH_4^+/NH_3H_2O$  buffer solution in our study,  $[NH_4^+]$  is constantly  $2 \text{ mol}\cdot\text{L}^{-1}$ . Thus, the concentration of free ammonia in the solution can be given by further transformation of Eq. 3 as below,

$$[NH_3] = \frac{k_{NH_4^+} \cdot [NH_4^+]}{[H^+]} \quad S14$$

Bjerrum<sup>16</sup> provided values for 2 mol·L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> solution at 295.15 and 303.15 K, respectively. Therefore, values in or close to this interval can be evaluated by interpolation.

Water activity,  $a_w$ , is a measure of the energy status of the water in a system. It can be assumed unity in 2 mol·L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> solution at low ammonia concentration (smaller than 1 mol·L<sup>-1</sup>). Nevertheless, assuming  $a_w$  equal to unity will lead to erroneous results at higher ammonia concentrations<sup>16, 18</sup>. The activity of free ammonia is presented in terms of activity coefficient in Eq. 10. One way to estimate the values of water activity and activity coefficient of free ammonia is interpolation according to ten sets of experimental data obtained between 1.01 and 10.57 mol·L<sup>-1</sup> of free ammonia in 2 mol·L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub><sup>16</sup>. These available experimental data correspond to our experimental conditions; the interpolated values are deemed more straightforward.

With known  $[NH_3]$ ,  $a_w$  and  $f_{NH_3}$ , the respective concentration of various ammoniacal cobalt(II) complexes can be described in terms of  $[Co(H_2O)_6^{2+}]$  from Eqs. S1 - S6. According to mass balance,

$$[Co^{2+}]_T = [Co(H_2O)_6^{2+}] + \sum_{i=1}^6 [Co(NH_3)_i(H_2O)_{6-i}^{2+}] \quad S15$$

Therefore, the concentration of  $Co(H_2O)_6^{2+}$  is solved, followed by the knowledge of each complex concentration. Accordingly, the cobalt(II) – ammonia system is known.

#### **After The Introduction of Nitric Oxide**

After the introduction nitric oxide into the absorbent system, two more equilibria, as shown in Reactions 5 and 6, exist apart from those tabulated in Table S1. In order to determine the concentrations of various cobalt(II) compounds, the equilibrium concentration of  $(NH_3)_5Co(N_2O_2)Co(NH_3)_5^{4+}$  is required. The specific calculation scheme for this concentration can be referred to Eqs. 22 – 25. Then conservation of mass gives,

$$[Co^{2+}]_T = [Co(H_2O)_6^{2+}] + \sum_{i=1}^6 [Co(NH_3)_i(H_2O)_{6-i}^{2+}] + 2[(NH_3)_5Co(N_2O_2)Co(NH_3)_5^{4+}]_e \quad S16$$

Since the temperature and ammonium nitrate concentration remain unchanged before and after the introduction of nitric oxide, the identical values of parameters such as  $K_n$  ( $n=1 - 6$ ) are used. Following the same method elaborated in the last section, the knowledge of cobalt(II) – ammonia system after NO introduction is obtained.

#### References:

- (16) Bjerrum J. *Metal ammine formation in aqueous solution*; P. Haase and Son: Copenhagen, 1957.
- (18) Simplicio, J.; Wilkins, R.G. Uptake of Oxygen by Ammoniacal Cobalt(II) Solutions. *J. Am. Chem. Soc.* **1969**, 91, 1325-1329.