

KINETICS OF CARBON MONOXIDE ABSORPTION IN CUPROUS AMMONIACAL CHLORIDE SOLUTIONS

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ABSTRACT

The kinetics of carbon monoxide absorption into aqueous cuprous ammoniacal chloride solutions has been investigated. A stirred cell of 98 mm diameter with flat interface was used to study the kinetics. The partial pressure of carbon monoxide was varied in the range of 2×10^3 to 1.01×10^5 N/m². The concentration of cuprous ammoniacal chloride was varied in the range of 0.32–2.4 kmol/m³. The value of rate constant has been reported at 30° C.

INTRODUCTION

CARBON monoxide is a key raw material for the synthesis of several chemical products¹. The separation of carbon monoxide from gas mixtures is necessary for an effective usage of carbon monoxide in the production of variety of chemicals. For the rational design of absorption equipment it is desirable to know the kinetics of reaction between carbon monoxide and a suitable chemical solvent. This information is not available in the published literature.

Cuprous ammoniacal chloride was selected for a preliminary study of the complexing reaction of carbon monoxide with various cuprous salts. It is known that cuprous ammoniacal chloride solutions are corrosive and are not used in commercial practice. However, such a study might provide some insight into the reactions of carbon monoxide with a variety of cuprous ammoniacal salts. Theory of mass transfer with chemical reaction was used to discern the kinetics. The details pertaining to the chemical method have been described in detail by Doraiswamy and Sharma².

EXPERIMENTAL

A standard stirred cell, the design of which was similar to that used by Sharma and Danckwerts³, (98 mm i.d. and 1 lit capacity) was used. The gas-liquid interfacial area was 70 cm². A vertical

cruciform stirrer with four flat blades of 80 mm diameter intersected the gas liquid interface. The liquid volume in all the experiments was 660 cm³.

Schematic flow sheet of experimental set-up is shown in figure 1. The (CO-N₂) gas flow rate was measured using calibrated rotameter or soap film meter. The change in the reactant concentration was negligible (less than 2%) during the experimental run. Thus the liquid reactant concentration was taken equal to initial concentration. Inlet and outlet gases were analysed for carbon monoxide using gas chromatography (the packing material was 13X molecular sieve). Liquid reactant solution was analysed for cuprous and

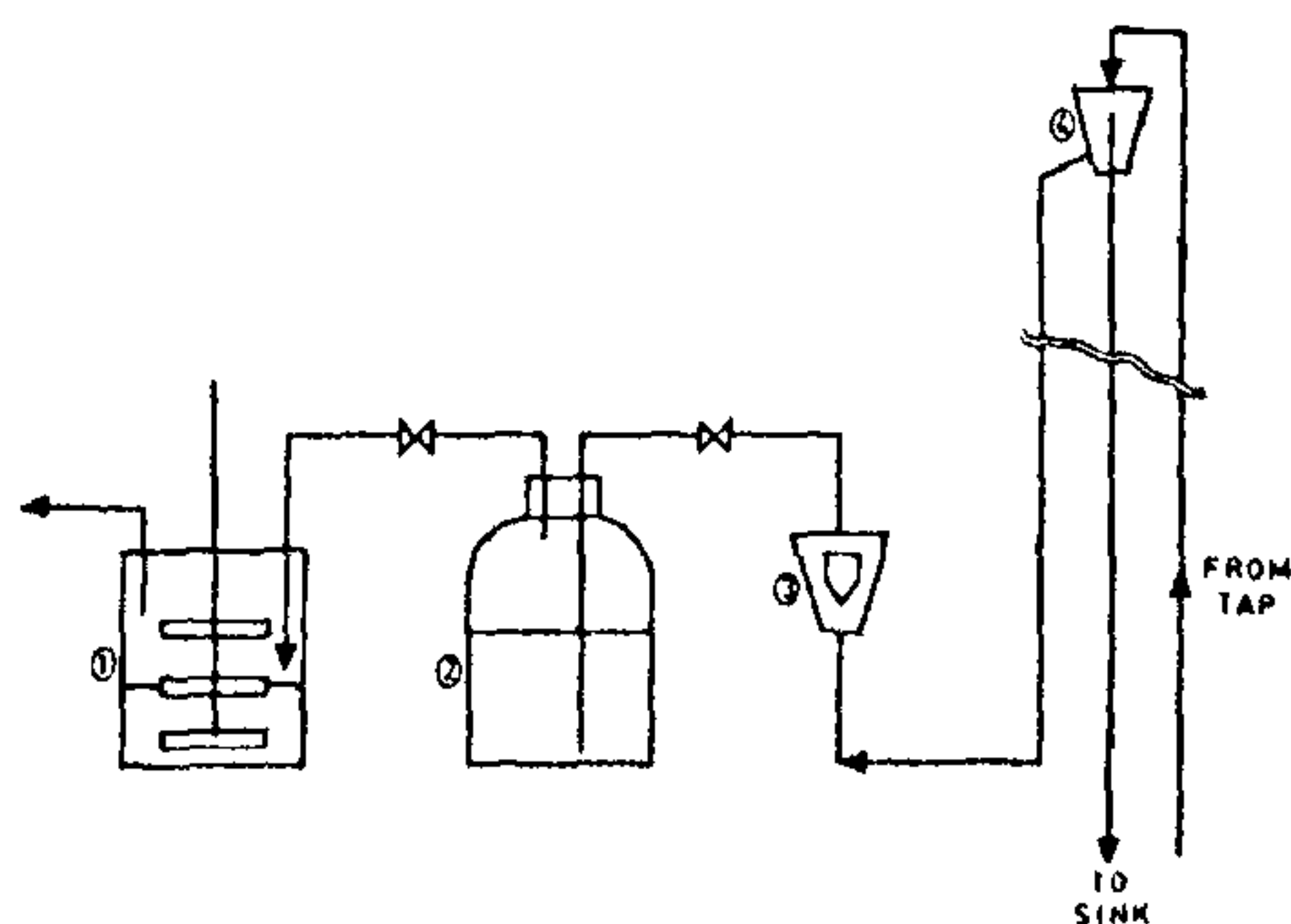
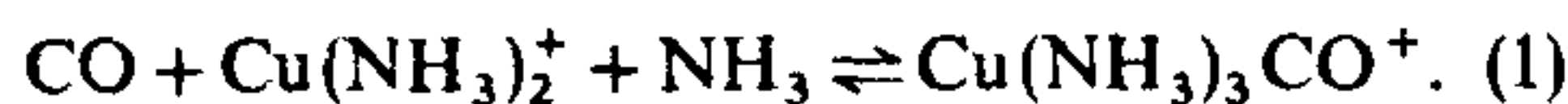


Figure 1. Experimental set-up. 1—Stirred cell. 2—Reservoir for CO-N₂ mixture. 3—Rotameter. 4—Constant head device.

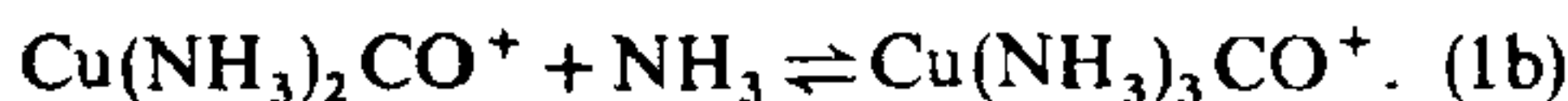
cupric concentrations. The solubility of carbon monoxide in aqueous cuprous ammoniacal chloride was estimated using the solubility reduction parameter proposed by van Krevelen and Hoftijzer⁴. The temperature in all the experiments was $29 \pm 0.5^\circ\text{C}$.

THEORY

van Krevelen and Baans⁵ studied the reaction between carbon monoxide and cuprous ammoniacal salts. The reaction is represented by the following overall stoichiometric equation:

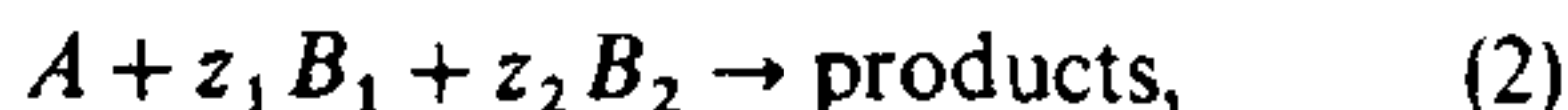


Equation (1) is the combination of the following two equations:



van Krevelen and Baans⁵ showed that (1) represents the overall reaction when the ammonia concentration is larger than 1×10^{-3} kmol/m³. At high ammonia concentrations, (1b) is sufficiently fast and the overall reaction can be represented by (1). In the present work, the ammonia concentration was in the range of 0.88–2.57 kmol/m³ which is much higher than that indicated by van Krevelen and Baans⁵.

The reaction given by (1) is reversible. However, in the present work, the forward reaction was carried out to a maximum of 2%. Therefore, the backward reaction can be neglected. Further, it can be seen that one gas species (CO) reacts with two liquid phase reactants namely $\text{Cu}(\text{NH}_3)_2^+$ and the free ammonia. Doraiswamy and Sharma² discussed the theory of absorption accompanied by a reaction where two liquid phase reactants are involved. A generalised reaction can be written as follows:



where A is the gaseous species and B_1, B_2 are liquid phase reactants. When the following conditions are satisfied:

$$\sqrt{M} = \frac{\left(\frac{2}{1+1} D_A k_{lmn} [A^*]^{1-1} [B_{10}]^m [B_{20}]^n \right)^{\frac{1}{2}}}{k_L} > 3 \quad (3)$$

$$\sqrt{M} > [(B_{10})/z_1(A^*)] = q_1, \quad (4)$$

$$\sqrt{M} > [(B_{20})/z_2(A^*)] = q_2. \quad (5)$$

Also, if the gas side resistance is negligible (shown later), the overall rate of absorption of CO is given by the following equation:

$$R_A a = a \left(\frac{2}{1+1} D_A k_{lmn} [A^*]^{1+1} [B_{10}]^m [B_{20}]^n \right)^{\frac{1}{2}} \quad (6)$$

The validity of conditions given by expressions (3)–(5) will be shown later.

The absorption of carbon monoxide was carried out in a standard stirred cell. The stirrer speeds were 0.417, 0.967 and 1.583 rev/sec. In this range there was practically no effect of stirrer speed on the absorption rate (figure 2), which indicates that the gas side mass transfer resistance does not prevail in the range of conditions covered in this work.

RESULTS AND DISCUSSION

When the concentrations of $\text{Cu}(\text{NH}_3)_2^+$ and the free ammonia are kept constant, it can be seen from (6) that the overall absorption rate depends

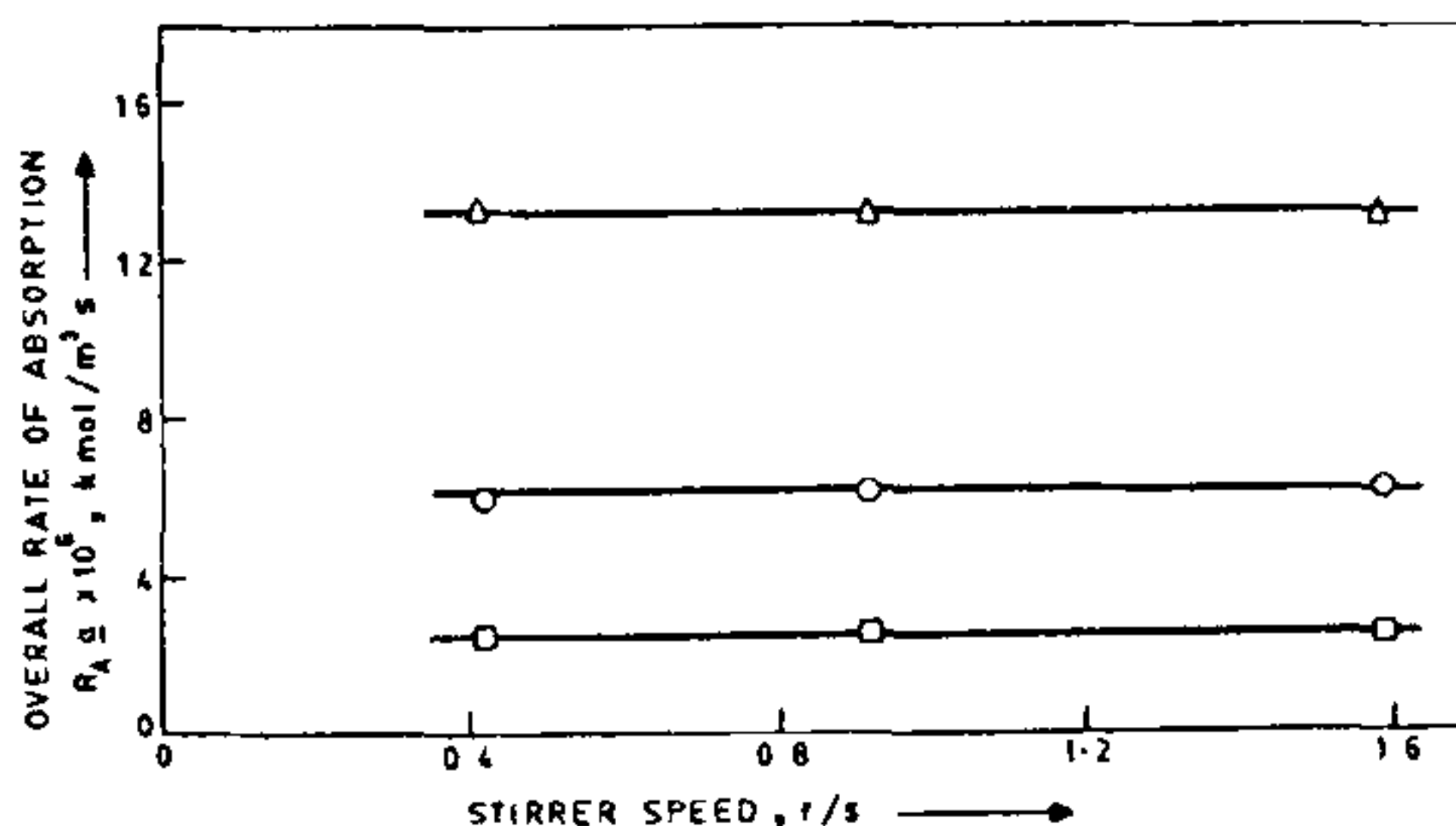


Figure 2. Effect of stirrer speed on carbon monoxide absorption. System: Carbon monoxide-cuprous ammoniacal chloride. □ 0.7203 kmol/m³, ○ 0.6790 kmol/m³, Δ 0.6818 kmol/m³.

upon the partial pressure of carbon monoxide. Equation (6) takes the following form:

$$R_A a = C_1 p_G^{(l+1)/2}, \quad (7)$$

where the constant C_1 is given by:

$$C_1 = a H^{(l+1)/2} \left(\frac{2}{l+1} D_A k_{lmn} \times [B_{10}]^m [B_{20}]^n \right)^{1/2}. \quad (8)$$

In order to find the value of l , $[B_{10}]$ and $[B_{20}]$ were maintained constant at the levels of 0.7 kmol/m^3 and 2.5 kmol/m^3 respectively. The partial pressure of carbon monoxide was varied in the range of $1682\text{--}8886 \text{ Pa}$ (more than five-fold variation). It can be seen from figure 3 that the overall absorption rate varies linearly with CO partial pressure or the order with respect to CO is one or the value of l is one.

Similarly, the order with respect to free ammonia (B_2) can also be found out. For this purpose, the concentration of $\text{Cu}(\text{NH}_3)_2^+$ and the

partial pressure of CO were maintained constant and the concentration of free ammonia was varied in the range of $0.88\text{--}2.57 \text{ kmol/m}^3$. It was found that the order with respect to free ammonia was one or n equals one.

In order to find the dependence of $\text{Cu}(\text{NH}_3)_2^+$ concentration on the absorption rate, the concentration was varied in the range of 0.322 to 2.413 kmol/m^3 (table 1). Equation (6) can be written in the following form ($l = 1, n = 1$):

$$\frac{R_A a}{H p_G ([B_{20}])^{1/2}} = C_2 [B_{10}]^{m/2}, \quad (9)$$

where

$$C_2 = a (D_A k_{lmn})^{1/2}. \quad (10)$$

It was assumed that the gas phase is completely back-mixed. Therefore, p_G in (9) corresponds to the outlet partial pressure. From (10), it can be seen that the liquid phase diffusivity of CO has been assumed to be constant. It is known that the diffusivity depends upon the liquid viscosity. van Krevelen and Baans⁵ showed that the viscosity of cuprous ammoniacal chloride solutions is practically constant over the ionic strength range of $0.66\text{--}2.5 \text{ kions/m}^3$, (most of the experiments in the present work were performed in this range of ionic strength). The value of effective interfacial area for the stirred cell used in this work was $10.6 \text{ m}^2/\text{m}^3$.

The experimental results reported in table 2 have been plotted according to (9) in figure 4. The value of m was found from the slope which works out to be two. Therefore, the order with respect to $\text{Cu}(\text{NH}_3)_2^+$ is two.

Now, let us see whether the conditions given by expressions³⁻⁵ are satisfied. In the case of a stirred cell, the value of k_L is in the range² of $3 \times 10^{-5}\text{--}1 \times 10^{-4} \text{ m/sec}$. This range of k_L was obtained by using similar stirred cell and the stirrer speed in the range of 0.3 to 2 rev/sec . In the present work, the stirrer speed was in the range of 0.5 to 1.5 rev/sec . Therefore, the hydrodynamic conditions in the present work are within the range of hydrodynamic conditions under which the value of k_L were obtained. Further, the value of k_L varies as square root of diffusivity⁶. Doraiswamy and Sharma² reported k_L values for

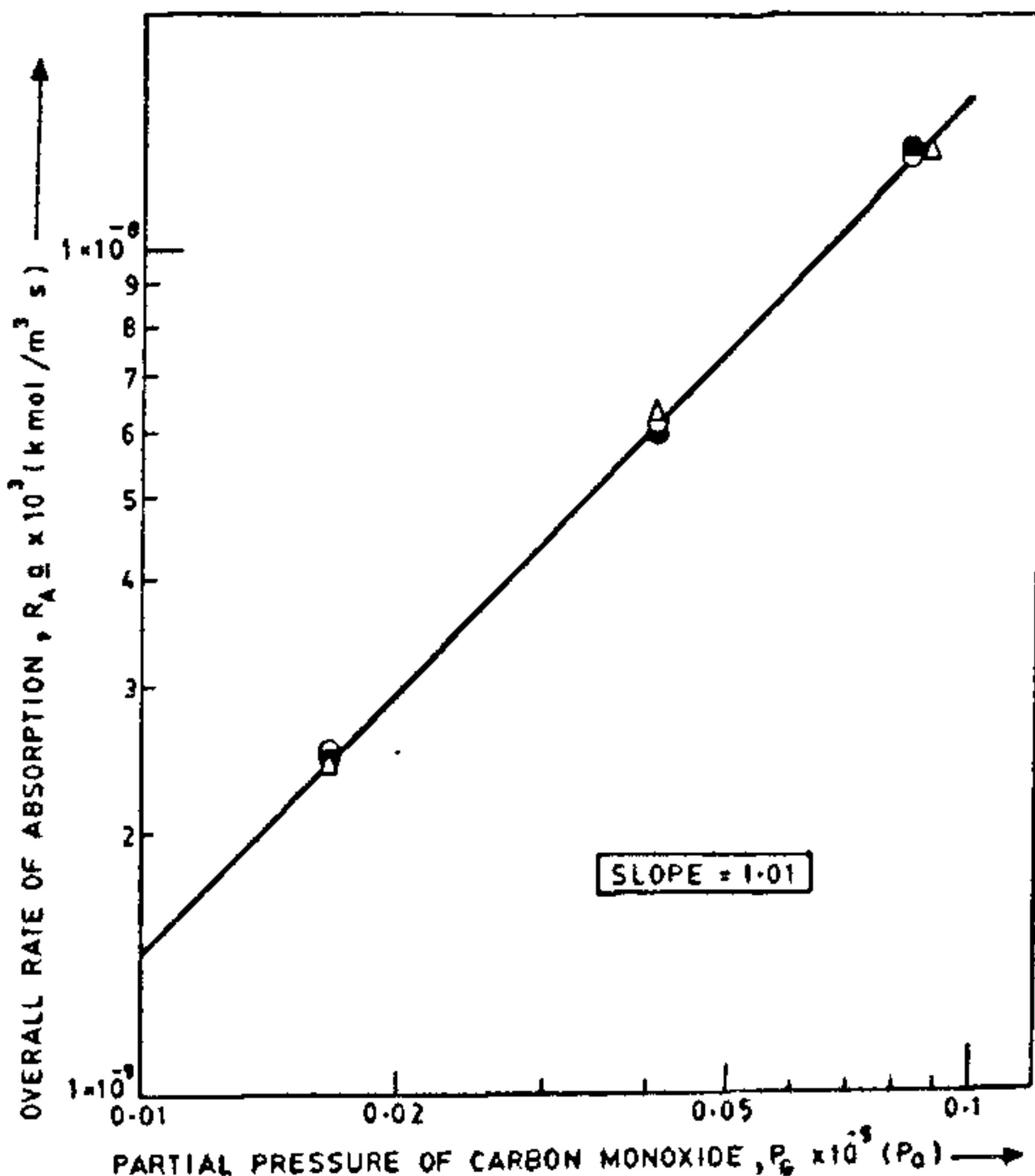


Figure 3. Reaction order with respect to carbon monoxide. System: Carbon monoxide-cuprous ammoniacal chloride. ● 0.417 rev/sec, ○ 0.917 rev/sec, Δ 1.583 rev/sec.

Table 1 Composition of aqueous cuprous ammoniacal chloride solution

Composition in kmol/m ³					Ionic strength kion/m ³
Cu(NH ₃) ₂ ⁺	Cu(NH ₃) ₄ ²⁺	NH ₄ ⁺	CL ⁻	Free NH ₃	
0.322	0.013	0.190	0.538	0.465	0.552
0.620	0.029	0.242	0.920	0.878	0.949
1.294	0.048	0.337	1.727	1.639	1.775
2.413	0.182	0.525	3.302	3.068	3.484

Table 2 Experimental results

No.	Concentration kmol/m ³		Partial pressure of carbon monoxide, Pa			H × 10 ⁹ kmol m ³ .Pa	R _A a × 10 ⁶ kmol m ³ .s
	Cu(NH ₃) ₂ ⁺ [B ₁₀]	Free ammonia [B ₂₀]	In	Out	log mean		
1.1	0.322	0.465	10906	9180	10018	7.87	2.068
1.2	0.620	0.878	10748	8369	9509	7.10	3.762
1.3	1.294	1.639	10858	7336	8982	5.72	4.791
1.4	2.413	3.068	10908	4580	7292	3.66	8.042
2.1	0.620	0.878	10676	7822	9175	7.10	4.544
2.2	1.294	1.639	10517	6059	8064	5.72	6.844
2.3	2.413	3.068	10750	3627	6556	3.66	8.994
3.1	0.322	0.465	10685	8836	9731	7.87	2.426
3.2	0.620	0.878	10550	7579	8983	7.10	4.871
3.3	1.294	1.639	10901	5279	7753	5.72	8.171
3.4	2.413	3.068	10372	2959	5910	3.66	8.891

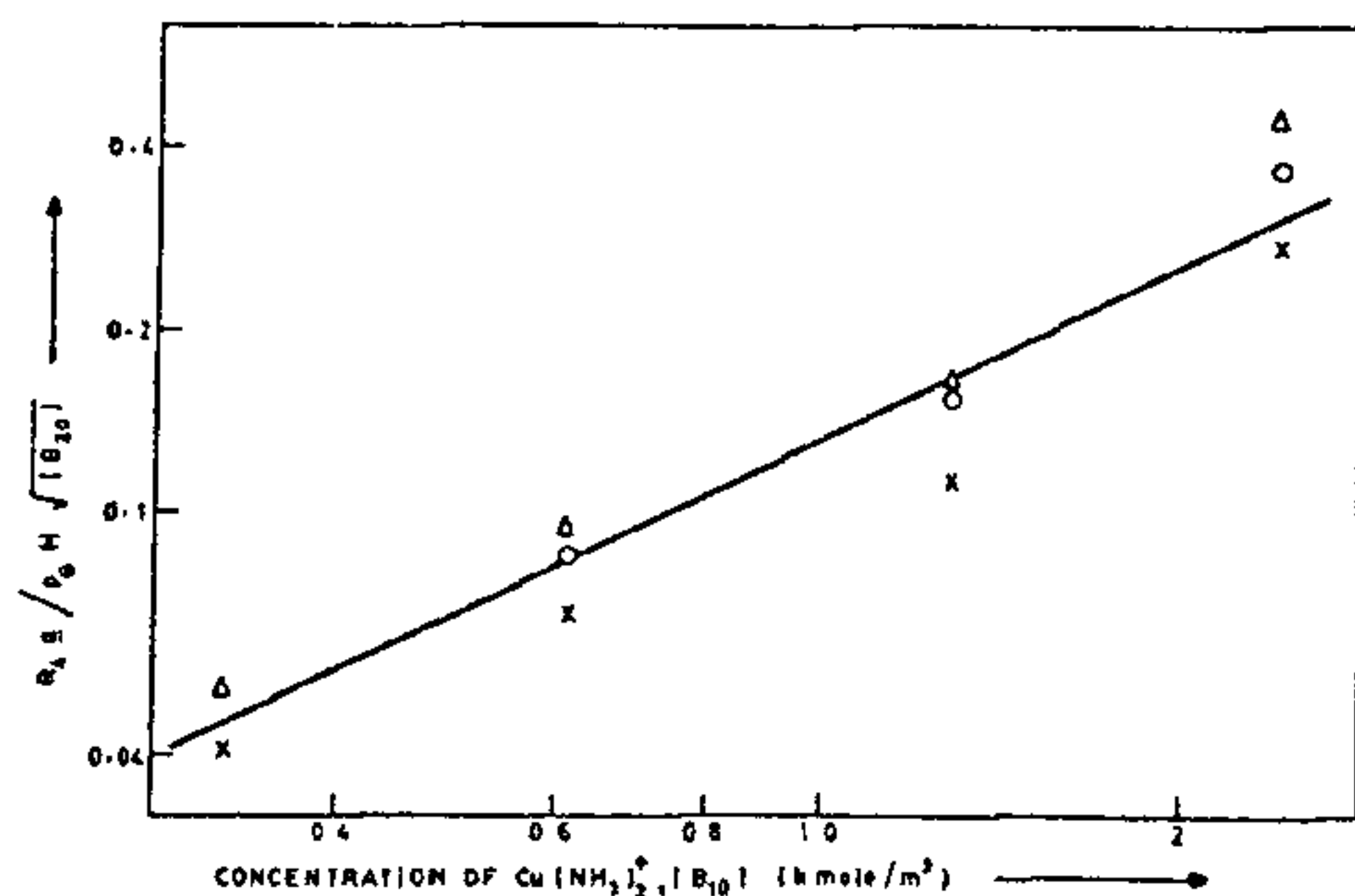


Figure 4. Reaction order with respect to liquid phase reactant. System: Carbon monoxide-cuprous ammoniacal chloride. X 0.417 rev/sec, O 0.967 rev/sec, Δ 1.567 rev/sec.

the system: lean CO₂ – NaHCO₃ + Na₂CO₃. In addition, the following relationship holds upto liquid viscosity of 5 mPa.s:

$$D\mu/T = \text{constant}, \quad (11)$$

where D is the diffusivity, μ is the liquid viscosity and T is absolute temperature.

The diffusivity of carbon dioxide in water at 25°C is 1.96×10^{-9} m²/sec and that of carbon monoxide in water is 2.5×10^{-9} m²/sec. When the liquid viscosities are substituted in (11) the following range of diffusivity ratio was obtained:

$$D_{\text{CO}}/D_{\text{CO}_2} = 0.8 \text{ to } 1.2. \quad (12)$$

From the above discussion it can be seen that the value of k_L for the stirred cell used in this work lies in the range of $3 \times 10^{-5} - 2 \times 10^{-4}$ m/s.

Table 3 Validity of conditions given by expressions (3)–(5)

B_{10} kmol/m ³	B_{20} kmol/m ³	Range of \sqrt{M}	q_1	q_2
0.322	0.465	27–90	35,000	50,500
2.413	3.068	450–1500	5.3×10^5	6.7×10^5

Further, it may be emphasised that the conditions for (3) are satisfied even for the k_L range of $5 \times 10^{-6} - 1 \times 10^{-3}$. From table 3 it can be seen that the necessary conditions are satisfied. It can also be shown that the necessary conditions are satisfied even if the value of k_L is as low as 5×10^{-6} m/s.

From figure 4 the value of $(D_A k_{lmn})^{1/2}$ works out to be 0.0125.

CONCLUSIONS

The reaction of carbon monoxide with cuprous ammoniacal chloride was found to be first order with respect to carbon monoxide, first order with respect to free ammonia and second order with respect to cuprous ammoniacal species. The value of rate constant at 29°C has been reported.

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NOTATION

a	effective gas-liquid interfacial area (m ² /m ³)
$[A^*]$	concentration of carbon monoxide at interface in equilibrium with gas at interface (kmol/m ³)
$[B_{10}]$	bulk concentration of $\text{Cu}(\text{NH}_3)_2^+$
$[B_{20}]$	bulk concentration of free ammonia
D_A	diffusivity of carbon monoxide in liquid (m ² /sec)

H	solubility of carbon monoxide in aqueous cuprous ammoniacal chloride solution (kmol/m ³ Pa)
k_{lmn}	rate constant for reaction; l th order in solute gas, m th order in $\text{Cu}(\text{NH}_3)_2^+$, n th order in free ammonia (kmol/m ³) ^{$l-m-n$} sec ⁻¹
k_G	true gas-side mass transfer coefficient (kmol/m ² s Pa)
k_L	true liquid-side mass transfer coefficient in the absence of reaction (m/sec)
l	order of reaction with respect to solute gas
m	order of reaction with respect to $\text{Cu}(\text{NH}_3)_2^+$
n	order of reaction with respect to free ammonia
p_G	partial pressure of solute gas in bulk gas (Pa)
R_A	average rate of absorption of carbon monoxide per unit interfacial area (kmol/m ² sec)
z_1, z_2	stoichiometric coefficients for the reaction represented by equation (2)

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