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Rate of absorption and interfacial area of chlorine into aqueous sodium hydroxide system

K. S. Agrawal

Department of Chemical Engineering, Faculty of Technology and Engineering,
The M. S. University of Baroda, Vadodara, Gujarat, India.

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Due to excellent mass transfer characteristics with energy efficiency jet ejectors can be used in place of conventional countercurrent systems, namely, packed bed contactors as well as venturi scrubbers, cyclones and airlift pumps. The removal of chlorine from certain gases by absorption in aqueous solutions of sodium hydroxide is industrially important in several chemical processes particularly in pollution control. Although, a number of papers have been published in the past, none of them provided a theoretical basis for the prediction of rate of absorption of chlorine from certain gases by absorption in aqueous solutions of sodium hydroxide in jet ejector. In this work, the rates of absorption of chlorine from different concentration of gas into aqueous sodium hydroxide solutions of various concentrations were measured at 30°C using a liquid jet ejector. The experimental results were analyzed on the basis of the penetration theory for gas absorption. The theoretical model to calculate rate of absorption is developed. The rate of absorption predicted from developed model is compared with experimental results. They were in good agreement. In this work, an attempt also has been made to develop mathematical model to estimate enhancement factor for jet ejector applying Higbie penetration theory.

Key words: Higbie penetration theory, jet ejector, chlorine, aqueous solutions, gases.

INTRODUCTION

There has been different reaction systems used to remove chlorine from gas. The commonly used systems are chlorine-water, chlorine-aqueous solution of alkaline carbonate, chlorine-aqueous alkaline hydroxide solution, chlorine- aqueous sulfite/bisulfite etc. The most commonly used system for chlorine removal is chlorine-aqueous sodium hydroxide solution.

Table 1 shows the summary of the rate constant developed by different researchers for absorption of chlorine in NaOH. Ashour et al. (1996) studied the absorption of Cl_2 into aqueous bicarbonate and aqueous hydroxide solutions both experimentally and theoretically. They estimated the reaction rate coefficient of reaction between Cl_2 and OH^- over the temperature range of 293 to 312 K and fitted by the Arrhenius equation:

$$k_2 = 3.56 \times 10^{11} \exp\left(\frac{-1{,}617}{T}\right) \qquad (1)$$

Table 1 indicates that there is variation in the value of the forward reaction rate coefficient of absorption between Cl_2 into aqueous solutions of NaOH from 10^7 to 10^{14}. Attempt has been made to develop the co-relation to predict k_2 on the basis of our experimental results.

Email: ksamsuce@gmail.com.

Table 1. The values of rate constant for Cl_2 - NaOH reaction system.

Author	Rate constant	Temperature (K)
Morris (1946)	$5 \times 10^{14} m^3/(kmol.s)$	298
Lifshitz and Perlmutter–Hayman (1961)	$(9 \pm 2) \times 10^{10} m^3/(kmol.s)$	283
Lifshitz and Perlmutter–Hayman (1962)	Of the order of $10^{10} m^3/(kmol.s)$	283
Spalding (1962)	Of the order of $10^{10} m^3/(kmol.s)$	298
Sandall et al.(1981)	$2.7 \times 10^7 m^3/(kmol.s)$	273
Ashour et al. (1996)	$1.2 \times 10^9 m^3/(kmol.s)$	298

REACTION MECHANISM AND RATE OF ABSORPTION OF CHLORINE INTO AQUEOUS NaOH SOLUTIONS

When Cl_2 is absorbed in aqueous NaOH solutions, the following reactions may take place:

$$Cl_2 + H_2O \overset{K_1,k_1}{\longleftrightarrow} HOCl + H^+ + Cl^- \qquad (2)$$

$$Cl_2 + OH^- \overset{K_2,k_2}{\longleftrightarrow} HOCl + Cl^- \qquad (3)$$

$$HOCl + OH^- \overset{K_3,k_3}{\longleftrightarrow} OCl^- + H_2O \qquad (4)$$

$$H_2O \overset{K_4,k_4}{\longleftrightarrow} OH^- + H^+ \qquad (5)$$

In this model, all reactions are assumed to be reversible. However reactions (2) and (3) have finite reaction rates, whereas reactions (4) and (5) are assumed to be an instantaneous.

Here three equilibrium constants K_1, K_3 and K_4 are independent and remaining K_2 can be obtained by following equation:

$$K_2 = \frac{K_1}{K_4}$$

The chemical species that are present in aqueous NaOH solutions are renamed as follows:

$$w_1 = C_{Cl_2}$$
$$w_2 = C_{HOCl}$$
$$w_3 = C_{Cl^-}$$
$$w_4 = C_{H^+}$$
$$w_5 = C_{OCl^-}$$
$$w_6 = C_{OH^-}$$
$$w_7 = C_{H_2O}$$
$$w_8 = C_{Na^+} = C_{NaOH,initial}$$

Bulk concentration of an individual chemical species in liquid

Assuming all the reactions are at equilibrium, the following equations can be derived by overall mass balance. Defining, L as molar ratio of chlorine to NaOH at initial condition.

Chlorine balance:

$$2w_1^0 + w_2^0 + w_3^0 + w_5^0 = C_{cl_2,initial} = LC_{NaOH,initial} \qquad (6)$$

Hydrogen balance:

$$w_2^0 + w_4^0 + w_6^0 + 2w_7^0 = LC_{NaOH,initial} + C_{H_2O,initial} \qquad (7)$$

Oxygen balance:

$$w_2^0 + w_5^0 + w_6^0 + w_7^0 = C_{H_2O,initial} + C_{NaOH,initial} \qquad (8)$$

Electro neutrality balance:

$$w_4^0 + w_8^0 - w_3^0 - w_5^0 - w_6^0 = 0 \qquad (9)$$

$$w_8^0 = C_{Na^+} = C_{NaOH,initial} \qquad (10)$$

As the reactions are at equilibrium the independent equilibrium constants are:

$$K_1 = \frac{w_2^0 w_4^0 w_3^0}{w_1^0} \qquad (11)$$

$$K_2 = \frac{w_2^0 w_3^0}{w_1^0 w_6^0} \qquad (12)$$

$$K_3 = \frac{w_5^0}{w_2^0 w_6^0} \qquad (13)$$

$$K_4 = w_6^0 w_4^0 \qquad (14)$$

We have $w_1^0 \; to \; w_8^0$ unknowns and equation 6 to 11, 13 and 14 algebraic independent equations. Thus we have 8 unknowns and 8 algebraic independent equations.

These equations are 'linear system' of equations and can be solved by minimal residual technique using MATLAB to get $w_1^0 \; to \; w_8^0$ (which converge to the solution). It may be noted that in case of aqueous NaOH solution do not contain any chlorine initially (means L = 0) then:

$$w_1^0 = w_2^0 = w_3^0 = w_5^0 = 0 \qquad (15)$$

$$w_6^0 = C_{NaOH,initial} \qquad (16)$$

Partial differential equations and nonlinear algebraic equations describing diffusion/ reaction process

By assuming all reactions reversible, the following reaction rate expression can be given:

$$R_1 = -k_1 w_1 + \frac{k_1}{K_1} w_2 w_3 w_4 \qquad (17)$$

$$R_2 = -k_2 w_1 w_6 + \frac{k_2}{K_2} w_2 w_3 \qquad (18)$$

The rate of reaction R_3 and R_4 are instantaneous having large values of rate of reaction and are eliminated. We also assume that:

i) Reactions are at equilibrium.
ii) The diffusivity of ionic spices are equal.
iii) The fluxes of the nonvolatile species at interface are equal to zero.

By considering the mass balance following differential equation are derived:

Cl_2 balance

$$\frac{\partial w_1}{\partial t} = D_1 \frac{\partial^2 w_1}{\partial x^2} + R_1 + R_2 \qquad (19)$$

Cl_2/Cl^- balance

$$\frac{\partial w_1}{\partial t} + \frac{\partial w_3}{\partial t} = D_1 \frac{\partial^2 w_1}{\partial x^2} + D_3 \frac{\partial^2 w_3}{\partial x^2} \qquad (20)$$

Total chlorine balance

$$2\frac{\partial w_1}{\partial t} + \frac{\partial w_2}{\partial t} + \frac{\partial w_3}{\partial t} + \frac{\partial w_5}{\partial t} = 2D_1 \frac{\partial^2 w_1}{\partial x^2} + D_2 \frac{\partial^2 w_2}{\partial x^2} + D_3 \frac{\partial^2 w_3}{\partial x^2} + D_5 \frac{\partial^2 w_5}{\partial x^2} \qquad (21)$$

Electro neutrality balance:

$$w_4 + w_8 - w_3 - w_5 - w_6 = 0 \qquad (22)$$

Where $w_8 = C_{Na^+} = C_{NaOH,initial}$

As it is assumed all reactions are reversible; hence, the instantaneous reactions are also at equilibrium and their equilibrium constant may be given as follows:

$$K_3 = \frac{w_5}{w_2 w_6} \qquad (23)$$

$$K_4 = w_4 w_6 \qquad (24)$$

There are 6 unknowns and 6 partial differential equations/algebraic equations which can be solved for the concentrations of all chemical species.

Initial condition and boundary condition

At t = 0 (for all $x \geq 0$) and at $x = \infty$ (for all $t \geq 0$), the concentration of chemical species are equal to bulk concentrations in liquid.

$$w_i = w_i^0, i = 1 \; to \; 6 \qquad (25)$$

$$i.e. (w_1 = w_1^0, w_2 = w_2^0, w_3 = w_3^0, w_4 = w_4^0, w_5 = w_5^0, w_6 = w_6^0)$$

Boundary conditions at interface

At the interface of gas-liquid $x = 0$
For non volatile species

$$\frac{\partial w_j}{\partial x} = 0, at \; x = 0, t > 0 \qquad (26)$$

for all j except j =1 (Cl_2)

For volatile species (Cl_2)

$$-D_j \frac{\partial w_j}{\partial x} = k_{g,j}[P_j - H_{ei} \, w_j \, (0,t)] \qquad (27)$$

Here in our system there is only one volatile species that is, chlorine and hence j = 1. The equation may be re-written as:

$$-D_1 \frac{\partial w_1}{\partial x} = k_{g,1}[P_1 - H_{e1} \, w_1 \, (0,t)] \qquad (28)$$

Where H_1 is the physical equilibrium constant (Henry's law constant) of Cl_2. In case of pure Cl_2 in the gas phase, mass transfer resistance in gas phase can be neglected.

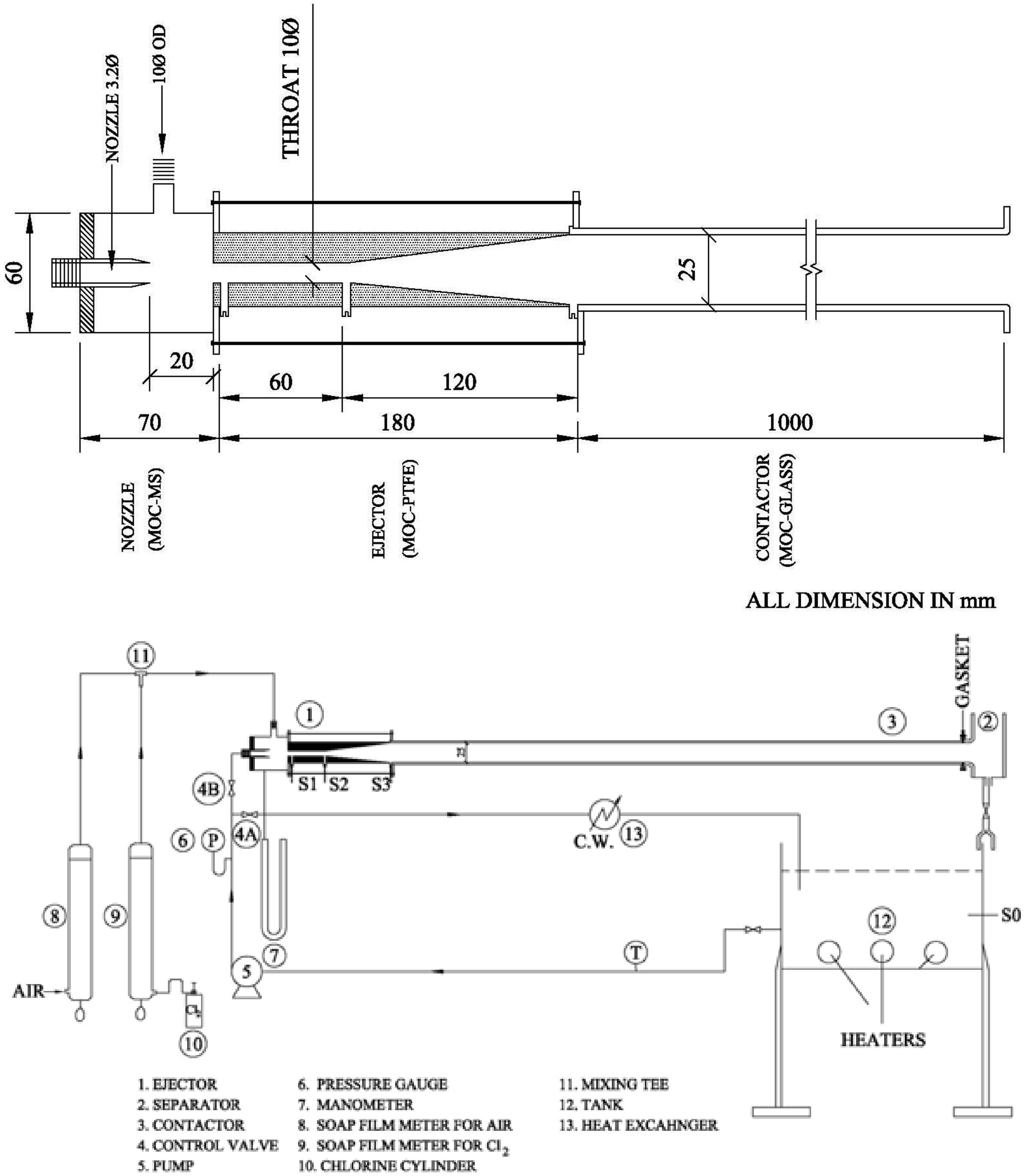

Figure 1. Detail of jet ejector and schematic diagram of experimental setup.

Hence $P_1^* = P_1$ and $(k_{g,1} \to \infty)$, the boundary condition for pure Cl_2 at the gas liquid inference reduces to:

$$w_1(0,t) = w_1^* = \frac{P_1}{H_1} \; at \; x = 0 \; t > 0 \tag{29}$$

EXPERIMENTALS

A detailed experimental set up for the ejector is shown in Figure 1. It consists of an ejector having detail as in Figure 1, an extended contactor, a gas liquid separator, aqueous caustic soda tank and other accessories. The ejector-head and extended contactor are made of transparent glass for visual observation of the flow and mixing patterns. The outlet of ejector and inside diameter of the contactor is 25 mm and length of the contactor 1 m. A high velocity liquid jet is produced through the nozzle (orifice) of the ejector which entrains air along with it. Known flow rate of aqueous solution of caustic soda whose concentration is predetermined is passed through the orifice of ejector. Then free suction of atmospheric air is allowed to enter. After measuring air flow rate, the chlorine flow rate is adjusted to achieve required gas concentration. Once steady state is achieved, samples are withdrawn from sample point S1, S2, S3 and S4. The available chlorine was analyzed by the iodometric method. The detailed experimental procedure has been discussed in an earlier paper (Agrawal, 2012). The rate of absorption of

Table 2. Densities and viscosities of aqueous NaOH solutions, Henery's law constants of Cl_2, and diffusion coefficients of Cl_2 (D_1), HOCl (D_2) and OH^- (D_6) (Ashour et al., 1996).

T K	$[NaOH]_{initial}$ $kmol/m^3$	$10^{-3}\ \rho$ kg/m^3	$10^{+3}\ \mu$ $kg/m.s$	H_3 $atm.m^3/kmol$	$10^9 D_1$ m^2/s	$10^9 D_2$ m^2/s	$10^9 D_6$ m^2/s
293	0.09985	0.9985	1.010	13.44	1.29	1.34	2.99
298	0.10000	0.9973	0.903	16.36	1.47	1.54	3.43
303	0.09960	0.9960	0.802	19.55	1.68	1.75	3.89
312	0.09970	0.9940	0.676	26.98	2.05	2.14	4.76

chlorine is computed using experimental result as follows:

$$R_{Cl_2} = N_{Cl_2} a = \left[C_{Cl_2,gas,in} - C_{Cl_2,gas,out}\right]/t_e\ kmol/m^3\, s \qquad (30)$$

Numerical implementation

The gas liquid exposure time for the jet ejector may be stated as:

$$t_e = \frac{Total\ volume\ of\ Jet\ ejector}{Sum\ of\ volumetric\ flow\ rate\ of\ aqueous\ solution\ and\ gas} \qquad (31)$$

$$t_e = \frac{V_J}{F_L + F_G}$$

The average rate of absorption of Cl_2 per unit interfacial area may be written as:

$$N_{Cl_2} = \frac{D_A}{t_e}\int_0^{t_e}\left(\frac{\partial w_1}{\partial x}\right)(0,t)\,dt \qquad (32)$$

and the enhancement factor of Cl_2 is determined from the following equation:

$$\beta = \frac{N_{Cl_2}}{k_L(w_1^* - w_1^0)} \qquad (33)$$

Where, w_1^* and w_1^0 are interfacial and bulk concentrations of Cl_2 in the liquid, respectively. k_L is the liquid phase mass transfer coefficient for physical absorption of Cl_2 is given by:

$$k_L = 2\sqrt{\frac{D_1}{\pi t_e}} \qquad (34)$$

The Finite Difference Method (FDM) is used to transform each partial differential equation into the system of ordinary differential equation in *t*. We choose following finite difference expressions to approximate the partial derivatives:

$$\frac{\partial w_{i,j}}{\partial x} = \frac{1}{2h_j}\left[w_{i,j+1} - w_{i,j-1}\right] + higher\ order\ terms \qquad (35)$$

$$\frac{\partial^2 w_{i,j}}{\partial x^2} = \frac{1}{h_j^2}\left[-2w_{i,j} + w_{i,j+1} + w_{i,j-1}\right] + higher\ order\ terms \qquad (36)$$

Where, i refer to the i^{th} chemical species, j, refers to the spatial node number and $h_j = x_{j+1} - x_j$. Typical values for the initial nodal spacing h_0 at the gas-liquid interface are about 10^{-4} mm. The system of partial differential equations /algebraic differential equations were transformed into large system of differential and algebraic equations that can be solved by MATLAB software by using ODE solver, BVP4c and preconditioning technique with special Jacobi pre-conditioner.

Physicochemical properties

The mathematical models is used to predict the rates of absorption and reaction (enhancement) factors of Cl_2 .We need the properties like densities and viscosities of the aqueous sodium hydroxide solutions, Henry's law constants of Cl_2 and the diffusion coefficients of all chemical species in these solutions which are tabulated in Table 2. We also need the equilibrium constants of all chemical reactions and the forward rate coefficients of reactions (2) to (5) which are tabulated in Table 3.

RESULTS AND DISCUSSION

The penetration model has been used to develop mathematical model for absorption of Cl_2 into aqueous solution of sodium hydroxide. The mathematical model to predict absorption rate is presented by equation (19) to (29). To solve this model the value of k_1, k_2, k_3 and k_4 were required. The value of k_1 was determined by the correlation given by Brian et al. (1966):

$$k_1 = 1.4527 \times 10^{10}\ exp.\left(\frac{-6138.6}{T}\right)$$

As the reactions are instantaneous, k_3 and k_4 are eliminated. There is large variation in the value of k_2 in the literature as clear from Table 1. Hence, attempt has been made to estimate value of k_2 by using data obtained for absorption of Cl_2 in aqueous sodium hydroxide solution in the jet ejector. The value of k_2 was adjusted until the theoretically predicted rate of absorption was

Table 3. Values for equilibrium constants of reactions 1 to 4 at various temperatures(Ashour et al., 1996).

T K	$10^4 K_1$ $(kmol/m^3)^2$	$10^{-10} K_2$	$10^{-6} K_3$ $m^3/kmol$	$10^{14} K_4$ $(kmol/m^3)^2$
293	3.890	5.722	3.726	0.6798
298	4.500	4.491	2.790	1.002
303	5.181	3.580	2.109	1.447
308	5.938	2.895	1.609	2.051
313	6.776	2.371	1.238	2.858

Table 4. The values of k_2 at atmospheric pressure for Cl_2- aqueous NaOH system.

T K	$(NaOH)_{initial}$ $kmol/m^3$	**Estimated k_2** $\frac{m^3}{kmol.s}$ **[Ashour et al. (1996) Equation (1)]**	**Experimental value k_2** $\frac{m^3}{kmol.s}$	**Estimated k_2** $\frac{m^3}{kmol.s}$ **present model Equation (37)**
293	0.09985	1.42×10^9	-	1.399×10^9
298	0.10000	1.566×10^9	-	1.669×10^9
303	0.09960	1.71×10^9	-	1.669×10^9
312	0.09970	1.99×10^9	-	1.945×10^9
303	0.03	1.399×10^9	1.662×10^9	-

within 1% of the experimentally measured rate of absorption of Cl_2. Thus, the following correlation is developed to predict the value of k_2:

$$k_2 = 3.39 \times 10^{11}\, exp.\left(-\frac{1610}{T}\right) \qquad (37)$$

The predicted values of k_2 from equation (1) reported by Ashour et al. (1996) and predicted value of k_2 from equation (37) by proposed model, along with the value obtained from the experimental result of present work are presented in Table 4 and plotted in Figures 2 and 3. The experimental value and value predicted by present model (equation 37) are comparable. The values estimated by Ashour et al. (1996) are a little higher by 2.7% at maximum and the present experimental k_2 value differs only negligibly from Equation 37. As the error is very less, it may be concluded that the proposed model is good. Figure 4 presents N_{Cl2} vs. $C_{Ag,in,}$ (C_{BO} as parameter). The values obtained by experiment result and proposed model are in good agreement. Thus, the chemical absorption mechanism proposed in the present work may be considered to be correct.

Conclusion

The value N_{Cl2} obtained by experiment and predicted from the proposed model are in good agreement. Hence, the proposed mathematical model may be used to predict the value of reaction rate (flux), N_{Cl2}. These values may be further utilized to predict enhancement factor β and interfacial area using following co-relations:

$$\beta = \frac{N_A}{k_L^0 (C_A^* - C_A^0)}$$

$$a = \frac{N_A . a}{N_A}$$

The correlation obtained to estimate rate constant for forward part of absorption of chlorine in aqueous NaOH is:

$$k_2 = 3.39 \times 10^{11}\, exp.\left(-\frac{1610}{T}\right)$$

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Nomenclature

Latin letters: a, Interfacial area (m^2/m^3); **C,** concentration

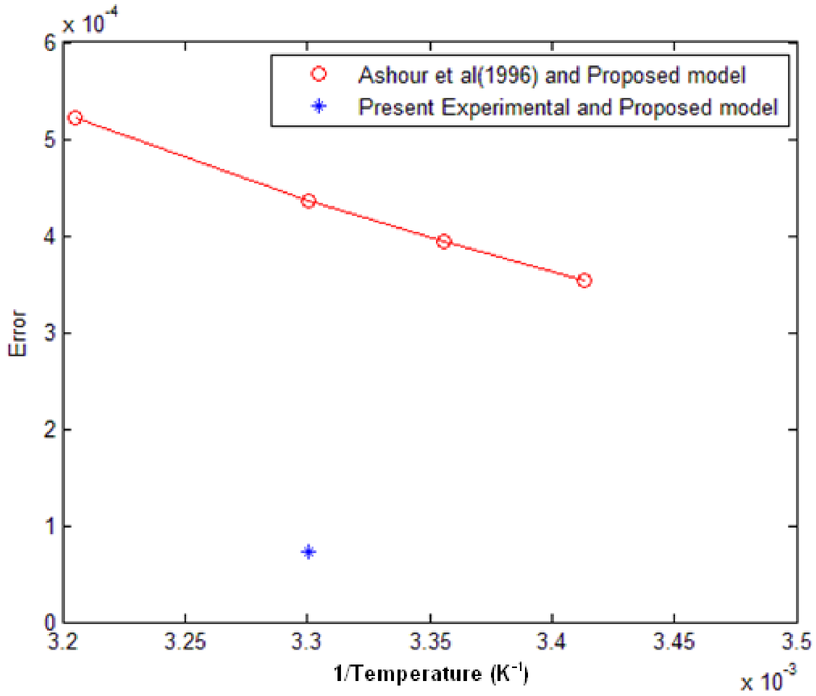

Figure 2. Comparison of k_2 obtained by proposed mathematical model with present experimental result.

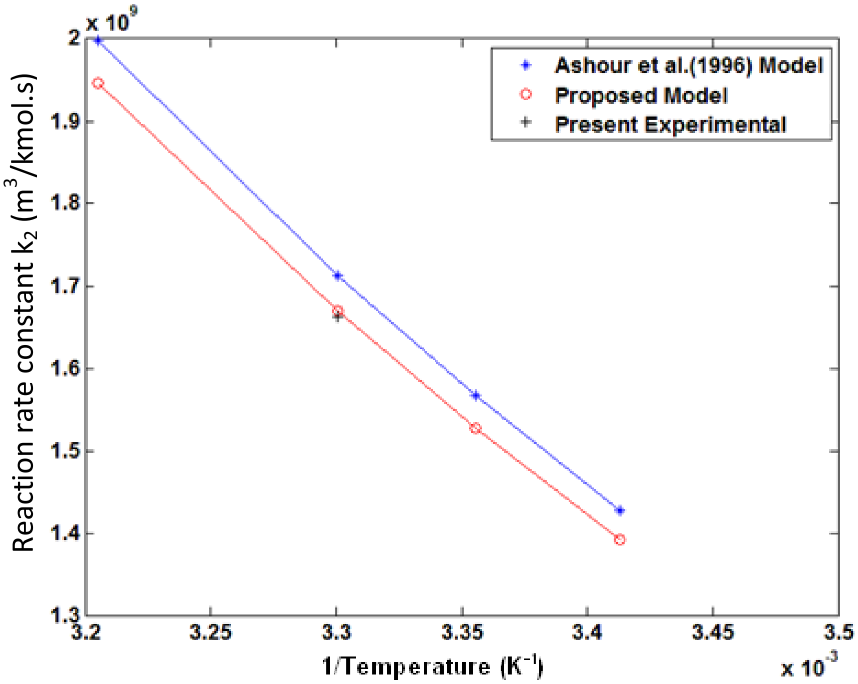

Figure 3. Error estimates for k_2 and proposed mathematical model.

of species indicated as subscript (kmol/m^3); **D,** diffusion coefficient of species indicated as (m^2 s^{-1}) subscript in the liquid phase; **F,** volumetric flow rate (m^3 s^{-1}); **H,** Henry's law coefficient (Pa m^3 mol^{-1}); **K,** equilibrium constants (-) k chemical reaction rate constant (as per order of reaction); **N_A*,** average rate of physical absorption (flux)

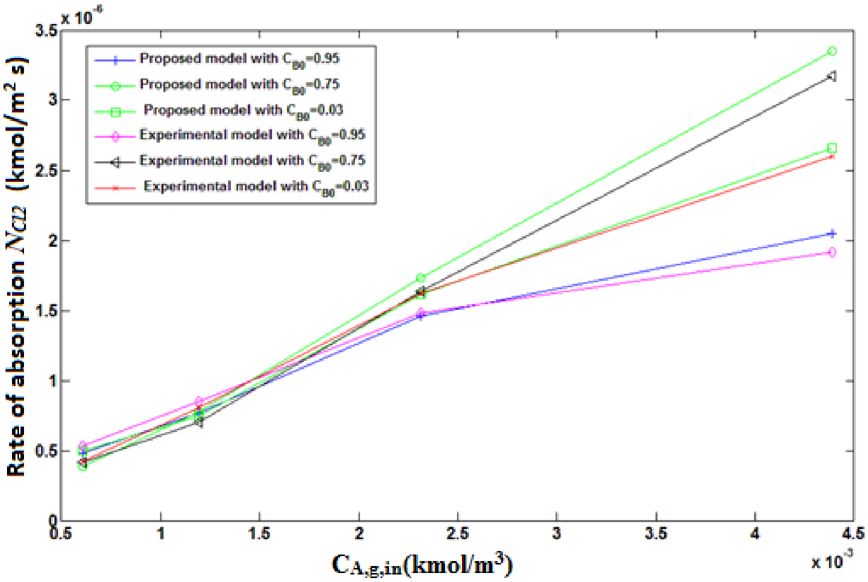

Figure 4. Comparison between the values for rate of absorption obtained experimentally and predicted by proposed model with respect to C_{A0} at different C_{B0}.

of A (kmol m^{-2} s^{-1}); **N,** rate of molar absorption with chemical reaction (kmol m^{-2} s^{-1}) (flux) of the species indicated by subscript; **k$_G$,** gas sided mass transfer coefficient (kmol m^{-3} Pa^{-1} s^{-1}); **k$_L$,** liquid sided mass transfer coefficient (m s^{-1}); **P,** system pressure (Pa); **R,** rate of reaction (kmol m^{-3} s^{-1}); **t,** time (s); **t$_e$,** exposure time (s); **T,** temperature (K); **V,** volume (m^3); **V$_J$,** volume of reactor/ejector (Figure 1) (m^3); **w$_i$,** concentration of species *i* in the liquid phase (kmol/m^3); **w$_{ij}$,** concentration of species *i* in the liquid phase at x_j (kmol/m^3); **x$_j$,** spatial variable at node j (mm).

Greek letters: **β,** Enhancement factor (-).

Subscripts: A, B…., Components A, B…..

Superscripts: ***,** Equilibrium, physical solubility; **i,** species number; **j,** node number; **g,** gas; **in,** at inlet of ejector; **out,** at outlet of ejector.
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REFERENCES

Agrawal KS (2012). Rate of absorption in laboratory scale jet ejector. Nat. J. Appl. Sci. Engr. 1(2):60-64.

Ashour SS, Edward RB, Orville C (1996). Absorption of chlorine into aqueous bicarbonate solutions and aqueous hydroxide solutions. AIChE J. 42(A3): 671-682.

Brian PLT, Vivian JE, Piazza C (1966). The effect of temperature on the ratio of absoraption of chlorine in to water. Chem. Eng. Sci. (21): 551-558.

Hikita H, Asai S, Himukashi Y, Takatsuka T (1973). Absorption of chlorine into aqueous sodium hydroxide solutions. Chem. Eng. J. (5):77-84.

Lahiri N, Yadav GD, Sharma MM (1983). Absorption of chlorine in aqueous solutions of sodium hydroxide desorption of hypochlorous acid followed by its dissociation to chlorine monoxide. Chem. Eng. Sci. 38(7):1119-1133.

Lifshitz A, Perlmutter HB (1962). The kinetics of the hydrolysis of chlorine III. The reaction in the presence of various bases and discussion of the mechanism. J. Phys. Chem. 66:701-705.

Lifshitz A, Perlmutter HB, (1961). The kinetics of the hydrolysis of chlorine II. The hydrolysis in the presence of acetate. J. Phys. Chem. 65:753-757.

Morris JC (1946). The mechanism of the hydrolysis of chlorine. J. Am. Chem. Soc. 68(9):1692-1694.

Roy S, Rochelle GT (2004). Chlorine Absorption in Sulfite Solutions. Sep. Sci. Technol. 39(13):3057-3077.

Sandall OC, Goldberg IB, Hurlock SC, Laeger HO, Wagner RI (1981). Solubility and rate of hydrolysis of chlorine in aqueous sodium hydroxide at 273K. AIChE J. 27(5): 856–859.

Spalding CW (1962). Reaction kinetics in the absorption of chlorine in to aqueous. AIChE J. (8):685-689.

Takahashi T, Hatanaka M, Konaka R (1967). Absorption of chlorine into still liquid in a simple stop-cock type absorber. Can. J. Chem. Eng. (45):145-149.