Absorption of Chlorine into Aqueous Bicarbonate Solutions and Aqueous Hydroxide Solutions

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The absorption of Cl_2 into aqueous bicarbonate and aqueous hydroxide solutions was studied both experimentally and theoretically. The rate coefficient of the reaction between Cl_2 and OH^- was estimated over the temperature range of 293–312 K and fitted by the Arrhenius equation:

$$k_{24} = 3.56 \times 10^{11} \exp\left(\frac{-1{,}617}{T}\right).$$

If Cl_2 were assumed to react only with water and OH^- in an aqueous bicarbonate solution, the predicted absorption rate would be much lower than that experimentally measured. This suggests that Cl_2 reacts with HCO_3^- in an aqueous bicarbonate solution. The rate coefficient of the reaction between Cl_2 and HCO_3^- was estimated over the temperature range of 293–313 K and fitted by the Arrhenius equation:

$$k_{21} = 5.63 \times 10^{10} \exp\left(\frac{-4{,}925}{T}\right).$$

More importantly, under absorption conditions, the amount of hydroxide consumed for absorbing a specific amount of Cl_2 into an aqueous hydroxide solution is almost twice the amount of bicarbonate consumed for absorbing the same amount of Cl_2 into an aqueous bicarbonate solution.

Introduction

Removal of chlorine from certain gas streams may be of industrial importance for certain chemical processes. One way of accomplishing this would be to absorb chlorine into basic aqueous solutions. There have been a few studies on the absorption of Cl_2 into aqueous sodium hydroxide solutions (Spalding, 1962; Takahashi et al., 1967; Hikita et al., 1973; Sandall et al., 1981; Lahiri et al., 1983). However, there has been a great deal of confusion and disagreement in the literature concerning the magnitude of the forward rate coefficient of the reaction between Cl_2 and OH^-. Morris (1946) estimated this rate coefficient to be about 5×10^{14} $m^3/(kmol \cdot s)$ at 298 K; Lifshitz and Perlmutter-Hayman (1961) first reported an approximate value of $(9 \pm 2) \times 10^{10}$ $m^3/(kmol \cdot s)$ for this rate coefficient at about 283 K, but they later estimated it to be of the order of 10^9 $m^3/(kmol \cdot s)$ (Lifshiftz and Perlmutter-Hayman, 1962); Spalding (1962) estimated it to be of the order of 10^6 $m^3/(kmol \cdot s)$ at 298 K; while Sandall et al. (1981) estimated it to be about 2.7×10^7 $m^3/(kmol \cdot s)$ at 273 K. On the other hand, other researchers (Takahashi et al., 1967; Hikita et al., 1973; Lahiri et al., 1983) have opted to treat the reaction between Cl_2 and OH^- as an instantaneous irreversible reaction, since it is much faster than the reaction between Cl_2 and water. One the other hand, there have not been any published studies regarding the absorption of chlorine into aqueous bicarbonate solutions.

In this article, the absorption of Cl_2 into aqueous solutions of sodium hydroxide and into aqueous solutions of potassium bicarbonate is studied both experimentally and theoretically. A laminar liquid jet absorber is used to acquire experimental absorption data, and a mathematical model that is based on

Higbie's penetration theory is developed. The mathematical model will be used to estimate the values of the rate coefficients of the reactions between Cl_2 and OH^- and between Cl_2 and HCO_3^-. It will also be used to further investigate various aspects of the absorption of Cl_2 into aqueous hydroxide solutions and into aqueous bicarbonate solutions.

Penetration Model for the Absorption of Chlorine into Aqueous Bicarbonate Solutions

When Cl_2 is absorbed into aqueous bicarbonate solutions, the following reactions may occur:

$$Cl_2 + HCO_3^- \overset{K_1, k_{21}}{\longleftrightarrow} CO_2 + HOCl + Cl^- \tag{1}$$

$$Cl_2 + CO_3^= \overset{K_2, k_{22}}{\longleftrightarrow} CO_2 + OCl^- + Cl^- \tag{2}$$

$$Cl_2 + H_2O \overset{K_3, k_{13}}{\longleftrightarrow} HOCl + H^+ + Cl^- \tag{3}$$

$$Cl_2 + OH^- \overset{K_4, k_{24}}{\longleftrightarrow} HOCl + Cl^- \tag{4}$$

$$CO_2 + H_2O \overset{K_5, k_{15}}{\longleftrightarrow} H_2CO_3 \tag{5}$$

$$CO_2 + OH^- \overset{K_6, k_{26}}{\longleftrightarrow} HCO_3^- \tag{6}$$

$$HOCl + OH^- \overset{K_7}{\longleftrightarrow} OCl^- + H_2O \tag{7}$$

$$HCO_3^- + OH^- \overset{K_8}{\longleftrightarrow} CO_3^= + H_2O \tag{8}$$

$$HCO_3^- + H^+ \overset{K_9}{\longleftrightarrow} H_2CO_3 \tag{9}$$

$$H_2O \overset{K_{10}}{\longleftrightarrow} OH^- + H^+ \tag{10}$$

In this model, all reactions are considered to be reversible. Reactions 1–6 have finite reaction rates, whereas reactions 7–10 involve only proton transfers and are assumed to be instantaneous with respect to mass transfer and to be at equilibrium.

Note that not all of the reaction equilibrium constants are independent. Only six equilibrium constants (K_3, K_6, K_7, K_8, K_9, and K_{10}) are independent. The remaining four can be obtained by appropriate combinations of the independent equilibrium constants. Hence, we have:

$$K_1 = \frac{K_3}{K_6 K_{10}}, K_2 = \frac{K_3 K_7}{K_6 K_8 K_{10}}, K_4 = \frac{K_3}{K_{10}}, K_5 = K_6 K_9 K_{10}.$$

The following reactions:

$$HOCl + HCO_3^- \overset{K_{11}}{\longleftrightarrow} H_2CO_3 + OCl^- \tag{11}$$

$$HOCl + CO_3^= \overset{K_{12}}{\longleftrightarrow} HCO_3^- + OCl^- \tag{12}$$

$$HCO_3^- + H_2O \overset{K_{13}}{\longleftrightarrow} H_2CO_3 + OH^- \tag{13}$$

involve only proton transfers and are hence considered to be instantaneous with respect to mass transfer and at equilibrium. Reactions 11, 12 and 13 are implicitly included in the reaction scheme just given, since reaction 11 can be obtained by adding the instantaneous equilibria reactions 7, 9 and 10, reaction 12 can be obtained by properly combining the instantaneous equilibria reactions 7 and 8, and reaction 13 can be obtained by adding the instantaneous equilibria reactions 9 and 10. Hence, we have $K_{11} = K_7 K_9 K_{10}$, $K_{12} = K_7/K_8$, and $K_{13} = K_9 K_{10}$.

For convenience, the chemical species that are present in an aqueous bicarbonate solution are renamed as follows:

$$\begin{array}{lll} u_1 = [Cl_2], & u_2 = [HCO_3^-], & u_3 = [CO_2], \\ u_4 = [HOCl], & u_5 = [Cl^-], & u_6 = [H^+], \\ u_7 = [OCl^-], & u_8 = [OH^-], & u_9 = [CO_3^=], \\ u_{10} = [H_2CO_3], & u_{11} = [H_2O]. & \end{array}$$

Liquid bulk concentrations of all chemical species

The liquid bulk concentrations of all chemical species can be estimated from the total concentration of bicarbonate, the initial Cl_2 loading of the aqueous bicarbonate solution, L_1, and the assumption that all reactions are at equilibrium. We have the following equations for the liquid bulk concentrations $u_1^0, \ldots, u_{11}^0$:

Overall Chlorine Balance:

$$2u_1^0 + u_4^0 + u_5^0 + u_7^0 = 2L_1[HCO_3^-]_{\text{initial}}. \tag{14}$$

Overall Carbon Balance:

$$u_2^0 + u_3^0 + u_9^0 + u_{10}^0 = [HCO_3^-]_{\text{initial}}. \tag{15}$$

Overall Hydrogen Balance:

$$u_2^0 + u_4^0 + u_6^0 + u_8^0 + 2u_{10}^0 + 2u_{11}^0 = [HCO_3^-]_{\text{initial}} + 2[H_2O]_{\text{initial}}. \tag{16}$$

Overall Oxygen Balance:

$$3u_2^0 + 2u_3^0 + u_4^0 + u_7^0 + u_8^0 + 3u_9^0 + 3u_{10}^0 + u_{11}^0 = 3[HCO_3^-]_{\text{initial}} + [H_2O]_{\text{initial}}. \tag{17}$$

Electroneutrality Balance:

$$u_6^0 + u_{12}^0 - u_2^0 - u_5^0 - u_7^0 - u_8^0 - 2u_9^0 = 0, \tag{18}$$

where $u_{12}^0 = [K^+] = [HCO_3^-]_{\text{initial}} = [KHCO_3]_{\text{initial}}$ is a constant.

Reactions at equilibrium (only independent equilibrium constants):

$$K_3 = \frac{u_4^0 u_5^0 u_6^0}{u_1^0} \tag{19}$$

$$K_6 = \frac{u_2^0}{u_3^0 u_8^0} \tag{20}$$

$$K_7 = \frac{u_7^0}{u_4^0 u_8^0} \tag{21}$$

$$K_8 = \frac{u_9^0}{u_2^0 u_8^0} \tag{22}$$

$$K_9 = \frac{u_{10}^0}{u_2^0 u_6^0} \tag{23}$$

$$K_{10} = u_6^0 u_8^0. \tag{24}$$

We have eleven unknowns ($u_1^0, \ldots, u_{11}^0$) and eleven algebraic equations. Hence, we can solve for the liquid bulk concentrations. We have found that Newton's method does not converge unless the initial guesses for the liquid bulk concentrations were very close to the (unknown) solution. Therefore, we used the Newton homotopy continuation method (Wayburn and Seader, 1987), which converged to the solution even when the initial guesses were not close to the solution.

Partial differential and nonlinear algebraic equations describing diffusion/reaction processes

For gas absorption into a laminar liquid jet when the gas–liquid contact times are relatively short, the penetration depth of the gas in the liquid would be small relative to the diameter of the jet. When chemical reaction accompanies the gas absorption, the penetration depth of the gas is even smaller than when only physical absorption takes place. In this case, the curvature effects of the cylindrical liquid jet can be neglected, and the gas absorption into the liquid jet can be modeled as gas absorption into an infinitely deep liquid with a flat surface. The average velocity of the laminar liquid jet, $\bar{v}$, can be computed from the following equation:

$$\bar{v} = \frac{4Q}{\pi d^2}, \tag{25}$$

where Q is the volumetric liquid flow rate, and d is the diameter of the laminar liquid jet. Let x be a length coordinate that denotes the position in the liquid as measured from the gas–liquid interface into the liquid bulk; $x = 0$ denotes the gas–liquid interface, and $x = \infty$ denotes the liquid bulk. Let y be a length coordinate that denotes the position along the liquid jet; $y = 0$ denotes the top of the liquid jet, and $y = l$ denotes the bottom of the liquid jet. Define a new variable, t, that denotes the position along the liquid jet, by the following equation:

$$t = \frac{y}{\bar{v}} = \frac{\pi d^2}{4Q} y. \tag{26}$$

Note that t has units of time, whereas y has unit of length.

Higbie's penetration model (Higbie, 1935; Danckwerts, 1970) was used to set up the diffusion/reaction partial differential equations that describe the absorption of Cl_2 into aqueous solutions of potassium bicarbonate in a laminar liquid jet absorber. All reactions were treated as reversible reactions. The first six reactions have finite reaction rates that are given by the following reaction rate expressions (R_i is the reaction rate expression for reaction i):

$$R_1 = -k_{21}u_1u_2 + \frac{k_{21}}{K_1}u_3u_4u_5 \tag{27}$$

$$R_2 = -k_{22}u_1u_9 + \frac{k_{22}}{K_2}u_3u_5u_7 \tag{28}$$

$$R_3 = -k_{13}u_1 + \frac{k_{13}}{K_3}u_4u_5u_6 \tag{29}$$

$$R_4 = -k_{24}u_1u_8 + \frac{k_{24}}{K_4}u_4u_5 \tag{30}$$

$$R_5 = -k_{15}u_3 + \frac{k_{15}}{K_5}u_{10} \tag{31}$$

$$R_6 = -k_{26}u_3u_8 + \frac{k_{26}}{K_6}u_2. \tag{32}$$

The partial differential equations were combined in such a way so as to eliminate the very large reaction rates for the instantaneous reactions (reactions 7–10). Since these reactions are assumed to be at equilibrium, their equilibrium constant expressions were used to complete the equations that are required to solve for the concentration profiles of all chemical species. Furthermore, the diffusion coefficients of the ionic species were assumed to be equal. With this assumption, the electrostatic potential gradient terms in the diffusion/reaction partial differential equations for the ionic species can be neglected while preserving the electroneutrality of the solution. The more rigorous approach of taking into account the electrostatic potential gradient terms with unequal diffusion coefficients for the ionic species requires much more computational effort with practically intangible effects on the predicted rates of absorption. The following equations describe the diffusion/reaction processes:

Cl_2 Balance:

$$\frac{\partial u_1}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + R_1 + R_2 + R_3 + R_4. \tag{33}$$

CO_2 Balance:

$$\frac{\partial u_3}{\partial t} = D_3 \frac{\partial^2 u_3}{\partial x^2} - R_1 - R_2 + R_5 + R_6. \tag{34}$$

Cl_2/Cl^- Balance:

$$\frac{\partial u_1}{\partial t} + \frac{\partial u_5}{\partial t} = D_1 \frac{\partial^2 u_1}{\partial x^2} + D_5 \frac{\partial^2 u_5}{\partial x^2}. \tag{35}$$

Total Chlorine Balance:

$$2\frac{\partial u_1}{\partial t} + \frac{\partial u_4}{\partial t} + \frac{\partial u_5}{\partial t} + \frac{\partial u_7}{\partial t} = 2D_1 \frac{\partial^2 u_1}{\partial x^2} + D_4 \frac{\partial^2 u_4}{\partial x^2} + D_5 \frac{\partial^2 u_5}{\partial x^2} + D_7 \frac{\partial^2 u_7}{\partial x^2}. \tag{36}$$

Total Carbon Balance:

$$\frac{\partial u_2}{\partial t}+\frac{\partial u_3}{\partial t}+\frac{\partial u_9}{\partial t}+\frac{\partial u_{10}}{\partial t}=D_2\frac{\partial^2 u_2}{\partial x^2}+D_3\frac{\partial^2 u_3}{\partial x^2}+D_9\frac{\partial^2 u_9}{\partial x^2}+D_{10}\frac{\partial^2 u_{10}}{\partial x^2}. \quad (37)$$

Electroneutrality Balance:

$$u_6+u_{12}-u_2-u_5-u_7-u_8-2u_9=0, \quad (38)$$

where $u_{12}=[K^+]=[HCO_3^-]_{\text{initial}}=[KHCO_3]_{\text{initial}}$ is a constant.

Instantaneous reactions assumed to be at equilibrium:

$$K_7=\frac{u_7}{u_4u_8} \quad (39)$$

$$K_8=\frac{u_9}{u_2u_8} \quad (40)$$

$$K_9=\frac{u_{10}}{u_2u_6} \quad (41)$$

$$K_{10}=u_6u_8. \quad (42)$$

We have ten unknowns ($u_1, \ldots, u_{10}$) and ten partial differential/algebraic equations that we can solve for the concentrations of all chemical species.

Initial Condition and Boundary Condition at $x=\infty$. At $t=0$ (for all $x \geq 0$) and at $x=\infty$ (for all $t \geq 0$), the concentrations of the chemical species are equal to their liquid bulk concentrations:

$$u_i=u_i^0, \qquad i=1, \ldots, 10. \quad (43)$$

Boundary Condition at Gas–Liquid Interface ($x=0$). At $x=0$ (gas–liquid interface), the fluxes of the nonvolatile species are equal to zero, which lead to the following equations:

$$\frac{\partial u_i}{\partial x}=0 \quad \text{at} \quad x=0, \qquad t>0 \quad (44)$$

for all i except $i=1$ (Cl_2) and $i=3$ (CO_2). For the volatile components (Cl_2 and CO_2), the mass-transfer rate in the gas near the interface is equal to the mass-transfer rate in the liquid near the interface. This leads to the following boundary condition:

$$-D_i\frac{\partial u_i}{\partial x}=k_{g,i}[P_i-H_iu_i(0,t)]$$
$$\text{for } i=1 \text{ and } 3 \quad \text{at} \quad x=0, t>0, \quad (45)$$

where H_i is the physical equilibrium constant (Henry's law constant) of gas i, which is defined as the interfacial partial pressure of gas i in the gas phase, P_i^*, divided by the interfacial concentration of gas i in the liquid, u_i^*. For the case of pure Cl_2 in the gas phase, the interfacial partial pressure of Cl_2, P_1^*, is the same as the bulk partial pressure of Cl_2, P_1, and there is no mass-transfer resistance in the gas phase ($k_{g,1} \to \infty$). Hence, the boundary condition for Cl_2 at the gas–liquid interface reduces to:

$$u_1(0,t)=u_1^*=\frac{P_1}{H_1} \quad \text{at} \quad x=0, \quad t>0. \quad (46)$$

On the other hand, since there is no CO_2 present in the gas phase, and since the solubility of CO_2 in aqueous bicarbonate solutions is relatively low, we will assume that all of the CO_2 that is present in the liquid at the gas–liquid interface will desorb from the liquid into the gas phase. This leads to the following boundary condition for CO_2 at the gas–liquid interface:

$$u_3(0,t)=0 \quad \text{at} \quad x=0, \quad t>0. \quad (47)$$

This boundary condition assumes that all of the mass-transfer resistance for CO_2 is in the liquid phase. Some preliminary model calculations showed that the results for the rate of Cl_2 absorption were not noticeably affected by this choice of boundary condition for CO_2.

Pentration Model for the Absorption of Chlorine into Aqueous Hydroxide Solutions

When Cl_2 is absorbed into aqueous hydroxide solutions, only reactions 3, 4, 7, and 10 can occur. Since the Cl_2-hydroxide system can be viewed as a subset of the Cl_2-bicarbonate system with respect to the reactions that take place and the chemical species that are present, we will maintain the same numbering scheme that has already been employed for the Cl_2-bicarbonate system. Note that for the Cl_2-hydroxide system, HCO_3^-, CO_2, $CO_3^=$ and H_2CO_3 are not present. Hence, we have $u_2=u_3=u_9=u_{10}=0$ for the Cl_2-hydroxide system.

Liquid bulk concentrations of all chemical species

The liquid bulk concentrations of all chemical species that are present can be estimated from the initial concentration of hydroxide, the initial Cl_2 loading of the aqueous hydroxide solution, and the assumption that all reactions are at equilibrium. For the case when the initial Cl_2 loading of the aqueous NaOH solution is zero ($L_1=0$), we have $u_1^0=u_4^0=u_5^0=u_7^0=0$, and the initial liquid bulk concentration of OH^- is practically equal to the initial NaOH concentration. Hence, we have:

$$u_8^0=[NaOH]_{\text{initial}} \quad (48)$$

and

$$u_6^0=\frac{K_{10}}{u_8^0}. \quad (49)$$

The partial differential and nonlinear algebraic equations that describe the diffusion/reaction processes

The equations for the Cl_2-hydroxide system can be obtained from those for the Cl_2-bicarbonate system by simply setting $u_2=u_3=u_9=u_{10}=0$ in Eqs. 27 through 32 and in

Eq. 38, setting $u_{12} = [\mathrm{Na}^+] = [\mathrm{NaOH}]_{\mathrm{initial}}$ in Eq. 38, and neglecting Eqs. 34, 37, 40, and 41. This results in six partial differential/algebraic equations in six unknowns (u_1, u_4, u_5, u_6, u_7, and u_8). Hence, we can solve for the concentrations of all chemical species. The same initial and boundary conditions apply here as for the Cl_2-bicarbonate system.

Numerical Implementation

The gas–liquid contact time for the laminar liquid jet absorber is given by

$$\tau = \frac{\pi d^2 l}{4Q}, \tag{50}$$

where l is the length of the liquid jet. The differential equations are integrated from $t = 0$ $(y = 0)$ to $t = \tau$ $(y = l)$. For Higbie's penetration model, the liquid-phase mass-transfer coefficient for physical absorption of Cl_2 is given by

$$k_{l,1}^0 = 2\sqrt{\frac{D_1}{\pi\tau}}. \tag{51}$$

The average rate of absorption of Cl_2 per unit interfacial area is then computed from the following equation:

$$RA_1 = -\frac{D_1}{\tau}\int_0^\tau \left(\frac{\partial u_1}{\partial x}\right)(0,t)\,dt, \tag{52}$$

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

$$E_1 = \frac{RA_1}{k_{l,1}^0 (u_1^* - u_1^0)}, \tag{53}$$

where u_1^* and u_1^0 are the interfacial and bulk concentrations of Cl_2 in the liquid, respectively.

The method-of-lines was used to transform each partial differential equation into a system of ordinary differential equations in t (Brenan et al., 1989). We chose to successively double the nodal spacing, h_j, as we proceeded from the gas–liquid interface into the liquid bulk (i.e., we used $h_{j+1} = 2h_j = 4h_{j-1}$). For this specific nodal spacing sequence, the following finite difference expressions were used to approximate the spatial derivatives:

$$\frac{\partial u_{i,j}}{\partial x} = \frac{1}{6h_j}[-8u_{i,j} + 9u_{i,j+1} - u_{i,j+2}] + O(h_j^2) \tag{54}$$

$$\frac{\partial^2 u_{i,j}}{\partial x^2} = \frac{1}{21h_j^2}[64u_{i,j-1} - 98u_{i,j} + 35u_{i,j+1} - u_{i,j+2}] + O(h_j^2), \tag{55}$$

where i refers to the ith 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^{-9} m, and for the total number of interior nodes used are about 15 nodes for the Cl_2-bicarbonate system, whereas these values are about 10^{-10} m and 20 nodes, respectively, for the Cl_2-hydroxide system. The systems of partial differential/algebraic equations were transformed into larger systems of ordinary differential/algebraic equations that were then solved by using the code DDASSL (Petzold, 1983; Brenan et al., 1989) in double precision Fortran on an Alliant FX-40 computer.

Physicochemical Properties

In order to use the mathematical models to predict the rates of absorption and enhancement factors of Cl_2, we need the values of the densities and viscosities of the aqueous potassium bicarbonate solutions and of the aqueous sodium hydroxide solutions, Henry's law constants of Cl_2, and the diffusion coefficients of all chemical species in these solutions, as well as the equilibrium constants of all chemical reactions and the forward rate coefficients of reactions 1 through 6.

The densities of the aqueous $KHCO_3$ solutions and of the aqueous NaOH solutions were measured by using a 2.5×10^{-5} m^3 Gay-Lussac pycnometer that was submerged in a large water bath where the temperature was maintained to within ±0.02 K with a constant-temperature circulator. The mass of the pycnometer was measured with an H-18 Mettler balance to within $\pm 2.0 \times 10^{-7}$ kg. The viscosities of the aqueous $KHCO_3$ solutions and of the aqueous NaOH solutions were measured by using a size-50 Cannon-Fenske viscometer that was submerged in the same water bath as that of the pycnometer. The densities and viscosities of the aqueous NaOH solutions are reported in Table 1 and those of the aqueous $KHCO_3$ solutions are reported in Table 2.

Henry's law constants for Cl_2 in aqueous $KHCO_3$ solutions and in aqueous NaOH solutions were estimated by using the method of van Krevelen and Hoftijzer (Danckwerts, 1970) for predicting gas solubility in electrolyte solutions. According to this method Henry's law constant of Cl_2 in an aqueous $KHCO_3$ solution or in an aqueous NaOH solution, H_1, is related to that in pure water, H_1^0, by the following equation:

$$\log_{10}\left(\frac{H_1}{H_1^0}\right) = -SI, \tag{56}$$

Table 1. Densities and Viscosites of Aqueous NaOH Solutions, Henry's Law Constants of Cl_2, and Diffusion Coefficients of Cl_2, HOCl, and OH^-, Respectively, in These Solutions

T K	$[\mathrm{NaOH}]_{\mathrm{initial}}$ kmol/m^3	$10^{-3}\rho$ kg/m^3	$10^3\mu$ kg/m·s	H_1 atm·m^3/kmol	$10^9 D_1$ m^2/s	$10^9 D_4$ m^2/s	$10^9 D_8$ 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

Table 2. Densities and Viscosites of Aqueous $KHCO_3$ Solutions, Henry's Law Constants of Cl_2, and Diffusion Coefficients of Cl_2, HOC_3^-, CO_2, and HOCl, Respectively, in These Solutions

T K	$[KHCO_3]_{initial}$ kmol/m^3	$10^{-3}\rho$ kg/m^3	$10^3\mu$ kg/m·s	H_1 atm·m^3/kmol	10^9D_1 m^2/s	10^9D_2 m^2/s	10^9D_3 m^2/s	10^9D_4 m^2/s
293	0.202	1.0136	1.0434	13.46	1.25	1.34	1.64	1.30
298	0.100	1.0005	0.9021	16.12	1.47	1.58	1.92	1.53
298	0.202	1.0072	0.9161	16.23	1.44	1.55	1.89	1.50
298	0.300	1.0140	0.9327	16.34	1.42	1.53	1.86	1.48
298	0.410	1.0209	0.9480	16.46	1.40	1.50	1.83	1.45
303	0.202	1.0056	0.8268	19.45	1.63	1.75	2.14	1.69
308	0.202	1.0042	0.7500	23.17	1.83	1.96	2.39	1.90
313	0.202	1.0023	0.6808	27.43	2.04	2.20	2.68	2.13

where S is the salting-out factor, and I is the ionic strength of the aqueous electrolyte solution. The salting-out factor, S, is defined in terms of the contributions of the positive and negative ions in the aqueous solution, S_+ and S_-, respectively, and the contribution of the Cl_2 gas, S_1:

$$S = S_+ + S_- + S_1, \tag{57}$$

where $S_+ = 0.074$ m^3/kmol for K^+ and $S_- = 0.021$ m^3/kmol for HCO_3^-, whereas $S_+ = 0.091$ m^3/kmol for Na^+ and $S_- = 0.066$ m^3/kmol for OH^- (Danckwerts, 1970), and the estimates of S_1 for Cl_2 at different temperatures were obtained from the paper by Ruiz-Ibanez et al. (1991). Ruiz-Ibanez et al. (1991) reported values for H_1^0 and S_1 over the temperature range of 283–298 K. Their results were extrapolated up to 313 K for our work. The ionic strength of the aqueous electrolyte solution, I, is defined in terms of the concentrations of the ionic species that are present in the solution, c_i, and their valences, z_i, according to the following equation:

$$I = \frac{1}{2}\sum_{ions} c_i z_i^2. \tag{58}$$

The estimated values of Henry's law constants for Cl_2 in aqueous NaOH solutions for the conditions of our experiments are reported in Table 1, and those for Cl_2 in aqueous $KHCO_3$ solutions are reported in Table 2.

The diffusion coefficients of Cl_2, CO_2, HOCl, and HCO_3^- in aqueous $KHCO_3$ solutions were estimated from the reported values of 1.48×10^{-9} m^2/s (Spalding, 1962; Hikita et al., 1973), 1.94×10^{-9} m^2/s (Tamimi et al., 1994), 1.54×10^{-9} m^2/s (Hikita et al., 1973), and 1.5×10^{-9} m^2/s (Kigoshi and Hashitani, 1963), respectively, in water at 298 K by correcting for the temperature and viscosity of the solutions according to the following Stokes–Einstein equation:

$$\frac{D_i\,\mu}{T} = \text{constant}, \tag{59}$$

where T is in units of K, μ is in units of kg/(m·s), and D_i is in units of m^2/s. The estimated values of the diffusion coefficients of these chemical species in aqueous $KHCO_3$ solutions are reported in Table 2. The diffusion coefficients of Cl^-, OCl^-, $CO_3^=$, H_2CO_3, OH^-, and H^+ were assumed to be equal to that of bicarbonate. For the aqueous NaOH solutions, we have assumed that the diffusion coefficients of the ionic chemical species (Cl^-, OCl^-, and H^+) are equal to that of OH^-. The value of the diffusion coefficient for OH^- in water at 298 K was taken to be 3.43×10^{-9} m^2/s (Hikita et al., 1973) and was corrected for temperature and viscosity of the aqueous NaOH solutions by using a Stokes–Einstein equation similar to Eq. 59. Values for the diffusion coefficients of Cl_2, HOCl, and OH^- in the aqueous NaOH solutions that were studied experimentally are reported in Table 1.

The following correlation for the water dissociation equilibrium constant, K_{10}, was reported by Olofsson and Hepler (1975) for the temperature range of 273–573 K:

$$\log_{10}(K_{10}) = 8{,}909.483 - \frac{142{,}613.6}{T} - 4{,}229.195\log_{10}(T) + 9.7384T - 0.0129638T^2 + 1.15068\times10^{-5}T^3 - 4.602\times10^{-9}T^4. \tag{60}$$

Data for (K_6K_{10}) were reported by Read (1975) for the temperature range of 273–523 K and were correlated according to the following equation:

$$\log_{10}(K_6K_{10}) = 179.648 + 0.019244T - 67.341\log_{10}(T) - \frac{7{,}495.441}{T}. \tag{61}$$

Estimates of K_8 were calculated from the following correlation for the temperature range of 273–323 K (Danckwerts and Sharma, 1966):

$$\log_{10}(K_8K_{10}) = 6.498 - \frac{2{,}902.4}{T} - 0.0238T. \tag{62}$$

Values of K_3 and K_7 were estimated at 298.15 K from the standard Gibbs energy change of reaction, $\Delta G_{298.15}^0$, by using the following equation:

$$K_i(298.15) = \exp\left(\frac{-\Delta G_{298.15}^0}{298.15R}\right). \tag{63}$$

On the other hand, the value of K_9 at 298 K was taken to be $(2\times10^{-4})^{-1} = 5{,}000$ m^3/kmol (Cotton and Wilkinson, 1966). K_3, K_7, and K_9 were corrected for temperature dependence according to the following equation:

Table 3. Values for Equilibrium Constants of Reactions 1–10 at Various Temperatures

T K	K_1 kmol/m^3	$10^{-5}K_2$ kmol/m^3	10^4K_3 (kmol/m^3)^2	$10^{-10}K_4$	10^3K_5	$10^{-7}K_6$ m^3/kmol	$10^{-6}K_7$ m^3/kmol	K_8 m^3/kmol	K_9 m^3/kmol	$10^{14}K_{10}$ (kmol/m^3)^2
293	1,013	6.148	3.890	5.722	2.024	5.651	3.726	6,137	5,270	0.6798
298	1,092	6.569	4.500	4.491	2.060	4.112	2.790	4,640	5,000	1.002
303	1,189	7.094	5.181	3.580	2.071	3.012	2.109	3,535	4,752	1.447
308	1,304	7.741	5.938	2.895	2.059	2.220	1.609	2,711	4,523	2.051
313	1,442	8.533	6.776	2.371	2.027	1.645	1.238	2,092	4,312	2.858

$$\ln\left(\frac{K_i(T)}{K_i(298.15)}\right)=\frac{-\Delta H^0}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right), \qquad (64)$$

where the standard enthalpy change of reaction, ΔH^0, is assumed to be independent of T and is approximated by its value at 298.15 K, $\Delta H^0_{298.15}$ (Smith and Van Ness, 1987). Since the temperature was varied over a relatively narrow range in the present work (293–313 K), this assumption would most likely be adequate. $\Delta G^0_{298.15}$ and $\Delta H^0_{298.15}$ were calculated from values reported in the *CRC Handbook of Chemistry and Physics* (Lide, 1990). Values of the equilibrium constants for reactions 1–10 at various temperatures are listed in Table 3.

The forward rate coefficients of reactions 1, 2, and 4 (k_{21}, k_{22}, and k_{24}) are not known. We have assumed in this work that k_{22} is equal to k_{21}. As mentioned earlier, there has been a great deal of disagreement in the literature concerning the value of the forward rate coefficient of reaction 4, k_{24}. In this work, we have attempted to estimate k_{24} by carrying out absorption experiments of Cl_2 into aqueous solutions of NaOH in the laminar liquid jet absorber and then using our penetration model to interpret the experimental data. Once k_{24} is known, k_{21} is estimated by using the penetration model along with the experimental results for the absorption of Cl_2 into aqueous solutions of $KHCO_3$ in the laminar liquid jet absorber.

Brian et al. (1966) reported values for the forward rate coefficient of reaction 3, k_{13}, over the temperature range of 288–313 K. These estimates were correlated according to the following equation:

$$k_{13}=1.4527\times10^{10}\exp\left(\frac{-6{,}138.6}{T}\right). \qquad (65)$$

Pinsent et al. (1956) reported the following correlation for the forward rate coefficient of reaction 5, k_{15}, over the temperature range of 273–311 K:

$$\log_{10}(k_{15})=329.85-110.541\log_{10}(T)-\frac{17{,}265.4}{T}. \qquad (66)$$

Values of the forward rate coefficient of reaction 6, k_{26}, were calculated from the following correlation, which was reported by Pinsent et al. (1956) for the temperature range of 273–313 K:

$$\log_{10}(k_{26})=13.635-\frac{2{,}895}{T}. \qquad (67)$$

Experimental Apparatus and Procedure

A laminar liquid jet absorber was used to measure the Cl_2 absorption rates in aqueous $KHCO_3$ solutions and in aqueous NaOH solutions. The experimental apparatus and procedure are similar to those that were described by Al-Ghawas et al. (1989). The diameter of the liquid jet was $d=5.33\times10^{-4}$ m. Our laminar liquid jet absorber was designed according to the recommendations of Raimondi and Toor (1959) in order to minimize boundary-layer effects and "end effects," and produce absorption rate results that are very close to the theoretical values for rodlike flow without interfacial resistance. For the Cl_2–NaOH system, the absorption experiments were performed with aqueous solutions of about 0.1 kmol/m^3 of NaOH over the temperature range of 293–312 K. The experimental data for the Cl_2–NaOH system are presented in Table 4. For the Cl_2–$KHCO_3$ system, absorption experiments were carried out with aqueous solutions of 0.202 kmol/m^3 of $KHCO_3$ over the temperature range of 293–313 K, and over the concentration range of 0.1–0.41 kmol/m^3 of $KHCO_3$ at 298 K. The experimental data for the Cl_2–$KHCO_3$ system are presented in Table 5, and the estimated initial liquid bulk concentrations of the major chemical species are reported in Table 6. All experiments were performed under atmospheric pressure with partial pressures of Cl_2 near 1 atm and with initial Cl_2 loadings of the aqueous sodium hydroxide and potassium bicarbonate solutions equal to zero.

Normally, the gas absorption rate is measured with a soap-film meter as the gas flows from the gas storage tube into the absorption chamber after turning off the feed gas flow (Al-Ghawas et al., 1989). However, this technique could not be used in the case of the absorption of Cl_2 into aqueous

Table 4. Experimental Data for the Absorption of Cl_2 into Aqueous Solutions of NaOH in a Laminar Liquid Jet Absorber at a Total Pressure of 1 atm, Along with the Estimated Rate Coefficient of Reaction 4, k_{24}*

T K	$[NaOH]_{initial}$ kmol/m^3	P_1 atm	10^6Q m^3/s	10^2l m	$10^3\tau$ s	$10^4k^0_{l,1}$ m/s	Measured 10^5 RA_1 kmol/(m$^2\cdot$s)	Estimated k_{24} m^3/(kmol$\cdot$s)
293	0.09985	0.969	0.787	2.535	7.19	4.7805	7.94	1.7×10^9
298	0.10000	0.962	0.836	2.580	6.89	5.2136	7.73	1.2×10^9
303	0.09960	0.950	0.750	2.565	7.63	5.2945	7.60	1.8×10^9
312	0.09970	0.922	0.829	2.550	6.86	6.1669	7.98	2.1×10^9

*$d=5.33\times10^{-4}$ m and $L_1=0$.

Table 5. Experimental Data for the Absorption of Cl_2 into Aqueous Solutions of $KHCO_3$ in a Laminar Liquid Jet Absorber at a Total Pressure of 1 atm, Along with the Estimated Rate Coefficient of Reaction 1, k_{21}*

T K	$[KHCO_3]_{initial}$ kmol/m^3	P_1 atm	$10^6 Q$ m^3/s	$10^2 l$ m	$10^3 \tau$ s	$10^4 k^0_{l,1}$ m/s	Measured $10^5\ RA_1$ kmol/(m$^2\cdot$s)	Predicted† $10^5 RA_1$ kmol/(m$^2\cdot$s)	Estimated‡ k_{21} m^3/(kmol$\cdot$s)
293	0.202	0.987	0.893	2.500	6.25	5.0477	6.62	3.99	2,800
298	0.100	0.974	0.845	2.505	6.61	5.3194	4.96	3.47	3,200
298	0.202	0.972	0.869	2.505	6.43	5.3391	6.69	3.56	4,090
298	0.300	0.969	0.866	2.505	6.45	5.2928	7.79	3.53	4,150
298	0.410	0.967	0.871	2.500	6.40	5.2758	9.36	3.53	4,900
303	0.202	0.967	1.02	2.470	5.40	6.1977	6.38	3.45	4,500
308	0.202	0.954	1.00	2.520	5.62	6.4374	6.41	3.04	6,490
313	0.202	0.935	1.04	2.475	5.31	6.9940	6.34	2.86	8,505

*$d = 5.33 \times 10^{-4}$ m and $L_1 = 0$.

†Reactions 3–10 are used in the model for predicting these rates of absorption; reactions 1 and 2 are neglected.

‡Estimated from the model by taking into account reactions 1–10 with $k_{22} = k_{21}$.

bicarbonate solutions, since carbon dioxide is produced as a result of the reaction between Cl_2 and HCO_3^- in the liquid phase and subsequently desorbs into the gas phase. Hence, the measured gas absorption rate would not accurately reflect the amount of Cl_2 that was absorbed. Therefore, the absorption rate of Cl_2 was determined by measuring the cup-mixed Cl^- concentration in samples of the liquid effluent by using an Orion Model 9617B chloride-selective electrode. The electrode was calibrated with standardized aqueous KCl solutions over a Cl^- concentration range of 0.001–0.1 kmol/m^3. It was also necessary to keep the chlorine flowing continuously through the absorption chamber during the experiments in order to prevent carbon dioxide from accumulating and changing the partial pressure of the chlorine in the absorption chamber. At a constant liquid flow rate, the chloride ion concentration reached a steady value within five minutes after start-up. The average rate of absorption of Cl_2 per unit interfacial area was calculated from the cup-mixed chloride ion concentration in the effluent of the laminar liquid jet absorber by using the following equation:

$$RA_1 = \frac{Q}{\pi d l}[Cl^-]_e, \qquad (68)$$

where $[Cl^-]_e$ is the cup-mixed chloride ion concentration in the liquid effluent of the jet in units of kmol/m^3. For consistency, we also used this technique to measure the average rate of absorption of Cl_2 per unit interfacial area for the Cl_2–NaOH system.

Results and Discussion

We used the penetration model for the Cl_2–NaOH system along with the experimentally measured rates of absorption of Cl_2 in the aqueous NaOH solutions (see Table 4) to estimate the rate coefficient of reaction 4, k_{24}, for the temperature range of 293–312 K. The value of k_{24} was adjusted until the theoretically predicted rate of absorption was within 1% of the experimentally measured rate of absorption of Cl_2. Our estimates for k_{24} are listed in Table 4 and are plotted in Figure 1. The estimates for k_{24} are fitted by the following Arrhenius equation over the temperature range of 293–312 K:

$$k_{24} = 3.558 \times 10^{11} \exp\left(\frac{-1{,}617}{T}\right), \qquad (69)$$

where T is in units of kelvin, and k_{24} is in units of m^3/(kmol s). The activation energy for k_{24} is estimated from Eq. 69 to be about 3.2 kcal/mol. Note that k_{24} is of the order of 10^9 m^3/(kmol$\cdot$s) (Table 4), which agrees very well with the prediction of Lifshitz and Perlmutter-Hayman (1962). Hence, it can be concluded that the estimate of Morris (1946) of 5×10^{14} m^3/(kmol$\cdot$s) at 298 K is too large and not very likely, whereas the estimate of Spalding (1962) of 10^6 m^3/(kmol$\cdot$s) at 298 K is too small.

When Cl_2 is absorbed into an aqueous bicarbonate solution, one might assume that Cl_2 reacts only with water and OH^-, and that it does not react directly with either HCO_3^- or $CO_3^=$. This mechanism corresponds to reactions 3–10

Table 6. Initial Liquid Bulk Concentrations of HCO_3^-, CO_2, OH^-, $CO_3^=$, and H_2CO_3, Respectively, for the Potassium Bicarbonate Solutions that were Studied Experimentally

T K	$[KHCO_3]_{initial}$ kmol/m^3	$[HCO_3^-]^0$ kmol/m^3	$10^3[CO_2]^0$ kmol/m^3	$10^6[OH^-]^0$ kmol/m^3	$10^3[CO_3^=]^0$ kmol/m^3	$10^6[H_2CO_3]^0$ kmol/m^3
293	0.202	0.1979	2.06	1.70	2.06	4.17
298	0.100	0.0979	1.04	2.29	1.04	2.14
298	0.202	0.1978	2.10	2.29	2.10	4.33
298	0.300	0.2938	3.12	2.29	3.12	6.42
298	0.410	0.4015	4.26	2.29	4.27	8.78
303	0.202	0.1977	2.14	3.07	2.14	4.43
308	0.202	0.1976	2.18	4.08	2.18	4.50
313	0.202	0.1975	2.23	5.39	2.23	4.52

Since the solutions are unloaded ($L_1 = 0$), the initial liquid bulk concentrations of Cl_2, Cl^-, HOCl, and OCl^- are equal to zero.

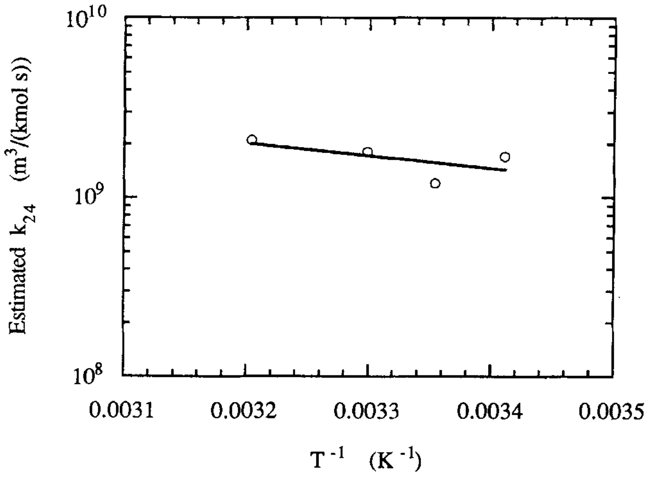

Figure 1. Arrhenius plot of the estimates for the second-order rate coefficient of reaction 4, k_{24}, for the 0.1 kmol/m^3 aqueous NaOH solutions.

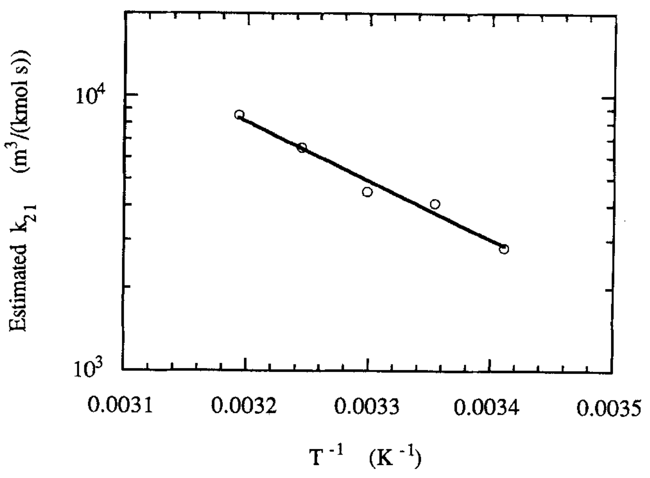

Figure 2. Arrhenius plot of the estimates for the second-order rate coefficient of reaction 1, k_{21}, for the 0.202 kmol/m^3 aqueous KHCO$_3$ solutions.

It was assumed that $k_{22} = k_{21}$, and k_{24} was estimated from Eq. 69.

without reactions 1 and 2. When this mechanism is used, the predicted rates of absorption turn out to be much smaller than the measured rates of absorption for our experimental data (see Table 5). This suggests that Cl_2 might react with other chemical species in an aqueous bicarbonate solution. It has been reported that Cl_2 reacts with the following anions: CH_3COO^-, $CHCl_2COO^-$, $SO_4^=$, CH_2ClCOO^-, $HCOO^-$, and $HPO_4^=$ in aqueous solutions (Lifshitz and Permutter-Hayman, 1961, 1962). In view of this, it seems reasonable to assume that Cl_2 reacts with HCO_3^- and possibly with $CO_3^=$. Hence, we have proposed reactions 1 and 2.

We turn our attention now to estimating the forward rate coefficient of the reaction between Cl_2 and HCO_3^-, k_{21}. In the Cl_2-bicarbonate system, we have two unknown rate coefficients: k_{21} and k_{22}. It seems reasonable to expect that the rate coefficient of the reaction between Cl_2 and $CO_3^=$, k_{22}, would be close to that of the reaction between Cl_2 and HCO_3^-, k_{21}. Hence, we assume that $k_{22} = k_{21}$. This reduces the number of unknown rate coefficients to only one: k_{21}. A detailed sensitivity analysis showed that the value of k_{22}, and subsequently reaction 2, did not have any major effects on the estimation of k_{21} or on the rate of absorption of Cl_2 for the conditions that were studied experimentally. Note that the carbonate concentration is about two orders of magnitude smaller than that of bicarbonate (see Table 6). Equation 69 was used to estimate the value of k_{24} at various temperatures. The penetration model for the Cl_2-bicarbonate system was then used along with the experimentally measured rates of absorption of Cl_2 in the aqueous $KHCO_3$ solutions (see Table 5) to estimate the rate coefficient of reaction 1, k_{21}, for the temperature range of 293–313 K. Our estimates for k_{21} are listed in Table 5 and are plotted in Figures 2 and 3. The following Arrhenius equation provides a fit for our k_{21} estimates for an aqueous solution of 0.202 kmol/m^3 of $KHCO_3$ over the temperature range of 293–313 K:

$$k_{21} = 5.63 \times 10^{10} \exp\left(\frac{-4{,}925}{T}\right), \qquad (70)$$

where T is in units of kelvin, and k_{21} is in units of m^3/(kmol·s). The activation energy for k_{21} is estimated from Eq. 70 to be about 9.8 kcal/mol. Note that the estimates for k_{21} for the 0.1, 0.202, 0.3, and 0.41 kmol/m^3 aqueous $KHCO_3$ solutions at 298 K exhibit a dependence on the bicarbonate concentration as shown in Figure 3. This is not surprising since it is known that the reaction rate coefficient may vary with composition, especially in nonideal systems (Froment and Bischoff, 1979). The estimates of k_{21} at 298 K can be approximated over the potassium bicarbonate concentration range of 0.1–0.41 kmol/m^3 by the following equation:

$$k_{21} = 2{,}811 + 5{,}034[KHCO_3]_{\text{initial}} \quad \text{at} \quad T = 298\ \text{K}, \qquad (71)$$

where $[KHCO_3]_{\text{initial}}$ is in units of kmol/m^3 and k_{21} is in units of m^3/(kmol·s).

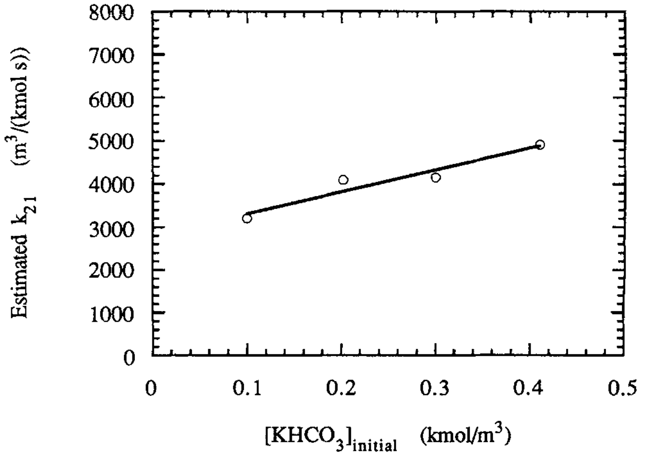

Figure 3. Concentration dependence of the second-order rate coefficient of reaction 1 at 298 K.

It was assumed that $k_{22} = k_{21}$, and k_{24} was estimated from Eq. 69.

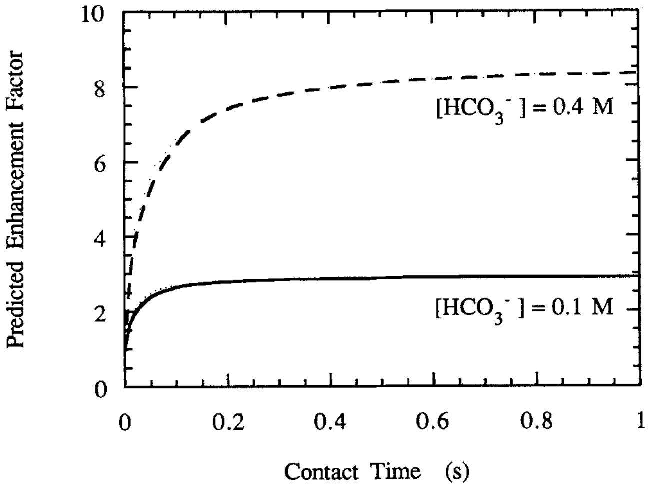

Figure 4. Predicted enhancement factors for the absorption of Cl_2 into aqueous bicarbonate solutions with concentrations of 0.1 and 0.4 kmol/m^3 as functions of gas-liquid contact time.
$T = 298$ K, $P_1 = 0.9$ atm, and $L_1 = 0$.

We would now like to use our mathematical models to further investigate different aspects of the absorption of Cl_2 into aqueous bicarbonate solutions and into aqueous hydroxide solutions. The predicted enhancement factors for the absorption of Cl_2 into aqueous bicarbonate solutions with concentrations of 0.1 and 0.4 kmol/m^3 as functions of the gas–liquid contact time at 298 K are plotted in Figure 4. For a given contact time, the enhancement factor increases with increasing bicarbonate concentration, since the contribution of the chemical reaction between Cl_2 and bicarbonate to the overall rate of absorption of Cl_2 increases, whereas that due to physical absorption decreases, as the bicarbonate concentration increases. Moreover, for a given bicarbonate concentration, the enhancement factor increases rapidly with increasing contact time initially and then levels off for longer contact times. The predicted enhancement factors for the absorption of Cl_2 into aqueous hydroxide solutions with concentrations of 0.1 and 0.4 kmol/m^3 as functions of the gas–liquid contact time at 298 K are plotted in Figure 5. It is clear that, for comparable gas–liquid contact times, the enhancement factors of Cl_2 in hydroxide solutions are higher than those in bicarbonate solutions of comparable concentrations. This is because the reaction between Cl_2 and OH^- is much faster than that between Cl_2 and HCO_3^-.

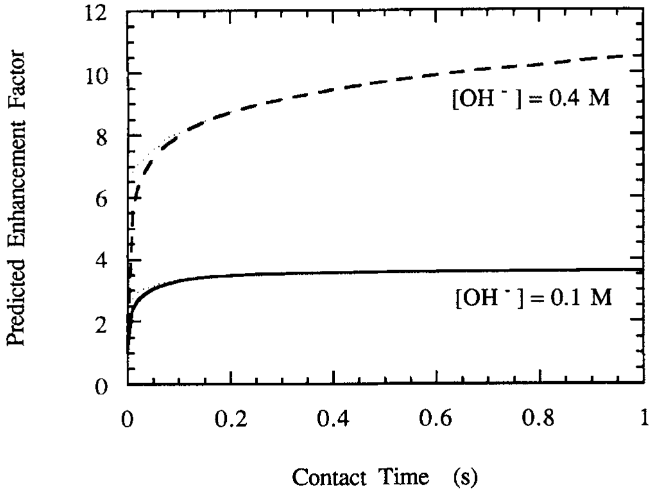

Figure 5. Predicted enhancement factors for the absorption of Cl_2 into aqueous hydroxide solutions with concentrations of 0.1 and 0.4 kmol /m^3 as functions of gas liquid contact time.
$T = 298$ K, $P_1 = 0.9$ atm, and $L_1 = 0$.

It is important to note that in an aqueous hydroxide solution, two moles of hydroxide are consumed for each mole of Cl_2 that reacts: one mole of OH^- reacts directly with one mole of Cl_2 according to reaction 4 to produce one mole of HOCl, which subsequently reacts instantaneously with a second mole of OH^- according to reaction 7. That is, the overall reaction between Cl_2 and OH^- is the sum of reactions 4 and 7:

$$Cl_2 + 2OH^- \xrightarrow{K_{72}} Cl^- + OCl^- + H_2O, \qquad (72)$$

where $K_{72} = K_4 K_7$, and $K_{72} = 1.25 \times 10^{17}$ m^3/kmol at 298 K. Whereas, in an aqueous bicarbonate solution, only one mole of bicarbonate is consumed for each mole of Cl_2 that reacts according to reaction 1. Note that the subsequent reaction between bicarbonate and HOCl according to reaction 11 is not favorable. This can be clearly seen when the equilibrium constants of reactions 7 and 11 are compared. For example, at 298 K, $K_7 = 2.79 \times 10^6$ m^3/kmol, whereas $K_{11} = 1.4 \times 10^{-4}$, which indicate that reaction 7 is very favorable, whereas reaction 11 is not. Hence, regardless of the solution concentration or the gas–liquid contact time, the amount of hydroxide that is consumed for absorbing a certain amount of Cl_2 into an aqueous hydroxide solution is almost twice the amount of bicarbonate that is consumed for absorbing the same amount of Cl_2 into an aqueous bicarbonate solution. Thus, it might be more economical to use aqueous bicarbonate solutions to absorb Cl_2 instead of aqueous hydroxide solutions. It should be pointed out, however, that the reaction between HOCl and HCO_3^- according to reaction 11 would continue to proceed, but at a very slow rate, if HCO_3^- is still present in sufficient amounts after the conclusion of the absorption of Cl_2 into the aqueous bicarbonate solution. This can be understood by realizing that HOCl and HCO_3^- react according to reaction 11 to produce H_2CO_3 which, in turn, dissociates slowly into CO_2 and water according to the reverse of reaction 5. The produced CO_2 would then desorb from the aqueous solution (to the extent that is allowed by the temperature of the system and the amount of CO_2 that is present in the gas phase), which enhances further dissociation of H_2CO_3. The removal of H_2CO_3 prompts reaction 11 to proceed even further, resulting in the consumption of more HCO_3^- by HOCl. Hence, the rate of the reaction between HOCl and HCO_3^- is controlled by the rate of dissociation of H_2CO_3 into CO_2 followed by desorption of CO_2. The rate coefficient for the dissociation of H_2CO_3 into CO_2 can be estimated as $k_{-15} = k_{15}/K_5$, which is about 13 s^{-1} at 298 K. This clearly shows that the dissociation of H_2CO_3 into CO_2 followed by the desorption of CO_2 from the bicarbonate solution into the gas phase is a slow process. However, if the conditions of the system are favorable for the occurrence of this sequence (higher temperatures or low CO_2 partial pressure in the gas phase, and $[HCO_3^-] \geq [HOCl]$), then after a relatively long time, most of the HOCl would react with an equal amount of HCO_3^-, and the net stoichiometry between Cl_2 and HCO_3^- would be two moles of HCO_3^- are consumed for each mole of Cl_2. Nevertheless, this would not happen to any significant extent if Cl_2 is being absorbed into the aqueous bicarbonate solution, because the rate of the reaction between HCO_3^- and Cl_2 is much faster than the rate of dissociation of H_2CO_3 followed by desorption of CO_2, and, hence, HCO_3^- would react much faster with Cl_2 than with HOCl. Moreover, in order to minimize the loss of HCO_3^- by further reaction with HOCl after the aqueous bicarbonate solution has been used to absorb Cl_2, the solution should be either immediately used to absorb more Cl_2, or it should be stored at lower temperatures or with sufficient CO_2 in the gas phase over the solution in order to prevent or minimize the desorption of CO_2 from the solution.

It is interesting to note that the standard heat of reaction for the reaction between Cl_2 and HCO_3^- at 298.15 K is $\Delta H^0_{298.15} = +3.238$ kcal/(mol of Cl_2), which indicates that reaction 1 is endothermic, whereas the standard heat of reaction for reaction 4 between Cl_2 and OH^- is $\Delta H^0_{298.15} = -8.282$ kcal/(mol of Cl_2), which indicates that reaction 4 is exothermic, and the heat of reaction for the overall reaction between Cl_2 and OH^- (reaction 72) is $\Delta H^0_{298.15} = -18.327$ kcal/(mol of Cl_2), which indicates that reaction 72 is even more exothermic than reaction 4. This implies that the forward path of reaction 1 is favored at higher temperatures, and that the reverse path of reaction 1 is favored at lower temperatures. Hence, regeneration of the spent bicarbonate solutions would be enhanced at lower temperatures. One possible method for regenerating spent aqueous bicarbonate solutions would be to absorb CO_2 into these solutions at lower temperatures, which enhances the reverse of reaction 1. The opposite is true for the Cl_2-hydroxide system: regeneration of the spent hydroxide solutions would be enhanced at higher temperatures. Furthermore, since the magnitude of the heat of reaction for reaction 72 is much more than that of reaction 1, the net energy costs for the absorption process followed by regeneration of the spent solutions would be higher for the Cl_2-hydroxide system than for the Cl_2-bicarbonate system.

Conclusions

The absorption of Cl_2 into aqueous bicarbonate solutions and into aqueous hydroxide solutions has been studied both experimentally and theoretically. A laminar liquid jet absorber has been used to carry out the absorption experiments, and a mathematical model that is based on Higbie's penetration theory has been developed and used to interpret the experimental data. The rate coefficient of the reaction between Cl_2 and OH^- has been estimated over the temperature range of 293–312 K, and the rate coefficient of the reaction between Cl_2 and HCO_3^- has been estimated over the temperature range of 293–313 K. The mathematical model was also used to further investigate the absorption of Cl_2 into aqueous bicarbonate and hydroxide solutions. It is important to note that the amount of hydroxide that is consumed for absorbing a specific amount of Cl_2 into an aqueous hydroxide solution is almost twice the amount of bicarbonate which is consumed for absorbing the same amount of Cl_2 into an aqueous bicarbonate solution, regardless of the solution concentration or the gas–liquid contact time. Moreover, since the magnitude of the heat of reaction for the reaction between Cl_2 and OH^- is much more than that of the reaction between Cl_2 and HCO_3^-, the regeneration energy costs of spent hydroxide solutions are expected to be higher than those for spent bicarbonate solutions, and it would probably be more economical to use aqueous bicarbonate solutions for absorption of Cl_2 than aqueous hydroxide solutions.

Acknowledgment

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Notation

$k_{g,i}$ = gas-phase mass transfer coefficient for gas i, kmol/(atm m^2 s)
R = gas law constant, 1.987 kcal/(mol·K)
u_i = concentration of species i in the liquid phase (which is a function of x and t), kmol/m^3
$u_{i,j}$ = concentration of species i in the liquid phase at x_j, kmol/m^3
x_j = discretized spatial variable at node j, m
ρ = density of the aqueous solution, kg/m^3

Subscripts

1 = Cl_2
2 = HCO_3^-
3 = CO_2
4 = HOCl
5 = Cl^-
6 = H^+
7 = OCl^-
8 = OH^-
9 = $CO_3^=$
10 = H_2CO_3
11 = H_2O
12 = K^+ or Na^+

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