The absorption of carbon dioxide or sulfur dioxide into aqueous sodium hydroxide solution has been performed in a packed column, and its application to the theory of gas absorption accompanied by chemical reaction has been studied. Furthermore, the effects of the heat of solution and heat of reaction on gas absorption rate have also been investigated.

The experimental values of reaction factor, which were evaluated from Eq.(7) by using the mean values of temperature and concentration at the top and the bottom of the column respectively, were in good agreement with theoretical values within an error of 30%, even though the liquid temperature difference between the inlet and the outlet of the column was as high as 30°C. Thus, the overall reaction factor in the packed column may be evaluated from Eq.(7) for other reaction systems.

A number of theoretical and experimental studies have been reported for gas absorption accompanied by chemical reaction in packed columns. Tepe and Dodge\textsuperscript{10}) and other investigators\textsuperscript{1-6}) have studied the overall capacity coefficients in packed columns for the absorption of carbon dioxide into sodium hydroxide solution when the concentration in gas phase is less than several percent. Therefore, the variation of sodium hydroxide concentration throughout the column is limited.

This paper discusses the absorption of pure carbon dioxide or pure sulfur dioxide by aqueous sodium hydroxide solutions in a packed column under adiabatic conditions. Furthermore, the effects of the heat of solution and heat of reaction on gas absorption rate are also investigated.

**Experimental**

The absorption column used in this study was 7.6 cm I.D. glass tube and was packed with 6 mm ceramic Raschig rings to a maximum height of 40 cm. The column consisted of a double tube evacuated and silver-coated like a vacuum bottle to avoid heat exchange through the column wall. Sodium hydroxide solution was irrigated on the top of the packed bed through a distributor with forty holes to obtain a uniform distribution. Exit liquid samples were withdrawn from the column through a sampling device fitted beneath the bottom of the packed bed to reduce the end effect. Gases of 99.8% purity were fed to the bottom of the column from commercial cylinders.

Inlet liquid temperature was adjusted to 15°C. Inlet gas temperature was also adjusted to about 15°C except for a few runs. Inlet and outlet liquid samples were analyzed for concentrations of total alkalis and
Fig. 1. Relation between the difference of concentration of NaOH and that of liquid temperature through a packed column

![Fig. 1](image)

Fig. 2. Variations of physico-chemical properties in a packed column for CO₂-NaOH system

Table 1. Effect of inlet gas temperature on gas absorption rate for CO₂-NaOH system

<table>
<thead>
<tr>
<th>Run</th>
<th>T₀ [°C]</th>
<th>Tᵣ [°C]</th>
<th>Tₛ [°C]</th>
<th>C₀₁ [kg-mol/m³]</th>
<th>Cₛ₁ [kg-mol/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>151</td>
<td>25.6</td>
<td>16.8</td>
<td>15.4</td>
<td>40.6</td>
<td>2.98</td>
</tr>
<tr>
<td>154</td>
<td>14.2</td>
<td>16.1</td>
<td>15.5</td>
<td>40.2</td>
<td>2.98</td>
</tr>
</tbody>
</table>

Hydroxides were investigated by the Warder method, using phenolphthalein and methylorange as indicators for CO₂-NaOH system and thymolphthalein and methylorange for SO₂-NaOH system. No effect of inlet gas temperature on gas absorption rate was observed, as shown in Table 1 for CO₂-NaOH system. However, the liquid concentration and temperature, respectively, varied markedly throughout the column. The difference in concentration of sodium hydroxide at top and bottom of the column is plotted against that of temperature in Fig. 1. The straight lines in Fig. 1 represent the thermal equation evaluated from the following assumptions, i.e., (1) the column is at adiabatic condition, (2) the variation of temperature in the column is due to the heat of reaction and heat of solution, (3) heat generated at gas-liquid interface is transferred only to the liquid phase and (4) the heat transfer between gas and liquid phases is negligibly small. For the case when above assumptions are satisfied, liquid temperature rise is evaluated by the following equation,

\[ T_r - T_0 = \frac{(C_{₀₁} - C_{ₛ₁})(-dH_r - dH_p)}{c_R \rho} \]

and Fig. 1 suggests the validity of Eq.(1).

Discussion

Based on the assumption that the liquid flow is piston-like, the material balance for any differential column height, \( dz \), leads to:

\[ u \frac{dC_B}{dz} + \beta k_B^a (C_A - C_{₅₅}) = 0 \]

(2)

where \( C_{₅₅} \) is considered to be zero. Thus, Eq.(2) gives:

\[ u \frac{dC_B}{dz} = -\beta k_B^a C_A \]

(3)

with boundary conditions

\[ C_B = C_{₀₁} \text{ at } z = 0 \]

(4)

\[ C_B = C_{ₛ₁} \text{ at } z = z_s \]

(5)

Eq.(3) is changed to dimensionless form by substituting the dimensionless quantities \( Y = C_B/C_{₀₁} \) and \( Z = z/z_s \), and then integrating with boundary conditions (4) and (5) to give:

\[ \frac{F C_{₀₁}}{V} \int_{1}^{Z} \frac{dY}{\beta k_B^* a C_A} = \frac{F C_{₀₁}}{V} \int_{1}^{Z} \frac{dY}{\beta N_A^*} = 1 \]

(6)

Values of \( \beta \) and \( N_A^* \) in Eq.(6) change along the packed height because liquid temperature and concentration of sodium hydroxide vary in the column. Thus, Eq.(6) must be integrated graphically. At first, the concentration of sodium hydroxide was assumed appropriately for the calculation of the values of \( \beta \) and \( N_A^* \). Then the liquid temperature was calculated from Fig. 1. The temperature of gas-liquid interface was estimated by the method of Kobayashi and Saito⁴ or Hiraoka and Tanaka². It was nearly equal to the bulk temperature of liquid. Values of \( k_B^* \), \( a \) and \( C_A \) were evaluated from the equations proposed by Onda et al.⁷ ⁸.

Figs. 2 and 3 show the variations of \( k_B^* \), \( T_r \), etc., calculated from the methods above mentioned. The variation of the product of \( \beta \) and \( N_A^* \) is smaller than that of other physico-chemical properties. Consequently, the product of \( \beta \) and \( N_A^* \) may be assumed to be constant throughout the column, and can be calculated based on the mean values of temperature and concentration.
concentration at the inlet and the outlet of the column. Thus, Eq.(6) becomes:

$$\beta = \frac{F_C}{V N_A} (1 - Y_t)$$  \hspace{1cm} (7)

In Fig. 4, the values of $\beta$ obtained from Eq.(7) are plotted against the theoretical ones estimated from the film theory. In the calculation of the theoretical value of $\beta$, the reaction between carbon dioxide and sodium hydroxide is considered to be an irreversible second-order reaction as given by Nijsing et al.\textsuperscript{5}. The reaction between sulfur dioxide and sodium hydroxide is considered to be a two-step consecutive instantaneous chemical reaction as given by Onda et al.\textsuperscript{9} or Hikita et al.\textsuperscript{3}, and reaction factor based on the film theory is evaluated by the following equations:

$$\beta = 1 + \frac{r_p}{r_p} \left( 1 + \frac{r_{p1}}{r_{p2}} \right) q + \frac{r_p}{r_p} q$$  , \hspace{1cm} (8)

where

$$r_p = \frac{12}{6 + Q + \kappa D_A}$$ \hspace{1cm} (9)

$$r_{p1} = \frac{-1 + 3D_p^{2}/D_A^{2} + v^{2} + 2AD_p^{2}/D_A^{2}}{2 - 2D_p^{2}/D_A^{2}}$$ \hspace{1cm} (10)

$$r_{p2} = \frac{9}{3 + (Q + \kappa) D_p^{2}/D_A^{2}}$$ \hspace{1cm} (11)

$$\kappa = v(6 - Q)^{3/2} + 24(D_p^{2}/D_A^{2} - 1)Q$$ \hspace{1cm} (12)

$$Q = C_{SL}/C_{CL}$$ \hspace{1cm} (13)

The product of $\beta$ and $N_A^*$ varied little for the systems studied in the present paper, though the liquid temperature difference between top and bottom of the column was as high as 30°C. Thus, the overall reaction factor in the packed column can be evaluated from Eq.(7) by using the mean values of temperature and concentration at top and bottom of the column respectively, and observed values of $\beta$ are in good agreement with theoretical values within an error of 30%.

Taking account of the liquid flow rate, the variation of liquid temperature in the column is considered to decrease with increasing liquid flow rate. This allows the overall reaction factor to be evaluated more accurately.

For other reaction systems, heat effect on gas absorption rate in liquid jet was negligibly small, not only for low solubility of gas, but also for high solubility of gas such as ammonia according to the result given by Onda et al.\textsuperscript{9}. Therefore, the overall reaction factor in a packed column for other reaction systems may be evaluated from Eq.(7) by using the mean values of temperature and concentration at top and bottom of the column, respectively.

### Nomenclature

- $a$ = interfacial area in packed bed $[\text{m}^2/\text{m}^3]$
- $C_A$ = concentration of gaseous species in liquid phase $[\text{kg-mol/m}^3]$
- $C_B$ = concentration of sodium hydroxide $[\text{kg-mol/m}^3]$
- $c_p$ = specific heat of liquid $[\text{kcal/kg} \cdot \text{°C}]$
- $D_A$ = diffusivity of gaseous species in liquid phase $[\text{m}^2/\text{hr}]$
- $D^*$ = ionic self-diffusivity, subscript indicating the species $[\text{m}^2/\text{hr}]$
- $F$ = volumetric flow rate of sodium hydroxide solution $[\text{m}^3/\text{hr}]$
- $H$ = holdup [—]
- $\Delta H_S$ = heat of solution (negative for an exothermic process) $[\text{kcal/kg-mol}]$
- $\Delta H_R$ = heat of reaction (negative for an exothermic reaction) $[\text{kcal/kg-mol}]$
- $k_f^*$ = liquid phase mass transfer coefficient $[\text{m/hr}]$
- $N_A^*$ = physical absorption rate defined by $k_f^* C_{SL} C_{CL}$ $[\text{kg-mol/m}^2 \cdot \text{hr}]$
YIELD FROM REACTORS WITH RECYCLE OF REACTANTS

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In a reactor with recycle of reactants, the relation between yield and recycle ratio of reactants is simply determined by the yield vs. feed-rate relation for single-pass operation of the reactor. If the reaction rate exhibits a maximum at a finite extent of reaction, a maximum yield is obtained at a finite recycle ratio of reactants. In this case, at yield less than the maximum value, dual values of recycle ratio are predicted for each desired yield. Operation with lower recycle ratio is only stable in a similar sense to concentration stability.

Yield from Single-pass Operation

Consider first a single reaction, for example, \( A + \beta B \rightarrow R \) being carried out in a flow reactor without recycle of reactants. The yield (or the production rate) of the product \( R \), \( Y_R \), is related to the feed rate of a specified reactant \( A \), \( F_A \), and to its fractional conversion at the reactor outlet, \( x_{A} \), by

\[ Y_R = \frac{F_A x_A}{J \rho} \]  

(1)

Plug Flow Reactor: The yield, in this case, is obtained by

\[ Y_R = V x_{A} / J \rho \]  

(2)

If the ratio of reactants, \( A \) to \( B \), in the feed is not changed and \( r_A \) does not depend on \( F_A \), \( F_R \) may be expressed in terms of \( x_A \). For a maximum value of \( F_R \) to exist at a constant value of \( V \), the necessary condition causing \( dF_R / dx_A \) to vanish is

\[ \int_0^{x_A} \frac{d^2x_A}{r_A} = -x_A \]  

(3)

where \( r_A(x_A) \) is the reaction rate at the reactor outlet condition. A maximum value of \( F_R \) at a finite value of \( x_A \) is obtained when the value of \( r_A \) changing with \( x_A \) has a maximum1,2).

This maximum in \( r_A \) is encountered in an isothermal reactor involving autocatalytic reactions, or else in a nonisothermal operation involving an exothermic reaction, especially in an adiabatic operation as pointed out by Konoki2).

When \( (1/r_A) \) increases monotonously with increasing \( x_A \), \( dF_R / dx_A \) cannot vanish at \( x_A = 0 \). The value of \( F_R \) corresponding to \( x_A = 0 \) is a maximum which corresponds to \( F_A \to \infty \). That this must be so

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\* Received on October 24, 1970

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